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TABLE 27.—ATOMIC WEIGHTS, 1939.

| | Symbol | At No | At wt |
|---|---|---|---|
| Aluminium | Al | 13 | 26 97 |
| Antimony | Sb | 51 | 121 76 |
| Argon | A | 18 | 39 944 |
| Arsenic | As | 33 | 74 91 |
| Barium | Ba | 56 | 137 36 |
| Beryllium | Be | 4 | 9 02 |
| Bismuth | Bi | 83 | 209 00 |
| Boron | B | 5 | 10 82 |
| Bromine | Br | 35 | 79 916 |
| Cadmium | Cd | 48 | 112 41 |
| Cæsium | Cs | 55 | 132 91 |
| Calcium | Ca | 20 | 40 08 |
| Carbon | C | 6 | 12 01 |
| Cerium | Ce | 58 | 140 13 |
| Chlorine | Cl | 17 | 35 457 |
| Chromium | Cr | 24 | 52 01 |
| Cobalt | Co | 27 | 58 94 |
| Copper | Cu | 29 | 63 57 |
| Dysprosium | Dy | 66 | 162 46 |
| Erbium | Er | 68 | 167 2 |
| Europium | Eu | 63 | 152 0 |
| Fluorine | F | 9 | 19 00 |
| Gadolinium | Gd | 64 | 156 9 |
| Gallium | Ga | 31 | 69 72 |
| Germanium | Ge | 32 | 72 60 |
| Gold | Au | 79 | 197 2 |
| Hafnium | Hf | 72 | 178 6 |
| Helium | He | 2 | 4 003 |
| Holmium | Ho | 67 | 163 5 |
| Hydrogen | H | 1 | 1 0081 |
| Indium | In | 49 | 114 76 |
| Iodine | I | 53 | 126 92 |
| Iridium | Ir | 77 | 193 1 |
| Iron | Fe | 26 | 55 84 |
| Krypton | Kr | 36 | 83 7 |
| Lanthanum | La | 57 | 138 92 |
| Lead | Pb | 82 | 207 21 |
| Lithium | Li | 3 | 6 940 |
| Lutecium | Lu | 71 | 175 0 |
| Magnesium | Mg | 12 | 24 32 |
| Manganese | Mn | 25 | 54 93 |
| Mercury | Hg | 80 | 200 61 |
| Molybdenum | Mo | 42 | 95 95 |
| Neodymium | Nd | 60 | 144 27 |
| Neon | Ne | 10 | 20 183 |
| Nickel | Ni | 28 | 58 69 |
| Niobium | Nb | 41 | 92 91 |
| Nitrogen | N | 7 | 14 008 |
| Osmium | Os | 76 | 190 2 |
| Oxygen | O | 8 | 16 000 |
| Palladium | Pd | 46 | 106 7 |
| Phosphorus | P | 15 | 30 98 |
| Platinum | Pt | 78 | 195 23 |
| Potassium | K | 19 | 39 096 |
| Praseodymium | Pr | 59 | 140 92 |
| Protactinium | Pa | 91 | 231 |
| Radium | Ra | 88 | 226 05 |
| Radon | Rn | 86 | 222 |
| Rhenium | Re | 75 | 186 31 |
| Rhodium | Rh | 45 | 102 91 |
| Rubidium | Rb | 37 | 85 48 |
| Ruthenium | Ru | 44 | 101 7 |
| Samarium | Sm | 62 | 150 43 |
| Scandium | Sc | 21 | 45 10 |
| Selenium | Se | 34 | 78 96 |
| Silicon | Si | 14 | 28 06 |
| Silver | Ag | 47 | 107 880 |
| Sodium | Na | 11 | 22 997 |
| Strontium | Sr | 38 | 87 63 |
| Sulphur | S | 16 | 32 06 |
| Tantalum | Ta | 73 | 180 88 |
| Tellurium | Te | 52 | 127 61 |
| Terbium | Tb | 65 | 159 2 |
| Thallium | Tl | 81 | 204 39 |
| Thorium | Th | 90 | 232 12 |
| Thulium | Tm | 69 | 169 4 |
| Tin | Sn | 50 | 118 70 |
| Titanium | Ti | 22 | 47 90 |
| Tungsten | W | 74 | 183 92 |
| Uranium | U | 92 | 238 07 |
| Vanadium | V | 23 | 50 95 |
| Xenon | Xe | 54 | 131 3 |
| Ytterbium | Yb | 70 | 173 04 |
| Yttrium | Y | 39 | 88 92 |
| Zinc | Zn | 30 | 65 38 |
| Zirconium | Zr | 40 | 91 22 |

# INTERMEDIATE CHEMISTRY

# INTERMEDIATE CHEMISTRY

BY

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# PREFACE

The purpose of the present volume is to provide a complete text-book of chemistry for Intermediate and Higher School Certificate Examinations It therefore includes under one cover sections on General and Theoretical, Inorganic and Organic, Analytical and Physical Chemistry In preparing it, the books already written by the senior author, either alone or in collaboration, have been drawn upon, especially as regards the figures and illustrations, so far as they were suitable for this purpose The inorganic section (Parts I to III) has been completely reconstructed, however, and bears only a remote resemblance to Lowry's " Inorganic Chemistry ", the four chapters on inorganic analysis (Part IV) and the whole of the section on " Principles of Organic Chemistry " (Part VI), with the exception of some of the organic preparations, are new , only the physical section (Part V), therefore, resembles at all closely those portions of Lowry and Sugden's " Class-book of Physical Chemistry " which have been adapted with relatively little change for their present use

The planning of an " Intermediate Chemistry " differs in many important respects from that of an elementary or of an advanced text-book Thus, in writing a book for the stage which immediately follows Matriculation, it may be assumed that the reader is already familiar with the great classical discoveries of the composition of air and of water, of the changes of weight which accompany the burning of chalk to lime and of metals to their calces, and in general with the main facts of chemical combination and decomposition, including the observations of Davy and Faraday on electrolysis Historical details, which may again become important in a more advanced study, need not therefore be stressed so strongly at the intermediate stage On the theoretical side, it may be assumed that the atomic and molecular theories have been expounded in the closing stages of the Matriculation or School Certificate course, and that the reader understands, at least in general terms, the meaning of chemical formulae and the significance of chemical equations, so that these can be used freely from the very beginning In these circumstances, it is a convenient and logical procedure to begin by setting out the theore-

tical conceptions in terms of which the facts of chemistry are now expressed Recent discoveries in the field of atomic and molecular physics are also in place, so far as they tend to increased orderliness and simplicity In particular, the introduction of atomic numbers is obviously essential , and even at this early stage there is much to be gained, and nothing to be lost, by contrasting the processes of electron transfer and electron sharing as alternative methods of forming chemical compounds from their elements

One other point of contrast is important The early stages in the study of chemistry are necessarily concerned mainly with the non-metals, and usually include only a fragmentary survey of the much larger range of the metals By contrast, the intermediate student may conveniently undertake the systematic study of the typical elements *in the sequence laid down in the periodic classification*, dealing first with the alkali metals, as elements which readily lose an electron, and finishing with the halogens, as elements which readily accept an electron, in order to acquire the configuration of an inert gas This reversal of the usual sequence has the advantage that the metals occupy the earlier pages, whilst the non-metals come up again for review only after their influence on the metals has been discussed The transitional elements are described after the typical elements, but in a sequence of valencies which is not the same as the sequence of atomic numbers

The organic section, under the title " Principles of Organic Chemistry," includes the subjects prescribed in the new syllabus recently issued by the University of London In harmony with the title, detailed descriptions of preparations and properties of organic compounds have been excluded, in principle, from the text, and transferred to the Experiments , but the underlying theories have been discussed more fully than has been customary hitherto, even in advanced text-books of organic chemistry Thus we have cited Lapworth's interpretation of the cyanhydrin reaction, and Robinson's explanation of the contrast between the unsaturation of olefines and of ketones, not merely because we accept them as true, but because they are too simple and clear to be overlooked, even in an elementary course of organic chemistry, at least when (as in the present instance) some knowledge of the structure of matter and of the electronic theory of valency can be assumed Teachers who may be interested in these recent developments in the theory of organic chemistry will find the materials which inspired this section of our work in a book on " Physical Aspects of Organic Chemistry " by Dr W A Waters, to which the senior author contributed an introduction and some portions of the text.

Experiments numbered from 1 to 190 are an important feature of the book They have survived the test of use in school classes, and it is believed that they will be of real value in practical work They include a series of preparations, which are attached to those paragraphs to which they are most closely related, but tables for use in qualitative analysis, and detailed instructions for volumetric and gravimetric analysis, have been placed together in Part IV of the book Since the book is intended to be used in the laboratory as well as in the classroom, it has been provided with a water-proofed cover Typical questions have been collected and classified into sections corresponding to successive groups of chapters, so that the reader may be able to test his progress in knowledge at convenient stages Solutions have been given to some of the problems in organic chemistry set in recent Scholarship Examinations More than fifty new figures have been prepared for the present volume, and many more have been modified or redrawn for the sake of greater clearness All temperatures are expressed in centigrade degrees

In conclusion, we wish to express our indebtedness to Sir Richard Gregory for expert advice and helpful sympathy, to Messrs J V S Glass and F. W Goddard for valuable suggestions in the composition of the inorganic section, to Messrs Imperial Chemical Industries for the prints used in preparing a diagram of the Gaillard tower, and for assistance in the preparation of certain other figures, to the Old Chemistry Department at the University of Oxford for permission to reproduce Experiments 10, 47 and 48, to Prof J R Partington for permission to reproduce Figs 57 and 85, to Dr S F Boys for data (in part not previously published) in reference to the absolute configurations of valeric, lactic and tartaric acids, to Mr R P Ayres of Leys School, Mr F E Hague of Culford School, and Mr A J V Gale for reading the slip-proofs and paged proofs of the book, to numerous pupils at Leys, Winchester and Uppingham who have tried out the experiments and helped in the correction of proofs, and finally to the Boards of Examiners whose questions we quote The authors will welcome information as to errors which may have escaped detection during numerous readings of the proofs

T M Lowry
A C Cavell

*June* 1936.

## PREFACE TO THE SECOND EDITION

THE subject matter has been thoroughly revised and brought up to date in the second edition of this book. New sections have been added on the electrochemical series and adsorption indicators, and extensive alterations have been made to a number of the experiments, especially in the organic section, by the insertion of fuller and improved details.

The junior author wishes to take this opportunity of expressing his great sorrow at the death of Prof. T. Martin Lowry, whose sympathetic collaboration was invaluable in the production of the original issue of this book.

A. C. CAVELL

Uppingham School,
Uppingham
*December* 1938

## PREFACE TO THE THIRD EDITION

IN this, the third edition, the subject matter has again been revised and brought up to date. In particular, extensive alterations have been made to the sections on carbon monoxide, the rusting of iron, the distillation of liquids, organic analysis and the organic derivatives of ammonia, whilst a large number of additional numerical problems has been added to the questions at the end of the book. Minor changes have been made in many other places where the subject matter was incomplete or out of date, as, for example, in the sections dealing with the effects of intense drying, the manufacture of bromine, catalysis, fermentation, etc.

The details of a number of the experiments have been rewritten, and a few new experiments have been added, but the abbreviation "c.c." has been retained for the present, since the change to "ml." would have caused an expenditure of labour and an increase in costs out of all proportion to the importance of the change.

The author would like to take this opportunity of thanking many friends, pupils and correspondents, who have made some very helpful suggestions for the improvement of the book.

A. C. CAVELL

Uppingham School,
Uppingham.
*May* 1942.

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# *PART I*

# GENERAL AND THEORETICAL

## CHAPTER I

### THE ATOMIC THEORY

**Is matter continuous or discontinuous?**—It has been a question of interest during many generations to know whether matter is really continuous, and therefore always capable of further subdivision, as it appears to be, for instance, in a pool of water, or whether this process of subdivision must ultimately reach a limit because the apparently continuous matter is really made up (like a sand-hill) of particles which may be separated quite easily but cannot readily be broken down into smaller units. Both theories can be found amongst the speculations of the Greek writers, but they were not accompanied by any experimental tests and therefore remained as unproved and almost barren expressions of opinion, with no claim to absolute truth or practical utility.

Two thousand years later, when the period of scientific experiment had begun, the thoughts of chemists and physicists turned increasingly towards the THEORY OF ATOMS (Greek, α, not, τέμνω, I cut), according to which matter was supposed to consist of tiny particles, which could not be divided by the means which were at man's disposal. Thus the great experimenter Robert Boyle (1627-1691) explained the "spring of the air" (or its tendency to expand on release of pressure) by assuming that air was composed of corpuscles whirling in a swiftly flowing ether, and Isaac Newton (1642-1726) suggested that matter was formed of "solid, massy, hard, unpenetrable, moveable particles" which were "so very hard, as never to wear or break in pieces."

Modern research has provided abundant evidence of the real existence of atoms and molecules, whilst at the same time demonstrating that they are neither indestructible nor indivisible. The atoms and molecules are, however, extremely small, since there are $0.6025 \times 10^{24}$ atoms in 16 grams of oxygen, and a similar number of molecules in 18 grams of steam.

**Dalton's atomic theory** — The theory of atoms was of little value until Dalton, about 1802, added to it certain novel features, and showed that it could then be used to explain the laws of chemical combination. Dalton suggested that

(1) The ultimate particles of a pure substance, whether simple or compound, are perfectly alike in size and weight.

(ii) The "simple atoms" of an elementary substance are indivisible, and can neither be created nor destroyed

(iii) The "compound atoms" (or "molecules") of a compound are formed by the union of two or more elementary atoms

(iv) Combination between atoms takes place in the simplest integral ratios, *e g* 1 atom of *A* with 1, 2, or 3 atoms of *B*

The groups of "simple atoms," which Dalton called "compound atoms," cannot be separated without destroying the compound, but as they are not indivisible, they are now generally described as **MOLECULES** (*i e* little masses, Latin, *moles*, a mass) rather than atoms

**Atomic symbols.**—Dalton represented the atoms by means of symbols, *e g* hydrogen ○, oxygen ⊙, water ○○ This pictorial representation was improved by Berzelius, who suggested in 1819 that the elements might be represented more conveniently by their initial letters, *e g* Hydrogen H, Oxygen O, Water $H_2O$ *

When several elements had the same initial letter, Berzelius proposed to use a single letter to represent the chief non-metallic element and to add a second letter to distinguish the metals, or other non-metals having the same initial As examples he gives

| | |
|---|---|
| S = Sulphur | C = Carbonicum (carbon) |
| Si = Silicium (silicon) | Co = Cobaltum (cobalt) |
| Sb = Stibium (antimony) | Cu = Cuprum (copper) |
| Sn = Stannum (tin) | |

The majority of Berzelius' symbols are easily recognised abbreviations, exceptions are found in the case of elements which are represented by entirely different names in Latin and in English, *e g*

| | | |
|---|---|---|
| Gold | Aurum | Au |
| Silver | Argentum | Ag |
| Copper | Cuprum | Cu |
| Iron | Ferrum | Fe |
| Lead | Plumbum | Pb |
| Tin | Stannum | Sn |
| Mercury | Hydrargyrum † | Hg |
| Antimony | Stibium | Sb |
| Sodium | Natrium | Na |
| Potassium | Kalium | K |

**The laws of chemical combination explained by the atomic theory.**—The chief merit of Dalton's atomic theory was the simple and obvious explanation which it gave of the laws of chemical combination, namely

(*a*) *The Laws of Conservation of Mass* and of the *Indestructibility of Matter*

(*b*) *The Law of Constant Proportions*

(*c*) *The Law of Multiple Proportions*

(*d*) *The Law of Reciprocal or Equivalent Proportions.*

* Unlike Dalton, Berzelius supposed that the molecule of water contained *two* atoms of hydrogen for each atom of oxygen

† From Greek ὕδωρ, water, ἄργυρος, silver, *i e* liquid silver or "quick-silver"

(*a*) **Conservation of mass.**—The law of INDESTRUCTIBILITY OF MATTER states that

*Matter can neither be created nor destroyed*

This law was postulated in unequivocal terms by Newton, who supposed that the atoms could not " wear or break in pieces, no ordinary power being able to divide what God Himself made one in the first creation " The LAW OF CONSERVATION OF MASS postulates that

*The mass of an atom or molecule is constant, e g that it is independent of temperature and is not altered by chemical combination*

Incidentally, the law of conservation of mass implies that

*Heat and light are imponderable*

This law had been tested experimentally by Lomonosoff in 1756, and by Lavoisier in 1774, when they calcined tin in a sealed flask and found that no change of weight took place until the flask was opened The law of conservation of mass was therefore firmly founded when Dalton developed his atomic theory, but it finds its simplest interpretation in his suggestion that chemical changes involve only a regrouping of the atoms to form different molecules, and that the mass of an atom is independent of the nature of the other atoms with which it is combined

Modern physics has made it necessary to qualify the Law of Indestructibility of Matter, in the sense in which it was understood by Newton and by Dalton, since the study of radioactivity has proved (i) that many of the heaviest atoms are unstable and undergo spontaneous disintegration into simpler atoms, and (ii) that this disintegration is so violent that the particles emitted in the process can shatter atoms which are otherwise quite stable

The Law of Conservation of Mass is also admitted to be inexact, since it is now agreed that mass $m$ and energy $E$ are interconvertible, the relation being expressed by the equation $E = mc^2$, where $c$ is the velocity of light The changes of mass due to liberation of energy are, however, extremely small, since the heat set free in burning a gram of hydrogen would represent a loss of only two millionths of a milligram On the other hand, the prolonged emission of radiation from the sun and stars is now explained by a wholesale conversion of matter into energy, but under conditions which cannot be realised in the laboratory

(*b*) **Constant composition of chemical compounds.**—The LAW OF CONSTANT PROPORTIONS states that

*Compounds are formed by the combination of elements in fixed proportions by weight*

This law was tacitly assumed and experimentally verified by Black in his experiments on the burning of chalk to lime, and by Cavendish and Lavoisier in their experiments on the composition of water It was formulated in a precise form in 1802 by the French chemist, Proust, who asserted that the proportions in which the elements combine are " fixed by nature " and that the " power of augmenting or diminishing " these proportions

" is not given to men " Thus his experiments showed that there was no difference of composition between natural and artificial carbonate of copper, and that " in art as in nature copper never oxidises beyond 26% "

The law of fixed proportions was challenged in 1803 by Berthollet, who, in his *Essay on Chemical Statics*, maintained that elements can combine in variable proportions, although products of constant composition may often be separated by distillation or crystallisation Thus *zinc* burns to a volatile oxide of constant composition , but *lead* on oxidation becomes progressively grey, yellow and red without giving any indication of forming an oxide of constant composition Proust, however, was able to appeal to the general experience of chemical workers when he made fixity of composition the hall-mark of a definite CHEMICAL COMPOUND Thus nitre can dissolve in water *in any proportions*, but the product is not a stable chemical compound but a mere SOLUTION, from which the nitre can be recovered by evaporation On the other hand, nitre itself is formed by the neutralisation of potash and nitric acid *in fixed proportions by weight* The product is therefore a chemical compound of constant composition It differs in every possible way from the materials from which it was made and cannot be reconverted into them by any simple process of crystallisation or distillation

From these statements, it is clear that the law of fixed proportions, like the law of conservation of mass, was developed independently of Dalton's atomic theory , but it found a simple explanation in the postulate that the atoms of each element are alike in weight, and that the composition of every compound is therefore fixed by the number and weight of the atoms of which its molecules are composed

(*c*) **Multiple proportions.**—Dalton's LAW OF MULTIPLE PROPORTIONS states that

> *When two elements combine together to form more than one compound, there is a simple ratio between the different weights of one element which combine with a fixed weight of the other element*

Thus, if two elements $A$ and $B$ unite to form two or more compounds, there is a simple integral ratio between the different weights of $A$ which combine with a fixed weight of $B$

Proust in 1802 had already recognised that many pairs of elements can combine together in more than one fixed proportion, *e g*

Sulphur to iron = 60 100 *minimum* (really 57 100),
" " = 90 100 *maximum* (really 114 100) ,

but he did not recognise any relationship between these quite incorrect minimum and maximum proportions Dalton, however, under the guidance of his atomic theory, concluded that combination between the atoms $A$ and $B$ of two elements *must* take place in simple integral ratios such as

$$A\ B,\ A\ 2B,\ 2A\ B,\ A\ 3B,\ 3A\ B, \text{ etc}$$

He was therefore able to recognise, in the equally doubtful analyses at his

disposal, evidence of the existence of "multiple proportions" in the oxides of carbon and nitrogen, *e g*

| | Dalton's symbol | | Berzelius' symbol |
|---|---|---|---|
| Carbon monoxide - - | ●○ | or | CO |
| Carbon dioxide - - | ○●○ | or | $CO_2$ |
| Nitric oxide - - - | ○① | or | NO |
| Nitrous oxide - - | ①○① | or | $N_2O$ |
| Nitrogen peroxide - - | ○①○ | or | $NO_2$ |

The accuracy of the law of multiple proportions was established by Berzelius in the following cases

$$PbO,\ PbO_2,\ SO_2,\ SO_3,\ CuO,\ Cu_2O,\ FeS,\ FeS_2,\ FeO,\ Fe_2O_3$$

It was afterwards confirmed by more precise analyses of the oxides of carbon, and by Stas's exact determinations of the ratio of silver to oxygen in $AgClO_3$ and $Ag_2SO_4$

(*d*) The **law of reciprocal proportions** is discussed in Chapter II

EXPT 1 **Conservation of mass during precipitation**

A test tube of silver nitrate solution is suspended in a corked conical flask containing sodium chloride solution, and the whole apparatus is then weighed On tipping the flask the following reaction takes place

$$NaCl + AgNO_3 \rightarrow NaNO_3 + AgCl$$

The flask is reweighed, no alteration in weight should be observed

EXPT 2 **Conservation of mass in combustion of phosphorus**

A round-bottomed Jena flask (500 c c ), fitted with a rubber stopper and containing a little sand and a small piece of yellow phosphorus is weighed The phosphorus is then ignited by warming the flask cautiously above a small flame, and the flask is rotated behind one's back until the phosphorus has burnt out The sand protects the flask from the intense heat of combustion, which otherwise might crack it When cold, the flask is reweighed and should weigh the same as before, in spite of the heat and light that are lost during the combustion

EXPT 3 **Conversion of silver into silver chloride**

The Law of Constant Proportions may be verified by synthesising silver chloride in two different ways, as expressed by the equations

(*a*) $2Ag + Cl_2 = 2AgCl$,

(*b*) $3Ag + 4HNO_3 = 3AgNO_3 + 2H_2O + NO$,

$AgNO_3 + HCl = AgCl + HNO_3$

(*a*) About half a gram of silver wire or foil is weighed into a boat, heated in a stream of dry chlorine until the silver has disappeared, and weighed again when cold The silver is thus converted into silver chloride and the amount of chlorine which combines with 1 gram of silver is calculated from the weights of silver and of silver chloride

(*b*) Silver foil (about a gram) is weighed out into a weighed dry boiling-tube and dissolved in the minimum quantity (7 c c or so) of nitric acid of about 25 % strength Concentrated hydrochloric acid is added to precipitate the silver as chloride, and the mixture evaporated to dryness by cautiously heating over a Bunsen flame, the boiling-tube being held in a sloping position to avoid loss through spraying The tube containing the dry chloride is reweighed and the amount of chlorine which combines with 1 gram of silver is calculated

EXPT 4 **Analysis of cupric and cuprous oxides.**

About two grams of "precipitated" ***cupric oxide,*** previously dried by ignition in air, are weighed out into a weighed test tube which has a hole

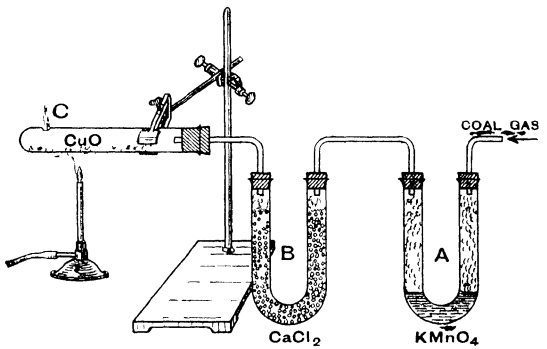



FIG 1 REDUCTION OF COPPER OXIDE

*C* (Fig 1) near the closed end Coal gas is purified from sulphur compounds by washing with strong alkaline permanganate in a U-tube *A* containing beads or glass-wool to increase the surface of contact It is then dried by calcium chloride in the U-tube *B*, and passed over the oxide, which is spread out to present as large a surface as possible When all the air has been expelled from the apparatus, the surplus gas is ignited at *C*, and the test tube heated strongly for about 15 minutes The finely divided copper is then allowed to cool in a stream of coal gas, to prevent oxidation by the air, and the test tube is reweighed It is advisable to place an evaporating dish under the cooling test tube as it often breaks The experiment is repeated with about one gram of *cuprous oxide*, which must be freshly prepared (p 315), and dried in a desiccator The weights of copper combined with 8 grams of oxygen in cupric and cuprous oxides are then calculated and should be in the ratio of 1 2

## CHAPTER II

## CHEMICAL EQUIVALENTS

**The law of reciprocal proportions.**—The LAW OF RECIPROCAL PROPORTIONS states that

> *The relative proportions in which two elements combine with a third element are in a simple ratio to those in which they combine* (a) *with one another or* (b) *with a fourth element*

(*a*) In *water*, hydrogen and oxygen are combined in the proportion

1 *part of hydrogen* 8 *parts of oxygen*

In *methane*, hydrogen and carbon are combined in the proportion

1 *part of hydrogen* 3 *parts of carbon*,

whilst in *ethylene*, the proportion is

1 *part of hydrogen* 6 *parts of carbon*

What will happen if oxygen, on the one hand, combines with carbon on the other? The Law of Reciprocal Proportions suggests that the elements will combine in the proportion of

8 *parts of oxygen* 3 *parts of carbon* or
8 *parts of oxygen* 6 *parts of carbon*

Actually, three oxides of carbon are known in which the proportions are as follows

| | | |
|---|---|---|
| Carbon dioxide, | *oxygen* *carbon* = 8 | 3 |
| Carbon monoxide, | *oxygen* *carbon* = 8 | 6 |
| Carbon suboxide, | *oxygen* *carbon* = 8 | 9 |

(*b*) Suppose that oxygen and carbon unite with a fourth element such as sulphur The Law of Reciprocal Proportions suggests that 3 *parts of carbon* and 8 *parts of oxygen*, which have been shown to unite with equal weights of hydrogen, will also unite with equal weights of sulphur, or that some simple multiples of these numbers will be involved In practice it is found that 16 *parts of sulphur* unite with 3 *parts of carbon* and with 16 *or* 24 *parts of oxygen*

**The law of reciprocal proportions and the theory of equivalents or combining-weights.**—The law of reciprocal proportions leads directly to the idea that each element has a definite COMBINING-WEIGHT or EQUIVALENT, and that when elements combine together they do so in simple multiples of these quantities Thus, in the examples already quoted, it is clear that

*one part of hydrogen*, *three parts of carbon*, *eight parts of oxygen*, and *sixteen parts of sulphur* represent in the simplest possible way the relative weights of these elements which are found in combination with each other or with other elements The importance of these equivalents or combining weights consists in the fact that, when they have once been determined by means of a small number of very careful analyses, they can be used to calculate the exact composition of all the other compounds of these elements This fact was realised for the first time in 1807 by Berzelius, who devoted most of his life to the accurate analyses that are needed to establish a correct table of equivalents Even greater care and painstaking accuracy were shown in the measurements of Stas extending over more than forty years, from 1840 to 1882 In more recent years much work of this character was carried out at Harvard University by Prof T W Richards

**Definition of equivalent or combining weights** —In establishing a table of combining weights or equivalents it is necessary to select a fixed weight of some one element as a standard Dalton in 1808 selected *one part of hydrogen* This standard has been used very widely, in accordance with the following definition

*The equivalent weight of an element is that weight which combines with or takes the place of one part by weight of hydrogen*

In this definition the smallest of the equivalents is selected as the standard, so that all the others are greater than unity In particular, since hydrogen and oxygen combine in the ratio H O = 1 8 (approx ) to form water, the equivalent of oxygen is approximately eight

At the present time oxygen has taken the place of hydrogen as the standard on which all other equivalent weights are based, in accordance with the following definition

*The equivalent weight of an element is that weight which combines with or takes the place of eight parts by weight of oxygen*

This change has been made for three principal reasons

(i) All the elements except a few inert gases (p 63) form compounds with oxygen, which are generally very stable, whereas only about one-third of them combine with hydrogen The combining weight of an element relatively to oxygen can therefore usually be determined directly by analysis of an oxide, whereas the determination of the combining weight relatively to hydrogen often involves the measurement of two ratios, *e g*

$$\text{Cu O} = 31\,5\ 8, \quad \text{H O} = 1\ 8, \qquad \text{Cu H} = 31\,5\ 1$$

The accuracy finally attained is obviously that of the less accurate of these two ratios

(ii) It is inconvenient to use a very light element as a standard, because of the wide inequality of the weights to be measured Thus the lightness of hydrogen is one of the principal difficulties that has to be surmounted when determining the composition of water, since the hydrogen ought to be weighed to one more decimal place than the oxygen or the water in

order to give the same proportional accuracy This difficulty is even more extreme in the case of chlorine, where the ratio of hydrogen to chlorine in hydrogen chloride is H Cl = 1 35 5 On the other hand, in potassium chlorate the oxygen-ratios are almost unity, namely

K Cl · O = 39 35 5 48

(iii) It happens that a considerable number of equivalents are almost exact integers when O = 8 and H = 1 0078, but deviate more widely from whole numbers when H = 1 and O = 7 939

**Experimental determination of equivalents** —In general, equivalents can be determined by (i) *synthesis*, as when hydrogen is burnt to water or copper to copper oxide in order to determine the ratios H O and Cu O, or (ii) *analysis*, as when copper oxide is reduced to copper in order to determine the proportion of metal in the oxide The methods finally selected are influenced by the nature of the element, as metal or non-metal, and by the magnitude of the equivalent, since it is desirable to avoid any wide disparity in the weights to be measured One of the best methods is to make a complete analysis of an oxy-salt, which contains oxygen in combination with a metal and a non-metal, so that the equivalents of both can be determined from the analysis of a single salt

**Equivalents of non-metals.**—(*a*) *Synthesis of hydrides* —This method can only be used in exceptional cases , but exact determinations of the equivalents of oxygen and chlorine have been made by burning known weights of hydrogen in weighed quantities of oxygen (p 83) and chlorine and weighing the water and hydrogen chloride produced

$$2H_2 + O_2 = 2H_2O \qquad H_2 + Cl_2 = 2HCl.$$

(*b*) *Synthesis and analysis of oxides* —Combustion in oxygen can be used to determine the equivalents of many non-metals relative to oxygen, but the only exact determinations of any importance are (i) the burning of hydrogen to water as described above, and (ii) the burning of carbon and of carbon monoxide to carbon dioxide (pp 143 and 145) in order to deduce the combining weight of carbon relatively to oxygen

$$C + O_2 = CO_2 \qquad 2CO + O_2 = 2CO_2$$

On the other hand, the equivalent of nitrogen has been deduced from an analysis of nitric oxide (p 193) For this purpose metallic nickel was burnt in the gas, as represented by the equation

$$2NO + 2Ni = 2NiO + N_2$$

The nitrogen was weighed as an element, and the oxygen as nickel oxide formed on the surface of electrically heated nickel

(*c*) *Analysis of oxy-salts* —Oxy-salts such as potassium chlorate, $KClO_3$, silver sulphate, $Ag_2SO_4$, and lead nitrate, $Pb(NO_3)_2$, were analysed by Berzelius and by Stas in order to determine the oxygen-equivalents of chlorine, sulphur and nitrogen, as well as of the metals which they contain The method has the advantage that direct determinations of the ratio of non-metal (or metal) to oxygen can be made under very favourable conditions, arising from the fact that the salts are readily prepared and purified, and often contain a conveniently large

proportion of oxygen * Thus in potassium chlorate the proportions of the elements are

*potassium chlorine oxygen* = 39 35½ 48

In order to determine the equivalent of chlorine relatively to oxygen from the analysis of a chlorate (or perchlorate) it is necessary to know how many equivalents of chlorine and oxygen are present in the salt, since the combining ratios are not the same as in the simple oxides of chlorine We therefore suppose that the approximate equivalents of chlorine and oxygen have already been determined as 35½ 8, and that the chlorate is therefore known to contain *six* equivalents of oxygen for each equivalent of chlorine Details of Stas's analyses of potassium chlorate are given below

(i) Potassium chlorate, which contains six equivalents of oxygen in combination with one of potassium and one of chlorine, was converted into potassium chloride by removing the oxygen

(a) by ignition,

(b) by heating with hydrochloric acid

It was found that 100 parts of potassium chlorate gave 60 846 parts of potassium chloride and therefore lost in this process 39 154 parts of oxygen; six equivalents, or 48 parts, of oxygen were therefore combined with $48 \times \frac{60\ 846}{39\ 154} = \mathbf{74\ 592}$ parts of potassium chloride This number is the equivalent of *potassium chloride*

(ii) The weight of potassium chloride was determined which was required to precipitate (as silver chloride) a known weight of silver dissolved in nitric acid It was found that 74 592 parts of potassium chloride would precipitate **107 943** parts of silver , this number is the equivalent of *silver*

(iii) By a variety of methods it was found that 100 parts of silver combined with 32 845 parts of chlorine to form 132 845 parts of silver chloride Since in these experiments 107 943 parts of silver combined with $\frac{32\ 845}{100} \times 107\ 943 = \mathbf{35\ 454}$ parts of chlorine, this number is the equivalent of *chlorine*

(iv) Subtracting 35 454 (the equivalent of chlorine) from 74 592 (the equivalent of potassium chloride), the equivalent of *potassium* is found to be **39 138**

(*d*) *Analysis of silver salts* —The determination of the ratios

$KClO_3$ KCl AgCl Ag, etc ,

has given a very exact value for the equivalent of *silver* relative to oxygen, namely Ag = 107 880 This number has therefore become an important secondary standard for determining the combining weights of the non-metals, *e g* the atomic weight of sulphur has been deduced by synthesis and analysis of silver sulphide, $Ag_2S$

* The oxy-salts were regarded by Lavoisier as formed by the union of the basic oxide of a metal with the acidic oxide of a non-metal Silver sulphate therefore contains the oxygen of silver oxide and of sulphur trioxide $Ag_2O + SO_3 = Ag_2SO_4$, and the ratio of oxygen to silver is four times as great as in silver oxide

**Equivalents of metals.**—The following methods are available for determining the equivalents of metallic elements

(*a*) *Displacement of hydrogen* —The equivalent of a metal which dissolves in dilute acid can be determined by measuring the volume of hydrogen liberated and deducing its weight from the known density of the gas As a laboratory exercise, this method can be used to determine the hydrogen equivalents of zinc and magnesium by dissolving the metal in dilute sulphuric acid, or of aluminium by dissolving it in caustic soda

$$Zn + H_2SO_4 = ZnSO_4 + H_2 \qquad Mg + H_2SO_4 = MgSO_4 + H_2$$
$$2Al + 2NaOH + 2H_2O = 2NaAlO_2 + 3H_2$$

During the period when hydrogen was still taken as a standard of combining weights, this method was also used for an exact determination of the ratio Zn $H_2$, but the principal interest of this work was to show that highly-purified zinc would not dissolve in dilute acids

(*b*) *Displacement of metals* —Zinc will displace copper from its salts, copper will displace silver, and in general a more "electropositive" metal (p 52) will displace a less electropositive metal from its salts The equivalents of metals may therefore be compared directly by displacement of one metal by another, *e g*

$$Zn + CuSO_4 = Cu + ZnSO_4 \qquad Fe + CuSO_4 = Cu + FeSO_4$$

This method provides good laboratory exercises, but is not usually suitable for exact measurements, since the precipitate of finely divided metal is often too impure for this purpose An exact determination of the ratio P = 5Ag has, however, been made by precipitating silver from silver sulphate by the addition of weighed quantities of pure phosphorus

$$2P + 5Ag_2SO_4 + 8H_2O = 10Ag + 2H_3PO_4 + 5H_2SO_4$$

(*c*) *Comparison of electrochemical equivalents* —Faraday's Second Law of Electrolysis (p 596) states that the weights of different metals deposited by the same current are proportional to their chemical equivalents By arranging a copper voltameter and a silver voltameter (p 596) in series, it is possible to compare the chemical equivalents of copper and silver This provides another interesting laboratory exercise, moreover, by working under carefully controlled conditions it is possible to avoid the complications that arise from the formation and decomposition of cuprous sulphate and to secure results which are in agreement with those obtained by other methods, but the results obtained are only of secondary importance

(*d*) *Interchange of radicals* —The combining weight of a metal can be deduced from a comparison of the weights of two of its salts Thus one part of barium chloride yields 1 12 parts of barium sulphate If, therefore, we assume the equivalents Cl = 35 5 and $\frac{1}{2}SO_4 = 48$, the equivalent of barium * can be deduced from the equation

$$\frac{BaSO_4}{BaCl_2} = \frac{x + 48}{x + 35\ 5} = 1\ 12, \text{ whence } x = 68{\cdot}5.$$

* The equivalents of calcium and barium are one half of their atomic weights The equivalent of oxygen is one half of its atomic weight, and those of the sulphate and carbonate radicals are one half of the formula weights of these radicals, namely $\frac{1}{2}SO_4 = 48$, $\frac{1}{2}CO_3 = 30$

The accuracy of this method obviously depends on using two radicals with widely different equivalents, and in the case cited above it is very small The conversion of a carbonate into an oxide has, however, been used for determining the equivalent of calcium* by burning chalk to lime, and gives results which are comparable in accuracy with the analysis of an oxy-salt as described above

$$\frac{CaO}{CaCO_3} = \frac{x+8}{x+30} = 0\ 56, \text{ whence } x = 20\ 0$$

(*e*) *Analysis and synthesis of oxides* —A direct determination of the combining weight of a metal relatively to oxygen can be made by synthesis or analysis of an oxide Thus copper may be converted to copper oxide by direct oxidation or by dissolving in nitric acid and igniting to the oxide, or the oxide may be reduced to metal by heating in a stream of hydrogen or purified coal gas

$$2Cu + O_2 = 2CuO \qquad 3Cu + 8HNO_3 = 3Cu(NO_3)_2 + 4H_2O + 2NO$$
$$2Cu(NO_3)_2 = 2CuO + 4NO_2 + O_2 \qquad CuO + H_2 = Cu + H_2O$$

These methods provide excellent laboratory exercises, and the results which can be obtained are comparable with those given by a comparison of electrochemical equivalents, but they do not lend themselves to measurements of the highest order of accuracy

(*f*) *Analysis of halides* —The analyses of oxy-salts (p 10) have established a series of very exact equivalents, especially

$$Ag = 107\ 880 \qquad Cl = 35\ 457 \qquad Br = 79\ 916$$

The most accurate method for determining the equivalent of a metal is therefore to take a known weight of the chloride of a light metal, or of the bromide of a heavy metal, and to determine the weight of pure silver which must be used (in the form of silver nitrate) to precipitate exactly the halogen which it contains The equivalent of the metal is then defined by the weight of metal which combines with the same weight of chlorine or bromine as 107 880 parts of silver In this way the exact equivalent of calcium has been deduced from the ratio $CaCl_2$ 2Ag, and that of lead from the ratio $PbBr_2$ 2AgBr 2Ag, using the equivalent of *silver* as a secondary standard

EXPT 5 **Equivalent of tin by the synthesis of stannic oxide**

Concentrated nitric acid, 2 c c , is added to 0 5 gram of pure tin in a weighed dry test tube, which is held nearly horizontal to prevent loss by spraying When the reaction has subsided, the mixture is cautiously heated to complete the oxidation of the tin to stannic oxide, $SnO_2$ (equations, p 165) and to drive off the excess acid and moisture When no more fumes are evolved the test tube is reweighed and the equivalent weight of tin is calculated from the weight of oxide thus produced

The above experiment may be repeated using copper or zinc in place of tin

* See footnote, p. 11.

**Expt 6 Analysis of calcium carbonate.** $CaCO_3 = CaO + CO_2$

Two grams of marble are ignited to constant weight in a crucible heated in a muffle furnace The percentage of lime is calculated from the weight of the residue The equivalent of the oxide can be deduced as the weight from which 22 parts of carbon dioxide have been lost To deduce the equivalent of calcium subtract eight from the equivalent of lime

**Expt. 7 Equivalent of magnesium or zinc by displacement of hydrogen**

The weighed metal (about 0 2 gram of magnesium ribbon, or 0 5 gram of zinc foil) is placed in the bottom of the conical flask *A*, which contains water and a small test tube of concentrated hydrochloric acid The flask, *A*, is connected to a large flask, *B*, full of water, and fitted with a cork and delivery tube leading to a measuring cylinder, *C* The tube, *Y*, is filled with water at the start of the experiment by sucking at its open end The latter is then placed in the cylinder, *C*, which is filled with water to the same level as that in *B*, so that the pressure of the air in *A* and *B* may be the same as that of the atmosphere The clips at *X* and *Y* are then put in position and the cylinder *C* emptied of water On tipping the flask, the acid attacks the metal and the hydrogen evolved displaces its own volume of water into the measuring cylinder *C*, the clips at *X* and *Y* being simultaneously released When the apparatus has cooled down, the water in *B* and *C* is adjusted to the same level, and its volume in *C* is read This volume is reduced to N T P and the equivalent of the metal calculated as that weight of it which liberates 1 gram of hydrogen from the acid

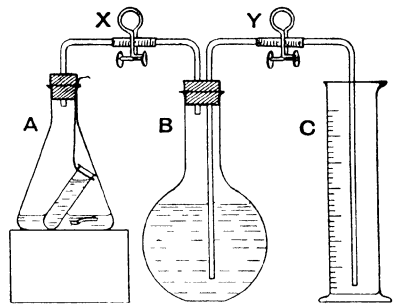



Fig 2 Displacement of Hydrogen by Metals

**Expt 8 Equivalents of potassium, chlorine and silver by analysis of potassium chlorate**

(*a*) About 1 gram of pure potassium chlorate is weighed out into a hard glass test tube, and ignited to constant weight The equivalent of potassium chloride is the weight which is left behind when 48 parts (6 equivalents) of oxygen have been set free

(*b*) About 2 grams of pure potassium chloride are weighed out and made up to 250 c c with water Portions of this are then titrated against a solution of silver nitrate containing a known weight, say 10 gm , of silver per litre (see p 431) The equivalent of silver is calculated as that weight of it which reacts with one equivalent weight of potassium chloride

(*c*) The synthesis of silver chloride (p 5) is then used to deduce the equivalent of chlorine, namely that weight of chlorine which combines with the equivalent of silver The equivalent of potassium can then be deduced by subtracting the equivalent of chlorine from that of potassium chloride

## CHAPTER III

### THE MOLECULAR THEORY

**The atomic and molecular theories.**—The chief purpose of Dalton's Atomic Theory was to explain the laws which determine the composition of chemical compounds This theory is therefore concerned with the masses of the *atoms* of different elements and the numerical ratios in which the atoms combine with one another, since these two factors control the composition of all their compounds The molecular theory, which we owe to Avogadro (1811), is concerned in the first instance with the relative masses of the *molecules* of which gaseous elements and compounds are composed, and was introduced in order to account for the extremely simple properties which characterise all substances when in the gaseous state Thus

(*a*) All gases behave in a similar way towards changes of pressure and temperature, since they obey, at least approximately,

(i) BOYLE'S LAW, $pv = k$, when $T$ is constant (Chapter XXXIII, p 454),

(ii) CHARLES' LAW, $v = kT$, when $p$ is constant (Chapter XXXIII, p 454)

No such simple relationship exists amongst solids and liquids, since each of these has its own characteristic coefficients of compressibility and of thermal expansion

(*b*) According to Gay Lussac's LAW OF VOLUMES *

*The volumes of gases entering into, or formed by, a chemical reaction bear a simple numerical relation to one another, when measured under the same physical conditions*

No equally simple relation is found in the combining *weights* of elements and compounds, even when these approximate (as they do in many cases) to integral values , and no relationship at all can be found amongst the

* The following examples of this law may be recalled with the help of equations

$$\underset{1\ vol}{C} + \underset{1\ vol}{O_2} = \underset{1\ vol}{CO_2} \qquad \underset{2\ vols}{2CO} + \underset{1\ vol}{O_2} = \underset{2\ vols}{2CO_2} \qquad \underset{1\ vol}{S} + \underset{1\ vol}{O_2} = \underset{1\ vol.}{SO_2}$$

$$\underset{2\ vols}{2H_2} + \underset{1\ vol}{O_2} = \underset{}{2H_2O} \qquad \underset{1\ vol}{H_2} + \underset{1\ vol.}{Cl_2} = \underset{2\ vols}{2HCl} \qquad \underset{2\ vols}{2NH_3} = \underset{1\ vol}{N_2} + \underset{3\ vols}{3H_2}$$

$$\underset{1\ vol}{CH_4} = \underset{}{C} + \underset{2\ vols}{2H_2}. \qquad \underset{1\ vol}{C_2H_4} = \underset{}{2C} + \underset{2\ vols.}{2H_2}$$

$$\underset{1\ vol}{CH_4} + \underset{2\ vols}{2O_2} = \underset{1\ vol}{CO_2} + \underset{}{2H_2O} \qquad \underset{1\ vol,}{C_2H_4} + \underset{3\ vols,}{3O_2} = \underset{2\ vols}{2CO_2} + \underset{}{2H_2O}$$

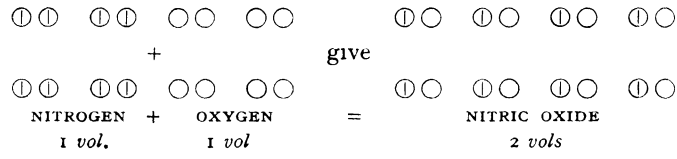
combining *volumes* of liquids and solids, so that this phenomenon is limited strictly to gases and vapours

**Dalton's theory of the equal spacing of particles in gases.**—Dalton in 1802 tried to explain the properties of gases by supposing that the spaces occupied by the ultimate particles of gases are all equal, so that a given volume of oxygen gas would contain the same number of particles as an equal volume of hydrogen gas, and so forth He abandoned this theory on the following grounds If it be assumed that the ultimate particles of nitrogen, oxygen, and nitric oxide all occupy equal volumes, it is evident (i) that the combination of a simple particle of nitrogen with a simple particle of oxygen to form a compound particle of nitric oxide must be accompanied by a decrease of volume, since the number of particles is reduced by combination , and (ii) that the density of the gas must be increased thereby Actually, Davy had shown that this combination was not accompanied by any change of volume, and that the density of nitric oxide was intermediate between those of nitrogen and oxygen, and therefore actually less than that of the oxygen which was one of its constituents Since these facts were completely at variance with his theory as to the equal spacing of the particles, Dalton was obliged to discard the simple views by which he had sought to explain the simple properties of gases

**Avogadro's hypothesis** —Dalton's theory was revived in 1811 by the Italian physicist Avogadro AVOGADRO'S HYPOTHESIS states that

*When the temperatures and pressures are the same, equal volumes of different gases contain equal numbers of molecules*

The difficulty which Dalton had found in applying this hypothesis was removed when Avogadro suggested that the molecules of an elementary gas need not be composed of single atoms, as Dalton had supposed, but might consist of groups of similar atoms, corresponding precisely with the groups of dissimilar atoms which form the molecules of a compound gas Thus, if the molecules of nitrogen and oxygen as well as those of nitric oxide were assumed to contain two atoms each, there need be no change of volume and no change of density when a mixture of nitrogen and oxygen was converted into nitric oxide This may be shown by means of the following diagrams




The chemical change is here represented, not as a direct combination of atoms of nitrogen with atoms of oxygen, but as a double decomposition in which an interchange of atoms takes place between diatomic molecules of the two elements

**Applications of Avogadro's hypothesis.**—Avogadro's hypothesis enables us (*a*) to compare the molecular weights of different gases and vapours,

(*b*) to determine the number of atoms in the molecule of a gaseous element and thus to deduce its atomic weight, (*c*) to determine the number of each kind of atom in the volatile compounds of volatile elements, and thus to deduce molecular formulae for these compounds, (*d*) to express by means of a chemical equation any chemical change involving only volatile elements and compounds These direct applications of Avogadro's hypothesis are described below , the indirect applications of Avogadro's hypothesis, to deduce the atomic weights of non-volatile elements, as well as the molecular formulae of non-volatile compounds, are described in Chapter IV

(*a*) **Comparison of molecular weights by means of Avogadro's hypothesis.**—Avogadro's hypothesis tells us that equal volumes of different gases at the same temperature and pressure contain equal numbers of molecules The ratio of the weights of single molecules of gases is therefore given by the ratio of their densities, *i e* by the ratio of the weights of one litre of each gas at S T P

Since Avogadro's hypothesis only gives the relative weights of the molecules, it is necessary to select a standard gas, with the density and molecular weight of which those of other gases and vapours can be compared Hydrogen was first selected for this purpose, because it was the lightest gas, so that the relative densities * of all other gases were then greater than unity The molecular weight of an element or compound was then defined as the number of times its molecule was heavier than the atom of hydrogen, the latter being taken as unity The molecule of hydrogen, however, contains *two atoms* (see below), so that its molecular weight is 2 and not 1 The molecular weights of other gases and vapours were therefore deduced by doubling the density relative to hydrogen

At the present time, relative densities are calculated and molecular weights are deduced relatively to oxygen, on the assumption that the molecule of oxygen also is diatomic and that its molecular weight is 32 On this basis the molecular weight of hydrogen is not 2, but $2 \times 1\ 0081$ , but the difference between the two standards is so small that it is unnecessary to discriminate between them in the following discussion

(*b*) **Atomicity of gaseous elements.**—In accordance with Avogadro's hypothesis, we can substitute *molecules* for *volumes* in all chemical changes in which gaseous elements and compounds are involved, *e g*

| | | |
|---|---|---|
| hydrogen + chlorine = hydrogen chloride. | | |
| 1 *vol* | 1 *vol* | 2 *vols* |
| 1 *mol* | 1 *mol* | 2 *mols* |

| | | |
|---|---|---|
| hydrogen + oxygen = water (gaseous). | | |
| 2 *vols* | 1 *vol* | 2 *vols* |
| 2 *mols* | 1 *mol* | 2 *mols* |

* The term VAPOUR DENSITY is often used to describe the ratio wt of gas or vapour/wt of an equal volume of hydrogen under the same physical conditions, but it is hardly satisfactory to speak of the vapour density of a permanent gas, nor does the term itself imply a ratio, hence in this book the above ratio is called the RELATIVE DENSITY

| nitrogen | + oxygen | = nitric oxide |
|---|---|---|
| 1 *vol* | 1 *vol* | 2 *vols* |
| 1 *mol* | 1 *mol* | 2 *mols* |

| nitrogen | + hydrogen | = ammonia |
|---|---|---|
| 1 *vol* | 3 *vols* | 2 *vols* |
| 1 *mol* | 3 *mols* | 2 *mols* |

From these equations it appears that no subdivision of the molecule of hydrogen takes place when this gas combines with oxygen to form an equal number of molecules of water vapour, but the molecule is obviously halved when *one* molecule of hydrogen yields *two* molecules of hydrogen chloride, or when *three* molecules of hydrogen are distributed equally amongst *two* molecules of ammonia. Since no further subdivision has been observed in any reaction in which gaseous hydrogen is involved, we conclude that the molecule of hydrogen contains two atoms and assign to it the formula $H_2$.

In the same way we notice that the molecules of oxygen and nitrogen are halved when they combine with one another to form two molecules of nitric oxide, the molecule of chlorine is also halved when it combines with hydrogen to form two molecules of hydrogen chloride. Since no further subdivision has been observed in other changes involving gaseous oxygen, nitrogen or chlorine, we conclude that the molecules of these gases are also diatomic, and assign to them the formulae $O_2$, $N_2$, $Cl_2$.

The complexity of these gaseous molecules has also been established by a purely physical method, namely by measuring the ratio of the specific heats at constant pressure and at constant volume (Ch. XXXIII, p. 460). The ratios for hydrogen, oxygen, nitrogen and chlorine are 1·41, 1·40, 1·40 and 1·34, whilst the kinetic theory of gases gives 1·66 for a monatomic gas and 1·40 for a diatomic gas. These gaseous elements are therefore diatomic. It must not be supposed, however, that the ATOMICITY of an elementary gas (*i.e.* the number of atoms in the molecule) is always *two*, since the inert gases of the atmosphere (p. 63) are monatomic, as are also most of the molecules in the vapours of metallic sodium, potassium and mercury. On the other hand, the molecules of ozone and of the vapours of phosphorus, arsenic and sulphur contain polyatomic molecules of $O_3$, $P_4$, $As_4$, $S_8$.

(*c*) **Atomic weights of gaseous elements.**—When the molecular weight and the formula of an elementary gas have been deduced by means of Avogadro's hypothesis, as described above, it is only necessary to divide the molecular weight by the atomicity in order to get the atomic weight of the element. Thus from the relationships

$$H_2 = 2,\ N_2 = 28,\ O_2 = 32,\ P_4 = 124,\ Cl_2 = 71,\ Hg = 200,$$

we deduce at once the following atomic weights

$$H = 1,\quad N = 14,\quad O = 16,\quad P = 31,\quad Cl = 35\tfrac{1}{2},\quad Hg = 200$$

(*d*) **Formulae of gaseous compounds.**—When the atomicities of the gaseous or volatile elements have been determined by means of

Avogadro's hypothesis, the formulae of their volatile compounds can be deduced from their volumetric composition, as follows

(i) *Steam* is formed by the explosion of two volumes of hydrogen and one volume of oxygen

| hydrogen | + oxygen | = steam | |
|---|---|---|---|
| 2 *vols* | 1 *vol* | 2 *vols* | (by experiment), |
| 2 *mols* | 1 *mol* | 2 *mols* | (by Avogadro's hypothesis), |
| ∴ 4 *atoms* | + 2 *atoms* | = 2 *mols* | (since hydrogen and oxygen are diatomic), |

or 2 *atoms* + 1 *atom* = 1 *mol*

The molecule of steam therefore contains two atoms of hydrogen and one atom of oxygen and is represented by the formula $H_2O$, instead of by the formula HO suggested by Dalton

(ii) *Ammonia* is decomposed by sparking as follows

| ammonia | = hydrogen + | nitrogen | |
|---|---|---|---|
| 2 *vols* | 3 *vols* | 1 *vol* | (by experment), |
| 2 *mols* | 3 *mols* | 1 *mol* | (by Avogadro's hypothesis), |
| ∴ 2 *mols* | = 6 *atoms* + | 2 *atoms* | (since hydrogen and nitrogen are diatomic), |

or 1 *mol* = 3 *atoms* + 1 *atom*

Hence the molecule of ammonia contains three atoms of hydrogen and one atom of nitrogen and is represented by the formula $NH_3$

It must be emphasised that Avogadro's hypothesis only enables us to pass from *volumes* to *molecules*, and not directly from volumes to *atoms* The fact that water is composed of hydrogen and oxygen in the ratio of two volumes to one volume does not prove by itself that the formula of water is $H_2O$, the coincidence between the number of atoms of hydrogen and oxygen in the molecule of steam and the combining volumes of these two gases is a mere accident depending on the fact that hydrogen and oxygen are both diatomic gases A similar statement may be made in reference to ammonia

The danger of omitting the intermediate step in the sequence *volumes*, *molecules*, *atoms* may be illustrated by the case of phosphine, where molecules containing unequal numbers of atoms are involved in the same equation

(iii) *Phosphine* can be decomposed at high temperatures, as shown in the following equations

| phosphine | = phosphorus + | hydrogen | |
|---|---|---|---|
| 4 *vols* | 1 *vol* | 6 *vols* | (by experiment), |
| 4 *mols* | 1 *mol* | 6 *mols* | (by Avogadro's hypothesis), |
| ∴ 4 *mols* | = 4 *atoms* | 12 *atoms* | (since the molecules are $P_4$ and $H_2$), |

or 1 *mol* = 1 *atom* + 3 *atoms*

The formula of phosphine is therefore $PH_3$ In this case the volumes of phosphorus and of hydrogen are in the ratio 1 : 6, but it would be incorrect to suppose that the formula of phosphine is therefore $PH_6$

(*e*) **Chemical equations.**—When the formulae of the molecules taking part in a gaseous reaction have been deduced as described under (*d*), it is only necessary to insert the appropriate symbols in order to express the reaction by means of a CHEMICAL EQUATION, *e g*

$$2H_2 + O_2 = 2H_2O,$$
$$2NH_3 = N_2 + 3H_2,$$
$$4PH_3 = P_4 + 6H_2$$

In each equation the numbers of molecules correspond with the volumes recorded above

**Absolute molecular weights.**—As we have already stated, Avogadro's hypothesis enables us to deduce the relative molecular weights of gases and vapours by measuring their densities, but it does not enable us to deduce the ABSOLUTE MOLECULAR WEIGHT, that is to say, the weight in grams of one molecule of the gas or vapour This figure has been deduced, however, by measuring $N$, the so-called AVOGADRO CONSTANT or AVOGADRO NUMBER, which represents the number of molecules in one gram-molecular weight (=number of grams numerically equal to the molecular weight) of an element or compound Many different methods have been employed to measure $N$, and the results generally agree with one another to a surprising degree, but the most accurate value is probably $6\ 025 \times 10^{23}$, and was obtained recently by the new X-ray method Since the gram-molecular weight of oxygen is 32 00 grams, it follows that the weight of one oxygen molecule is

$$\frac{32\ 00}{6\ 025 \times 10^{23}} = 5\ 310 \times 10^{-23} \text{ grams},$$

whilst the weight of the hydrogen molecule, the lightest of all molecules, is

$$\frac{2\ 016}{6\ 025 \times 10^{23}} = 0\ 3346 \times 10^{-23} \text{ grams}$$

# CHAPTER IV

## THE DETERMINATION OF ATOMIC WEIGHTS

**Atomic weights and equivalents.**—The atomic weight deduced by means of Avogadro's hypothesis is sometimes identical with the equivalent or combining weight of an element, but in other cases it is an integral multiple of it. The ratio is called the VALENCY of the element, thus

$$\text{Atomic weight} = \text{equivalent} \times \text{valency}$$

Equivalents can be determined very accurately by gravimetric analysis, as described in Chapter II Atomic weights, determined by the volumetric methods of Chapter III, are usually much less accurate , but they can be used to determine the whole number by which the equivalent must be multiplied in order to give the exact atomic weight The determination of atomic weights therefore takes place in the following stages

(i) The equivalent is determined as accurately as possible by gravimetric analysis

(ii) The atomic weight is determined approximately by one of the methods set out below

(iii) The valency is deduced by dividing the equivalent into the atomic weight, and taking the nearest integer as the correct number

(iv) The equivalent multiplied by the valency gives the *exact atomic weight*

(*a*) **Avogadro's method** —(i) The *molecular weight* of a gaseous element is deduced from its density (relatively to $O_2 = 32$) (ii) The *atomicity* of the gaseous element is determined by finding the largest number of parts into which the molecule can be divided in forming gaseous compounds (iii) The molecular weight divided by the atomicity gives the *atomic weight* of the element

This method is limited to gaseous (or volatile) elements which form gaseous (or volatile) compounds, and only gives exact atomic weights if the exact molecular weight of the gas has been determined by the methods described in Chapter XXXIII (p 468)

(*b*) **Cannizzaro's method.**—This is an extension of Avogadro's method which makes it applicable to non-volatile elements, such as carbon, provided that they form a number of volatile compounds The following definition is used

> *The atomic weight of an element is the smallest weight of it which is found in the molecular weight of any of its compounds*

The method depends on determining the molecular weights and per-

centage compositions of a large number of compounds of the element The weight of the element present in the molecular weight of each compound is calculated, and the smallest of these quantities (or the highest common factor) is taken as the atomic weight of the element The application of this method to *carbon* may be illustrated by the following table

| Compound | Molecular weight | Percentage of carbon | Weight of carbon per molecule |
|---|---|---|---|
| Carbon monoxide | 28 | 42 9 | 12 |
| Carbon dioxide - | 44 | 27 3 | 12 |
| Chloroform - | 119 5 | 10 0 | 12 |
| Methane - - | 16 | 75 0 | 12 |
| Ethylene - - | 28 | 85 7 | 24 |
| Acetylene - - | 26 | 92 3 | 24 |
| Benzene - - | 78 | 92 3 | 72 |

The smallest weight of carbon in the molecular weight of the above compounds is 12, and since this is also the smallest weight ever found in any carbon compound it is assumed to be the atomic weight

(*c*) **Dulong and Petit's method.**—The two methods described above are not usually available for determining the atomic weights of metallic elements, since the metals are nearly all difficult to vaporise and form very few volatile compounds, *e g* in the case of iron we have the following data

| Compound | Molecular weight | Weight of iron in molecular weight * |
|---|---|---|
| Ferrous chloride - | 125 6 | 56 (about) |
| Ferric chloride - - | 332 2 | 112 ,, |
| Iron carbonyl - - | 199 0 | 56 ,, |

This table suggests that the atomic weight of iron is probably 56, but the total number of volatile compounds is too small to exclude a risk that other compounds might be found to contain a smaller weight of iron, *e g* 28 parts. For this reason the atomic weights of the metals are usually determined by the method of Dulong and Petit Dulong and Petit's LAW OF ATOMIC HEATS (1819) states that

*The atoms of all simple substances have the same capacity for heat*

If we define the ATOMIC HEAT of an element as the product of its specific heat and atomic weight, we can express the law in an algebraic form as follows.

specific heat × atomic weight = atomic heat = 6 3 (approx).

An approximate value for the atomic weight of a metal can therefore be obtained by dividing its specific heat into 6 3

* The last column shows the weight of iron in the molecular weight, rounded off to the nearest multiple of the equivalent of iron.

The law of Dulong and Petit was based upon a study of the specific heats of elements whose atomic weights had been deduced by the methods described in the preceding chapters. It applies only to solid elements, and breaks down completely at low temperatures (p 59), but, if a few of the lighter elements are excluded, the atomic heats of the remaining metals do not vary much from an average value of 6 3 in the range from 20° to 100° The application of the method to some common metals is illustrated in Table 1.

TABLE 1 —SPECIFIC AND ATOMIC HEATS OF THE METALS

| Element | Equivalent | Sp ht (20° to 100°) | Approx. atomic weight | Valency | Exact at wt (Equiv × valency) | At ht (At wt × sp heat) |
|---|---|---|---|---|---|---|
| *1* | *2* | *3* | *4* | *5* | *6* | *7* |
| Iron - | 27 92 | 0 1146 | About 55 | 2 | 55 84 | 6 4 |
| Tin - | 59 5 | 0 0556 | About 113 | 2 | 119 0 | 6 6 |
| Lead - | 103 55 | 0 031 | About 203 | 2 | 207 10 | 6 4 |
| Copper | 31 785 | 0 0936 | About 67 | 2 | 63 57 | 6 0 |
| Silver - | 107 88 | 0 0566 | About 111 | 1 | 107 88 | 6 1 |
| Gold - | 65 73 | 0 0316 | About 199 | 3 | 197 2 | 6 2 |
| | | | | | Mean | 6 3 |

In this table the " approximate atomic weights " of column *4* are obtained by dividing the specific heats of column *3* into a fixed number, 6 3, representing the average atomic heat of the metals A comparison of columns *2* and *4* gives the integral valencies of column *5*. The exact atomic weights of column *6* are then obtained by multiplying together the equivalent (column *2*) and the valency (column *5*) In column *7* the individual values for the atomic heat (specific heat × exact atomic weight) are given in order to show the variations from the average value 6 3 of this " constant "

(*d*) **The law of isomorphism.**—The atomic weights of the metals can also be deduced by means of Mitscherlich's LAW OF ISOMORPHISM (1819), which states that

*Substances which are similar in crystalline form and in chemical properties can usually be represented by similar formulae*

Thus, the phosphates and arsenates represented by the following pairs of formulae

| | | |
|---|---|---|
| $NaH_2PO_4,H_2O$ | $KH_2PO_4$ | $(NH_4)H_2PO_4$ |
| $NaH_2AsO_4,H_2O$ | $KH_2AsO_4$ | $(NH_4)H_2AsO_4$ |

are isomorphous, and one set of formulae can be changed into the other merely by writing As instead of P Since 31 is the atomic weight of phosphorus, and 31 *parts of phosphorus* are replaced by 75 *parts of arsenic* on passing from one compound to the other, it follows that **75** must be the atomic weight of *arsenic*.

In the same way, in the isomorphous perchlorates and permanganates (*e.g* $KClO_4$ and $KMnO_4$), 35 5 *parts of chlorine* are replaced by 55 *parts of manganese*, and **55** is therefore the atomic weight of *manganese*. Again, in the isomorphous sulphates and chromates (*e g* $K_2SO_4$ and $K_2CrO_4$), 32 *parts of sulphur* are replaced by 52 *parts of chromium*, and **52** is therefore the atomic weight of *chromium*

These examples of isomorphism were used in order to bridge the gap between the non-metals chlorine and sulphur, of which the atomic weights can be determined directly from Avogadro's hypothesis, and those metals to which atomic weights cannot be assigned by this method. Thus, having once established suitable values for manganese and chromium, it is easy to deduce values for the atomic weights of other metals by making use of other isomorphous series, such as

(i) the alums, $RX(SO_4)_2$, $12H_2O$ (p 134),
where R is a univalent metal, Na, K, Ag, Tl, etc.,
X is a tervalent metal, Fe, Cr, Al, etc

(ii) the double sulphates, $R_2X(SO_4)_2$, $6H_2O$ (p 112),
where R is a univalent metal, Na, K, etc ,
X is a bivalent metal, Mn, Fe, Cu, Mg, Zn, etc

The law of isomorphism is, however, not a very sure guide, since many cases are known in which isomorphous compounds have dissimilar formulae Thus the atomic weights of silver and lead are 108 and 207, although in their isomorphous sulphides, $Ag_2S$ and PbS, 216 parts of silver replace 207 parts of lead The final test in fixing the atomic weights of the metals is therefore the Periodic Classification of the Elements (Chapter VII), in which each metal should fall into a suitable position as soon as its atomic weight has been determined correctly

## CHAPTER V

### THE STRUCTURE OF MATTER

**The real existence of atoms and molecules.**—The German physicist, Sommerfeld, has cited three lines of evidence as proof of the real existence of atoms and molecules

(*a*) **The Brownian movement** —The botanist Brown discovered in 1827 that tiny particles of pollen floating in water, when viewed under a microscope, were in incessant motion This was found to be a general property of small particles suspended in a fluid medium It gives the impression of a body being incessantly buffeted by other bodies in a state of chaotic movement , as if Boyle's " whirling corpuscles," although too small to be seen themselves, could nevertheless produce visible movement in larger corpuscles introduced amongst them The French physicist, Perrin, showed in 1908 that the velocities of translation and of rotation, and the variations of concentration in a tiny vertical column of the particles of a carefully-graded suspension of gum-mastic in water, agreed exactly with those which could be predicted on the hypothesis that the particles behave like molecules of large dimensions The BROWNIAN MOVEMENT makes it possible for solid particles to remain suspended in a liquid for an indefinite period, and is a principal characteristic of the important group of COLLOIDAL SUSPENSIONS Another characteristic is a potential difference between the particles and the medium , this gives a charge of similar sign to all the particles and so creates a repulsion which prevents them from coalescing with one another (p 645)

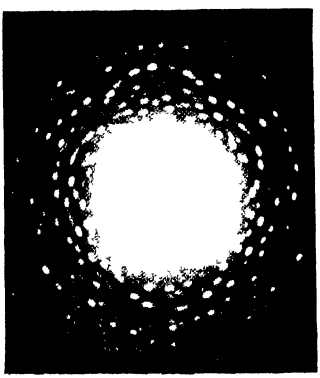


FIG. 3 LAUE DIAGRAM

(*b*) **Diffraction of X-rays by crystals** — It is well known that prismatic colours are produced by the reflection of light from (or the transmission of light through) thin films of liquid, *e g* of oil on the surface of water This phenomenon is attributed to INTERFERENCE of waves of light when reflected from the front and back of the film Laue in 1912 showed that similar phenomena can be observed with X-rays, and thus proved that they are similar in character to light waves but about 10,000 times smaller This was done by passing a pencil of X-rays through a crystal before receiving it on a photographic

plate A DIFFRACTION PATTERN, such as that shown in Fig 3, was obtained, which could only be accounted for by supposing that the crystal was built up of regularly spaced layers, separated from one another by a few ten-millionths of a millimetre The existence of these layers is at once explained by the molecular theory, if we suppose that a crystal is an orderly aggregate of atoms, molecules or ions, arranged in a regular pattern like tennis balls in a box or canned goods in a packing-case

(*c*) **The law of multiple proportions.**—Ostwald in 1904 claimed that the laws which govern chemical combination could be explained without assuming the real existence either of atoms or of molecules This is certainly true of the Law of Constant Proportions (p 3), since many examples of constant composition can be found which do not depend on Dalton's rules for the combination of atoms with one another Thus, when a mixture of alcohol and water is distilled, the most volatile portion of the distillate is a mixture of constant composition and constant properties, as follows

Alcohol, 95 59% Water, 4 41% Boiling-point, 78 13°

Again, two layers of constant composition and constant properties can be produced by shaking together two partially miscible liquids such as ether and water, thus

| | | |
|---|---|---|
| *Upper layer* | Ether, 98 7% | Water, 1 3% |
| *Lower layer* | Water, 94 2% | Ether, 5 8% |

Sommerfeld points out, however, that Dalton's Law of Multiple Proportions (p 4) cannot be explained by any similar device, and therefore provides a valid proof of the atomic theory Thus, in the case cited above, there is no simple numerical relation between the compositions of the two layers of ether and water such as exists between those of the two oxides of carbon (p 21) The relation between these oxides follows at once if we postulate with Dalton that one atom of carbon combines with one or with two atoms of oxygen to form the two oxides, but it is inexplicable unless the two elements are composed of atoms of constant weight

**The atom of electricity** —The electric current, produced by Volta in 1790 with the help of the "voltaic pile," was at first explained by the theory of an electric fluid, or alternatively of two fluids, positive and negative This raises once more the old question "Is this fluid really continuous or discontinuous?" Until recently, all physical theories and calculations were based upon the theory of a continuous electrical fluid Conclusive evidence on this point was, however, already available in the two Laws of Electrolysis, which Faraday enunciated in 1834 (p 595)

By these laws it was established that each atom carries a constant charge of electricity, when it migrates in the form of an ion to the anode or cathode in electrolysis Since the electrolyte is divided into atoms, it is reasonable to suppose that the electric charge is divided in a similar way, and that each atom of matter in a binary electrolyte bears one or more atoms of electricity An analogy to Dalton's Law of Multiple Proportions can then be found in the Second Law of Electrolysis, which states that equivalent quantities of different elements carry equal charges

If therefore a univalent sodium ion carries a single " atom " of positive electricity, as represented by the symbol $Na^+$, it follows that each atom of bivalent copper must carry two " atoms " of positive electricity, as represented by the symbol $Cu^{++}$ Similarly in the case of the anions, if the univalent chloride ion $Cl^-$ carries a single " atom " of negative electricity, the sulphate ion $SO_4^{--}$ must carry two negative " atoms "

This deduction from Faraday's Laws was made in 1891 by Helmholtz, and in the same year Johnston Stoney proposed that the atom of electricity should be described as an ELECTRON This term is now restricted to the *negative* atom of electricity, which is carried by the atoms of the *anion* A POSITIVE ELECTRON was also discovered in 1932, but is much more difficult to separate from ponderable matter

The magnitude of the electron, like that of the atom, is extremely small Thus the charge of 96,540 coulombs which are carried by one equivalent of an electrolyte must be divided amongst $0\ 6064 \times 10^{24}$ atoms, so that each univalent atom carries an electronic charge $e = 4\ 77 \times 10^{-10}$ electrostatic units This conclusion was established by Millikan, who studied the movement of electrified oil-drops under the combined action of gravity and of a vertical electric field, and showed in 1913 that the charge on the drop was always a multiple of $4\ 77 \times 10^{-10}$ e s u Conversely, Millikan's measurements have been used to deduce the value of the Avogadro number as cited above

**Discovery of the free electron.**—In 1858, Plucker observed that, when an electric discharge was passed through a rarefied gas in a VACUUM TUBE (Fig 4), a phosphorescent light was produced on the surface of the glass

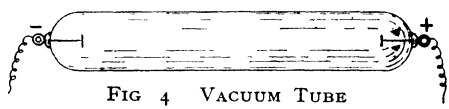



FIG 4 VACUUM TUBE

opposite to the cathode by which the current was led out from the tube This phenomenon is produced by CATHODE RAYS (Goldstein, 1876), which are projected in straight lines from the surface of the cathode, since, when an obstacle is interposed, they cast a shadow on the walls of the tube Crookes concluded in 1879 that these rays consisted of sub-atomic particles, which he described as a " fourth state of matter "

The nature of the cathode rays was established by J J Thomson, who showed that they were deflected by magnetic and electric fields in the same way as a moveable conductor, thus proving that they were electrically charged Since they were projected *from* the cathode, the charge was obviously negative in sign, as Perrin found when he allowed the cathode rays to fall on an insulated plate, which thus acquired a negative charge

J J Thomson was the first to characterise the electron by means of numerical measurements For this purpose, a stream of cathode rays was deflected in two directions at right angles to one another by magnetic and electric fields From these deflections the ratio of the charge $e$ to the mass $m$ of the electron was determined and found to have the value $e/m = 1\ 769 \times 10^7$ c g s units This ratio is 1830 times greater than for

the hydrogen ion, where a charge of 96,500 coulombs (9650 c g s units) is carried by a mass of 1 0078 grams of hydrogen If therefore the charge of the electron is equal and opposite to that of the hydrogen ion, its mass must be 1830 times smaller

Thomson found that the ratio $e/m$ for the electron was always the same , in particular, it was independent (1) of the nature of the material from

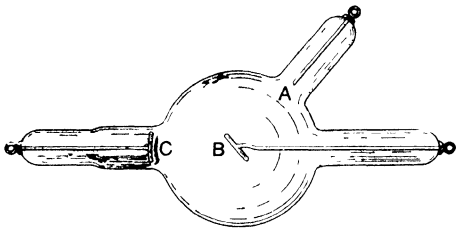



FIG 5 VACUUM-TUBE AS USED FOR THE PRODUCTION OF X-RAYS

Cathode rays are projected at right angles from the surface of the CATHODE $C$ and are concentrated on an ANTI-CATHODE $B$ X-rays are emitted from the anti-cathode $B$, which is also heated by the bombardment of the cathode rays The current enters the bulb by the ANODE $A$, but this does not play any conspicuous part in its operation

which the cathode was made and from which the electrons were projected, and (11) of the residual gas in the vacuum tube It therefore appears that *the electron is a common constituent of all forms of matter* and always has the same properties

**Positive rays** —In addition to the negatively charged cathode rays, the operation of a vacuum tube produces positively-charged rays, which travel with the current to the cathode instead of being projected from it In order to detect them, it is necessary to pierce the cathode with a narrow canal, when CANAL RAYS (Goldstein, 1866) can be seen as a stream of violet light emerging from the back of the cathode These were studied in Germany by Lenard, and in England by J J Thomson and found to be positively charged They are therefore known as POSITIVE RAYS Thomson measured the ratio $e/m$ by the same method as for the electron He found that it was no longer constant, but depended on the nature of the residual gas in the tube Since the values of this ratio were comparable with the values of $e/m$ for the ions of aqueous electrolytes, *e g* $Hg^{++}$, it appeared that the *positive rays consist of atoms and molecules which have become positively charged* Moreover, since a stream of electrons was always produced at the same time, it was likely that these positive ions had been formed from neutral atoms or molecules by the removal of electrons

**The atom as a planetary system.**—We have seen that, in a vacuum tube, neutral atoms give rise to (1) negatively charged electrons, which are much lighter than any atom, since their electrochemical equivalent is 1830 times smaller than that of hydrogen, (11) positively charged particles, which are of similar mass to the atoms, since their electrochemical equivalents

are of similar magnitude The atom is therefore pictured as a system in which a positively charged NUCLEUS is surrounded by PLANETARY ELECTRONS in sufficient numbers to balance its positive charge, and thus produce a neutral atom The planetary electrons are supposed to occupy a series of ORBITS, in which they are held, not by gravity as in the solar system, but by the electrostatic forces between the positive and negative charges The orbits have a radius of a few Ångstrom units ($10^{-8}$ cm ), whilst that of the nucleus is of the order $10^{-12}$ cm

**The mass-spectrograph.**—Aston in 1919 constructed an apparatus for the study of positive rays, in which the magnetic and electric fields produced deflections in the same plane (but in opposite directions) instead of in planes at right angles to one another as in Thomson's apparatus The apparatus was designed in such a way that all particles with the same value of $e/m$ were brought to a common focus on a photographic plate, whatever their velocity might be, whereas those with different values of this ratio were focused at other points on the plate By this method the value of the ratio $e/m$ can now be determined within 1 part in 10,000

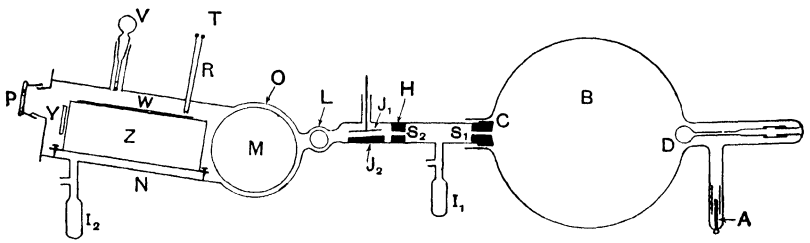



FIG 6 APPARATUS FOR PRODUCTION OF MASS-SPECTRA (Aston)

In this figure $I_1$, $I_2$ are charcoal-tubes cooled in liquid air to maintain a vacuum in the apparatus , $V$ is a device for moving the photographic plate, and $T$ is a lamp which makes a spot on the plate through the tube $R$ in order to record its position in the camera

Fig 6 shows the general structure of the mass-spectrograph The gas to be examined is introduced at very low pressure into the bulb $B$ This carries an anode $A$, a cathode $C$, and an insulated anticathode $D$ to dissipate the energy of the cathode rays The positive rays, which are propelled towards the cathode, pass through an aperture $S_1$, and are reduced to a narrow ribbon by a second slit $S_2$ They are deflected downwards by an electrostatic field between the plates $J_1$ and $J_2$, and upwards by an electromagnetic field between the poles $M$ of an electromagnet, and are finally received on a photographic plate at $W$ They are there spread out as a MASS-SPECTRUM, in which all particles having the same value of $e/m$ are brought to a common focus on the plate, the heavier particles being focused on the left and light particles on the right hand side of the plate

**The proton.**—Aston found that multiply-charged atoms of certain elements, *e g* mercury, were formed in an electric discharge and were readily detected by the mass-spectrograph , but it was impossible to remove more than *two* electrons from an atom of helium or *one* from an atom of hydrogen Moreover, the singly-charged atom of hydrogen was found

to have a higher value of $e/m$ than any other positive ion, in agreement with the fact that its atomic weight is less than that of any other element This very light positively charged particle has been described as a PROTON In accordance with Aston's WHOLE NUMBER RULE, the masses of all other atoms, as deduced with the help of the mass-spectrograph, were found to be very nearly integral multiples of the mass of the proton

Aston's rule is a modern version of PROUT'S HYPOTHESIS (1815), according to which the atomic weights of all the heavier elements were supposed to be multiples of that of hydrogen, because they were built up from this primary material Prout's hypothesis was contradicted by Stas's experiments on the atomic weight of chlorine, but the mass-spectrograph has confirmed it, by showing that elements with fractional atomic weights are mixtures of atoms with unequal but integral atomic weights Thus chlorine, with an atomic weight of 35 457, is a mixture of two kinds of atoms, with MASS NUMBERS 35 and 37, which are distinguished as $^{35}Cl$ and $^{37}Cl$ These atoms, which differ in mass but are almost identical in every other respect, are known as ISOTOPES Elements which contain two or more isotopes are described as COMPLEX ELEMENTS, whilst those of which all the atoms are alike are known as SIMPLE ELEMENTS

**Atomic numbers** —The atom of hydrogen consists of a single proton and a single planetary electron In other atoms the nucleus carries a multiple charge and is surrounded by several planetary electrons The number of units of positive electricity on the nucleus is known as the ATOMIC NUMBER of the atom and is represented by the symbol $Z$ In a neutral atom, the number of planetary electrons is equal to the atomic number, but in ions such as $K^+$ and $Cl^-$ it is either smaller or greater than this number

The atomic number of an element can be determined most readily by Moseley's method, namely by examining the X-rays which are given out when the element or one of its compounds is bombarded by cathode rays It is then found that *the square root of the frequency of vibration of the X-rays is proportional to the nuclear charge and therefore to the atomic number of the element* The different isotopes which are present in a complex element have identical atomic numbers, the modern definition of an ELEMENT therefore includes all those atoms which have a given atomic number

If the nuclei of the heavier elements consisted only of protons, the ratio $e/m$ would be the same for all nuclei, and the *mass number* would always be identical with the *atomic number* Actually, however, apart from hydrogen itself, the *mass number of an atom is always at least twice as great as its atomic number* Thus the MASS NUMBER of helium is *four*, whilst its ATOMIC NUMBER is *two* If the mass number is printed on the left of the atomic symbol at the top and the atomic number at the bottom, the symbols of some of the commonest of the lighter elements may be set out as follows

$$^{1}_{1}H\ ^{2}_{1}D\ ^{4}_{2}He\ ^{12}_{6}C\ ^{14}_{7}N\ ^{16}_{8}O\ ^{19}_{9}F\ ^{20}_{10}Ne\ ^{22}_{10}Ne\ ^{23}_{11}Na\ ^{35}_{17}Cl\ ^{37}_{17}Cl$$

In this list, D is a heavy isotope of hydrogen, and isotopes of neon and chlorine are also shown

The difference between the mass number and the atomic number of an atom is attributed to the presence in the nucleus of one or more NEUTRONS These are particles having a similar mass to the proton, *but no electric charge* The number of neutrons can be deduced at once by subtracting the numbers shown in the symbols set out above Except in the case of hydrogen, *the number of neutrons is either equal to or greater than the number of protons in the nucleus, e g*

2 for $^{4}_{2}$He, 6 for $^{12}_{6}$C, 8 for $^{16}_{8}$O, but 12 for $^{23}_{11}$Na

The isotopes of a given element contain the same number of protons, but different numbers of neutrons, *e g*

18 for $^{35}_{17}$Cl and 20 for $^{37}_{17}$Cl,

the proportion of neutrons and protons, however, can only vary within narrow limits, beyond which the nuclei are no longer stable

**Radioactivity** —The nuclei of the lighter atoms which occur in nature are quite stable, but those of the heaviest atoms are often unstable, and disintegrate spontaneously after a longer or shorter life The explosive disintegration of these atoms gives rise to three types of radiation, which are known as $\alpha$-, $\beta$- and $\gamma$-rays, the phenomenon is therefore known as RADIOACTIVITY

(i) ALPHA RAYS (which are emitted by most of the radioactive elements, including uranium, thorium and radium) consist of helium nuclei $He^{++}$, and are identical with the doubly-charged positive rays formed in a vacuum-tube containing helium (p 65) On account of their mass and the high velocity with which they are expelled from the atom, they are only deflected with difficulty by a magnetic field

(ii) BETA RAYS, which are formed by the disintegration of actinium and other less stable radioactive elements, are high-velocity electrons, comparable with cathode rays formed under a very high voltage They are negatively charged and, on account of their small mass, are bent more easily (and in the opposite direction) by a magnetic field

(iii) GAMMA RAYS, which accompany the emission of both $\alpha$- and $\beta$-rays, are light waves of very short wave-length, like the "hard" X-rays which are emitted when elements of high atomic weight are bombarded by cathode rays

**Thorium and uranium.**—Natural radioactivity has its source in two of the heaviest known elements

90 Thorium. Th = 232 12 92 Uranium Ur = 238 14

These are radioactive, but with an average life of the order of $10^{10}$ years, and have therefore survived since the earth was separated from the sun When, however, the atoms of these two elements disintegrate, by liberation of an $\alpha$-particle, they give rise to less stable atoms, with a life which can often be measured in days, minutes or seconds, instead of millions of years These elements are therefore more powerfully radioactive than uranium or thorium

The final product of disintegration is *lead*, of which one isotope is formed from thorium, whilst two others are formed from uranium and

its isotope **actino-uranium**, by expulsion of a series of $\alpha$- and $\beta$-particles as represented by the following equations, in which the $\alpha$-particle is represented by the symbol $^{4}_{2}\mathrm{He}$ and the $\beta$-particle or electron by the symbol $_{-1}^{0}e$

| | | |
|---|---|---|
| *Thorium* | $^{232}_{90}\mathrm{Th}$ | $= {}^{208}_{82}\mathrm{Pb} + 6\,{}^{4}_{2}\mathrm{He} + 4\,{}_{-1}^{0}e$ |
| *Actino-uranium* | $^{235}_{92}\mathrm{AcUr}$ | $= {}^{207}_{82}\mathrm{Pb} + 7\,{}^{4}_{2}\mathrm{He} + 4\,{}_{-1}^{0}e$ |
| *Uranium* | $^{238}_{92}\mathrm{Ur}$ | $= {}^{206}_{82}\mathrm{Pb} + 8\,{}^{4}_{2}\mathrm{He} + 6\,{}_{-1}^{0}e$ |

The atomic weight of lead derived from thorium minerals therefore approximates to 208, and that from uranium minerals to 206, as compared with 207 22 for ordinary lead

**Radium.**—One of the 14 intermediate stages in the disintegration of uranium is the radioactive element

88 Radium Ra = 225 97

This belongs to the family of alkaline earths, like barium (p 123), and can be separated from uranium minerals as an isomorphous mixture of barium and radium bromides It has a half-life period * of 1600 years, and is therefore, as the Curies found, far more powerfully radioactive than the purest uranium salt On disintegration, it gives rise, by expulsion of an $\alpha$-particle, to a gaseous emanation,

86 Radon. Rn = 222,

which exhibits the chemical properties of an inert gas, but is intensely radioactive, since it has a half-life period of only four days This disintegration can be represented by the equation

$$^{222}_{88}\mathrm{Ra} = {}^{218}_{86}\mathrm{Rn} + {}^{4}_{2}\mathrm{He}$$

**Radioactive isotopes**—In each disintegration series, $\alpha$-particles, $^{4}_{2}\mathrm{He}$, are expelled one at a time from the atom Each time this happens the mass-number of the atom is decreased by *four* and the atomic number by *two* The change of mass-number is not of first-rate importance, but the change of atomic number implies that a new element has been formed Moreover, since the periodic classification of the elements (p 54) is now based upon a sequence of atomic numbers, the loss of an $\alpha$-particle (and the consequent diminution of the atomic number by two units) gives rise to a disintegration-product which is displaced *two places to the left* in this classification Conversely, the expulsion of a $\beta$-particle, $_{-1}^{0}e$, *increases the atomic number by one unit*, without altering the mass-number The product is again a new element, but it is shifted *one place to the right* in the periodic classification It therefore follows logically that the successive expulsion of *one* $\alpha$-particle and *two* $\beta$-particles must give rise to a disintegration product with the same atomic number as the original atom, *i e* to an isotope and not a new element Thus, by emission of an $\alpha$-particle, Radium A gives Radium B,

* The half-life period is the time which experiment shows would be taken for half of the atoms to disintegrate

and then by the successive emission of two $\beta$-particles gives Radium C and C′, the latter being an isotope of Radium A, since $Z=84$ for both

$$^{218}_{84}\text{RaA} \xrightarrow{-\alpha} {}^{214}_{82}\text{RaB} \xrightarrow{-\beta} {}^{214}_{83}\text{RaC} \xrightarrow{-\beta} {}^{214}_{84}\text{RaC}'$$

Since the initial and final products are both radioactive, they are described as RADIOACTIVE ISOTOPES These isotopes are usually too unstable to be isolated in quantity, but they can be recognised by the fact that the radioactivity is precipitated with the same element when a qualitative analysis of the material is carried out

Radioactive isotopes are also formed when disintegration-products of equal atomic number are produced from uranium and thorium and actinium, *e g* each series yields an " inert gas " of atomic number 86, as follows

| | | |
|---|---|---|
| *Uranium series* | Radium-emanation | $^{222}_{86}\text{Rn}$ |
| *Actinium series* | Actinium-emanation | $^{219}_{86}\text{Rn}$, |
| *Thorium series* | Thorium-emanation | $^{224}_{86}\text{Rn}$ |

(Compare

Uranium lead, $^{206}_{82}\text{Pb}$, Actinium lead, $^{207}_{82}\text{Pb}$, Thorium lead, $^{208}_{82}\text{Pb}$)

It is of interest to note that the recognition of radioactive isotopes by Soddy preceded the discovery of the stable isotopes of neon by Thomson and Aston

**Artificial disintegration** —So far as is known at present, protons are never set free by the spontaneous disintegration of a radioactive element When, however, elements of small atomic weight are bombarded by $\alpha$-particles, an artificial disintegration may take place, in which the $\alpha$-particle is absorbed by the nucleus and a proton expelled The mass-number of the nucleus is thus increased by three units and its atomic number by one unit In this way the disintegration of nitrogen gives rise to an isotope of oxygen, $^{17}_{8}\text{O}$,

$$^{14}_{7}\text{N} + {}^{4}_{2}\text{He} = {}^{1}_{1}\text{H} + {}^{17}_{8}\text{O}$$

Conversely, when lithium is bombarded by swift protons, protons are absorbed and helium is produced,

$$^{7}_{3}\text{Li} + {}^{1}_{1}\text{H} = {}^{4}_{2}\text{He} + {}^{4}_{2}\text{He}$$

When, however, beryllium is bombarded by $\alpha$-particles, an entirely new phenomenon is encountered, since the absorption of the $\alpha$-particle is accompanied by the expulsion of a *neutron*, $^{1}_{0}n$,

$$^{9}_{4}\text{Be} + {}^{4}_{2}\text{He} = {}^{12}_{6}\text{C} + {}^{1}_{0}n$$

This is a particle with the mass of a proton, but no electric charge It is therefore less easy to detect than an $\alpha$-particle, a proton or an electron

**Induced radioactivity.**—$\alpha$-Particles and protons are of no use as disintegrating agents unless projected with sufficient velocity to overcome the repulsion between the positive charges of the two nuclei set out in the preceding equations. The neutron, however, carries no electric

charge and experiences no similar repulsion An atomic nucleus is therefore even more defenceless when bombarded by a shower of neutrons than a battleship attacked by aeroplanes For this reason, even slow neutrons can penetrate into the nucleus of atoms of nearly every kind The product may be an isotope, or an element of lower atomic number may be produced by the simultaneous expulsion of an $\alpha$-particle or proton, *e g*

$$^{14}_{7}\mathrm{N} + {}^{1}_{0}n = {}^{11}_{5}\mathrm{B} + {}^{4}_{2}\mathrm{He}.$$

In this case the product is the ordinary stable form $^{11}_{5}$B of the element boron , but in other cases an unstable isotope is produced, which disintegrates spontaneously, giving rise to the phenomenon of INDUCED RADIOACTIVITY Thus, when phosphorus $^{31}_{15}$P is bombarded by neutrons, it absorbs a neutron and loses an $\alpha$-particle, giving rise to **radio-aluminium**, $^{28}_{13}$Al, the nucleus of which contains one neutron more than ordinary aluminium, $^{27}_{13}$Al, and therefore disintegrates, with loss of an electron, to produce the ordinary stable form $^{28}_{14}$Si, of silicon

$$^{31}_{15}\mathrm{P} + {}^{1}_{0}n = {}^{28}_{13}\mathrm{Al} + {}^{4}_{2}\mathrm{He},$$
$$^{28}_{13}\mathrm{Al} = {}^{28}_{14}\mathrm{Si} + {}^{0}_{-1}e$$

# CHAPTER VI

## THE ELECTRONIC THEORY OF VALENCY

**Definitions of valency.**—(*a*) The *valency of an element* has already been defined (p 20) as the number of equivalents in the atomic weight of the element, *i e*

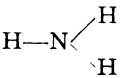
$$\text{Valency} = \frac{\text{Atomic weight}}{\text{Equivalent weight}}$$

(*b*) We can also define the *valency of an atom* as the number of atoms of hydrogen with which it can combine, *e g*

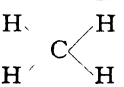
*Univalent* - - - H—H H—Cl

*Bivalent* - - - H—O—H H—S—H

*Tervalent* - - -



*Quadrivalent* -



The valencies are here represented by a series of CHEMICAL BONDS, of which hydrogen and chlorine possess *one*, oxygen and sulphur *two*, nitrogen *three*, and carbon *four* In general, the number of bonds by which an atom can be linked to other atoms is distinguished as its COVALENCE (p 38)

The two definitions (*a*) and (*b*) are really identical Thus, an atom of bivalent oxygen or sulphur combines with *two* atoms of univalent hydrogen , the atomic weight must therefore be divided by *two* in order to give the equivalent, since this is defined as the weight which combines with *one* part of hydrogen

(*c*) We can define the *valency of an ion* by the number of positive or negative charges which it carries, *e g*

*Univalent* - - - - - $H^{+}$, $Na^{+}$, $Cl^{-}$.

*Bivalent* - - - - $Ca^{++}$, $Fe^{++}$, $S^{--}$.

*Tervalent* - - - - $Al^{+++}$, $Fe^{+++}$

This type of valency is distinguished as ELECTROVALENCE, and can obviously be either positive or negative. It is again found to be identical with the definition given under (*a*). Thus, if we define the valency of a metal

as the ratio of its atomic weight to its chlorine-equivalent (*i.e* as the number of equivalents of chlorine, Cl = 35 457, with which the atom can combine), it is clear that bivalent iron, $Fe^{++}$, must combine with $2Cl^-$, and tervalent iron, $Fe^{+++}$, must combine with $3Cl^-$, in order to form the neutral compounds, ferrous chloride, $FeCl_2$, and ferric chloride, $FeCl_3$

**The dual character of valency.**—The dual character of valency (as indicated in the preceding definitions) led to a controversy which lasted nearly a century Thus, since chemical compounds are decomposed by electrolysis, Berzelius in 1812 supposed that chemical affinity is electrical in origin and depends on the mutual attraction of positive (metallic) and negative (non-metallic) elements for one another This ELECTROCHEMICAL THEORY explains many of the facts of inorganic chemistry, where we are concerned chiefly with the combination of *unlike* elements and compounds (*e g* metals and non-metals, alkalis and acids), which can often be separated from one another by the action of an electric current But the theory broke down completely when applied to the facts of organic chemistry, which is concerned mainly with the union of *like* elements (non-metals) with one another and in particular with the linkage of *carbon to carbon* to form the chains and rings of the carbon-skeletons of organic compounds It failed even more completely to explain the fact that two *identical* atoms of hydrogen or of chlorine can unite to form diatomic molecules, which are often quite as stable as the molecules of a chemical compound This controversy has been settled as a result of our knowledge of the electrical structure of matter , and a clear interpretation of the two kinds of chemical combination is provided by the ELECTRONIC THEORY OF VALENCY, which is set out below

**The electronic theory of valency.**—According to the electronic theory of valency, the chemical properties of an atom are determined by the behaviour of the planetary electrons which surround the nucleus In a neutral atom they are equal in number to the positive charge on the nucleus, as given by the atomic number $Z$ of the element The electronic theory of valency therefore depends on knowing the atomic numbers of the elements These were determined for a number of elements by Moseley, who showed in 1913 that, if the value $Z = 13$ were assigned to aluminium, the atomic number of gold must be $Z = 79$ This scale of atomic numbers has been confirmed by later work and extended to cover all the known elements, as set out in Table 26, p 304, from which it will be seen that the atomic numbers all fall within the range from 1 to 92

**The Rydberg series.**—When the atomic numbers had thus been determined, it was possible to look for relationships between the chemical properties of an element and the number of planetary electrons in it atoms The simplest case of all is found in the inert gases (p 63), which were separated from the atmosphere by Ramsay These "noble gases are even more inert than nitrogen, since it is only under exceptional conditions that they are able to form even unstable compounds, although solid argon can crystallise with six molecules of water of crystallisation The emanation, known as "radon," which is produced by the disintegration of radium, is a gas of similar type, since it forms no chemic

compounds and is therefore completely inert, in spite of its intense radioactivity The atomic numbers of these gases are as follows

| | Helium | Neon | Argon | Krypton | Xenon | Radon |
|---|---|---|---|---|---|---|
| $Z =$ | 2 | 10 | 18 | 36 | 54 | 86 |

This regular sequence of atomic numbers can be expressed by an algebraic series discovered by Rydberg and therefore known as the RYDBERG SERIES, namely

$$Z = 2 \times 1^2 + 2 \times 2^2 + 2 \times 2^2 + 2 \times 3^2 + 2 \times 3^2 + 2 \times 4^2$$

In this series we find an algebraic basis for the classification of the elements A corresponding physical basis has been provided by spectroscopic observations, which have enabled us to group the planetary electrons into SHELLS, which are described by the letters $K$, $L$, $M$, $N$, $O$, $P$ Thus the planetary electrons of the inert gases are classified as follows

ELECTRONIC CONFIGURATION OF THE INERT GASES

| Symbol of shell | | | | $K$ | $L$ | $M$ | $N$ | $O$ | $P$ |
|---|---|---|---|---|---|---|---|---|---|
| Serial number of shell | | | | 1 | 2 | 3 | 4 | 5 | 6 |
| Helium | - | - | $Z =$ 2 | = 2 | | | | | |
| Neon | - | - | = 10 | = 2 | + 8 | | | | |
| Argon | - | - | = 18 | = 2 | + 8 + | 8 | | | |
| Krypton | - | - | = 36 | = 2 | + 8 + 18 + | 8 | | | |
| Xenon | - | - | = 54 | = 2 | + 8 + 18 + 18 + | 8 | | | |
| Radon | - | - | = 86 | = 2 | + 8 + 18 + 32 + | 18 | + 8 | | |

**Duplets and octets** —The atom of helium contains a DUPLET or *pair* of electrons in the $K$-shell, and this group persists in all the heavier gases of this series The other inert gases contain an OCTET of *eight* electrons in the outermost shell This is not always the maximum number which the shell can contain, since the $N$-shell, which contains only 8 electrons in krypton, is occupied by 18 electrons in xenon and by 32 electrons in radon, but the stability of the two former gases is not affected by the incompleteness of this inner shell The stability of the inert gases towards chemical agents therefore appears to depend on the completion of an octet in the outer shell (or of a duplet in helium), supported by terms of the Rydberg series in all the inner shells Conversely, the chemical activity of other elements depends on the lesser stability of electronic groups which do not conform to the Rydberg series

The formation of molecules can be attributed to a rearrangement of electrons whereby other atoms are enabled to acquire the stable electronic configurations of an inert gas According to the electronic theory, this rearrangement (as is shown in the two following paragraphs) may be effected in two ways, namely by "electron-transfer" and by "electron-sharing," giving rise to two types of chemical combination These are characteristic respectively of salts and of carbon compounds, thus justifying in a striking way the familiar distinction between inorganic and organic chemistry

**Combination of metals and non-metals by electron-transfer.**—When their atomic numbers are determined, it is found that the inert gases are

preceded by a halogen and followed by an alkali-metal The actual sequence is as follows

| | | | | |
|---|---|---|---|---|
| | Hydrogen | Helium | Lithium | |
| $Z =$ | 1 | **2** | 3 | |
| Oxygen | Fluorine | Neon | Sodium | Magnesium |
| $Z = 8$ | 9 | **10** | 11 | 12 |
| Sulphur | Chlorine | Argon | Potassium | Calcium |
| $Z = 16$ | 17 | **18** | 19 | 20 |
| Selenium | Bromine | Krypton | Rubidium | Strontium |
| $Z = 34$ | 35 | **36** | 37 | 38 |
| Tellurium | Iodine | Xenon | Caesium | Barium |
| $Z = 52$ | 53 | **54** | 55 | 56 |

In general it appears that the elements which *follow* the inert gases are METALS, whilst those which *precede* the inert gases are NON-METALS *

The formation of binary salts is then attributed to a process of ELECTRON TRANSFER, whereby the surplus electrons of the metal are used to supply the deficiency of electrons of the non-metal, thus

| | Na | + | F | = | $^{+}$Na | $^{-}$F |
|---|---|---|---|---|---|---|
| Planetary electrons | 11 | | 9 | | **10** | **10** |
| Nuclear charge | 11 | | 9 | | 11 | 9 |
| Electrical charge | 0 | | 0 | | +1 | −1 |

| | K | + | Cl | = | $^{+}$K | $^{-}$Cl |
|---|---|---|---|---|---|---|
| Planetary electrons | 19 | | 17 | | **18** | **18** |
| Nuclear charge | 19 | | 17 | | 19 | 17 |
| Electrical charge | 0 | | 0 | | +1 | −1 |

| | Ca | + | S | = | $^{++}$Ca | $^{--}$S |
|---|---|---|---|---|---|---|
| Planetary electrons | 20 | | 16 | | **18** | **18** |
| Nuclear charge | 20 | | 16 | | 20 | 16 |
| Electrical charge | 0 | | 0 | | +2 | −2 |

In this process the metallic atoms are converted into cations and the non-metallic atoms into anions These ions have the electronic configuration (but not the nuclear charge) of an inert gas, and are therefore more stable than the neutral atoms from which the salt is formed, thus the sodium ion, $Na^{+}$, does not react with water

Until recently, it was believed that the atoms of sodium and chlorine in common salt were united in pairs to form molecules of sodium chloride An examination of crystals of rock salt by means of X-rays, however, has shown that every atom of chlorine is surrounded symmetrically by *six*

* The peculiar properties of hydrogen are discussed in Chapter X

atoms of sodium and conversely (Fig 129, p 493) There is therefore no indication of a selective union of *one* atom of chlorine with *one* atom of sodium The conclusion has therefore been drawn that these crystals are aggregates of ions, in which no individual molecules can be detected, thus

$$\begin{matrix} \overset{+}{\mathrm{Na}} & \overset{-}{\mathrm{Cl}} & \overset{+}{\mathrm{Na}} & \overset{-}{\mathrm{Cl}} \\ \overset{-}{\mathrm{Cl}} & \overset{+}{\mathrm{Na}} & \overset{-}{\mathrm{Cl}} & \overset{+}{\mathrm{Na}} \end{matrix}$$

These IONIC AGGREGATES are held together by the attraction between the positive and negative charges, and the forces between the atoms are believed to be purely electrostatic in character In a similar way the vapour, which has a density corresponding with the formula NaCl, is believed to consist of ION-PAIRS, $Na^+Cl^-$, in which the atoms are held together by opposite electrical charges and not by ordinary chemical bonds This conclusion does not apply, however, to volatile salts, such as calomel, which is formulated as ClHgHgCl and not as $Hg^+Cl^-$

The type of valency which depends on electron transfer is known as ELECTROVALENCE It may be either *positive* or *negative* and is measured by the number of electrons which the neutral atom *loses* or *gains* in forming an ion METALS may therefore be defined as elements which tend to lose electrons giving rise to positively charged cations, *e g*

$$\overset{+}{\mathrm{Na}},\ \overset{+}{\mathrm{K}},\ \overset{+}{\mathrm{Ag}},\ \overset{++}{\mathrm{Cu}},\ \overset{++}{\mathrm{Fe}},\ \overset{+++}{\mathrm{Fe}},$$

whilst NON-METALS tend to gain electrons and to form negatively charged anions, *e g* $Cl^-$, $Br^-$, $S^{--}$ The characteristic properties of METALLIC CONDUCTIVITY and METALLIC LUSTRE can be explained as due to the readiness with which electrons are liberated from a metal, since these properties depend on the presence of mobile electrons, which are unlikely to exist in non-metals with their characteristic property of electron-hunger

**Chemical combination by electron-sharing.**—The atoms of the non-metals unite readily with metallic atoms as described in the preceding paragraph , but they also unite with one another to form diatomic molecules, *e g*

$$\mathrm{H_2},\ \mathrm{N_2},\ \mathrm{O_2},\ \mathrm{F_2},\ \mathrm{Cl_2},\ \mathrm{Br_2},\ \mathrm{I_2}$$

These molecules are held together by the mutual attraction of two positively charged nuclei for the same pair of electrons This type of valency, which depends on electron-sharing, has been described as COVALENCE

The electronic theory of valency attributes the formation of covalent bonds in the first instance to the stability of the DUPLET Thus the atomic numbers of hydrogen, sodium and potassium are

| | Hydrogen | Sodium | Potassium |
|---|---|---|---|
| $Z$ = | 1 | 11 | 19 |

Each atom carries an odd electron, loosely bound either to a proton or to an ion with the electronic configuration of an inert gas The " coupling " of two of these electrons to form a duplet gives rise to a chemical bond

between two atoms, as in the diatomic molecules of hydrogen, sodium and potassium : *

H—H Na—Na K—K

The chemical bond between two atoms, which is so important in organic chemistry, is therefore composed of a pair of shared electrons Its structure can be indicated by using a colon to represent each pair of shared electrons, thus

H H Na Na K K

Modern physics postulates that the two coupled electrons are spinning in opposite directions and therefore give rise to opposite magnetic fields, which are neutralised in the process of coupling

Greater stability is found when a duplet of shared electrons forms part of an OCTET, *i e* when the sharing of two electrons enables one or both nuclei to acquire the electronic configuration of an inert gas with eight electrons in the outer shell This condition is fulfilled pre-eminently in the halogens, which are predominantly diatomic gases, whereas the vapours of the alkali metals (at temperatures above 800°) are mainly monatomic The electronic configurations of the atoms in question are as follows

| | | *K* | *L* | *M* | *N* | *O* |
|---|---|---|---|---|---|---|
| Fluorine | $Z = 9 = 2 + 7$ | | | | | |
| Chlorine | $Z = 17 = 2 + 8 + 7$ | | | | | |
| Bromine | $Z = 35 = 2 + 8 + 18 + 7$ | | | | | |
| Iodine | $Z = 53 = 2 + 8 + 18 + 18 + 7$ | | | | | |

In each case the outer shell contains one electron less than the complete octet of an inert gas , by sharing a pair of electrons each atom therefore acquires an octet, consisting of one pair of shared electrons and three LONE PAIRS of unshared electrons, thus

F F Cl Cl Br Br I I

In these ELECTRONIC FORMULAE only the outer shell of VALENCY ELECTRONS is shown, since the inner shells have very little influence on the chemical properties of the elements, as is shown by the close general similarity of all the halogens to one another

**Single, double and triple bonds.**—The sharing of electrons by adjacent nuclei may involve *one*, *two* or *three* duplets, giving rise to a SINGLE, DOUBLE or TRIPLE BOND These can be formulated as follows,

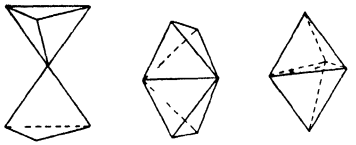
F—F O=O N≡N

or ·F F O O .N. N

where each line represents a bond and each colon a pair of electrons. A quadruple bond appears, however, to be impossible, as van't Hoff

* Spectroscopy has disclosed the existence of diatomic molecules, $Na_2$, $K_2$, $Hg_2$, etc , in vapours which were formerly supposed to be wholly monatomic

postulated when he used a tetrahedral model to represent a quadrivalent atom of carbon, and represented the formation of single, double and triple bonds by the sharing of an *apex*, an *edge* or a *face* between two contiguous tetrahedra (Fig 7)



SINGLE BOND DOUBLE BOND TRIPLE BOND

FIG. 7 VAN'T HOFF'S TETRAHEDRAL MODELS

**Dative bonds.**—A DATIVE BOND IS a covalent link in which *one atom provides both shared electrons* It is formed by the union of a DONOR ATOM, which contains a "lone pair" of unshared electrons, with an ACCEPTOR ATOM, the electronic shell of which can be expanded by the inclusion of two more electrons Thus the oxidation of a sulphide to a sulphate is supposed to take place by the sharing of the *four* lone-pairs of the sulphide ion with *four* oxygen atoms, each carrying only a sextet of electrons in the outer shell

$$\overline{\overline{S}} + 4O = SO_4 \quad \text{or} \quad \underset{\cdot\cdot}{S} + 4\ O \rightarrow O\ \underset{\cdot}{S}\ O \quad (O \text{ above and below } S)$$

The formation of a dative bond involves the transfer of a half-share of two electrons from the donor to the acceptor This is equivalent to the transfer of one electron from one atom to the other A dative bond between neutral atoms therefore takes the form of a SEMI-POLAR BOND, in which *an electrovalence is superposed on a covalence*, as in phosphorus oxychloride $Cl_3P^+—O^-$ A dative bond between *ions*, however, usually results in a neutralisation of their charges and the formation of a simple covalence, *e g*

$$\overset{+}{H} + \overset{-}{Cl} \rightarrow HCl \quad \text{or} \quad H + Cl \rightarrow H\ Cl$$

**Valency number and coordination number**—Werner defined the VALENCY NUMBER of an element by the number of *similar* atoms, *e g* of hydrogen or of a halogen, with which it could combine, as in

| $BF_3$ $NH_3$ | $CH_4$ $CCl_4$ |
|---|---|
| Tervalent | Quadrivalent |

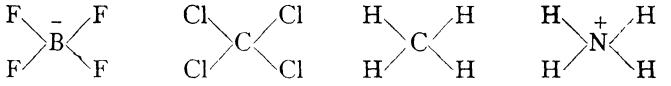
This number of atoms can often be increased, however, with the help of a third element, *e g.*

$$BF_3 + KF = KBF_4 \qquad NH_3 + HCl = NH_4Cl$$

The products are sometimes described as containing quinquevalent boron or nitrogen, but they are really *salts*, containing a polyatomic or COMPLEX ION, in which the central atom is linked directly to *four* similar atoms of fluorine or of hydrogen, thus

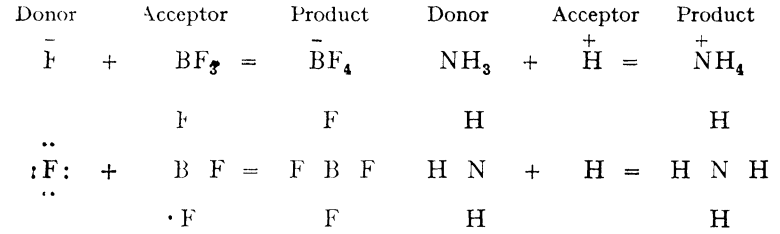
$$BF_3 + \overset{+}{K}\overset{-}{F} = \overset{+}{K}[BF_4] \qquad NH_3 + HCl = [NH_4]\overset{+}{\overset{-}{Cl}}$$

The maximum number of atoms which can be linked directly to the central atom, if necessary with the help of a third element, was described by Werner as the COORDINATION NUMBER of the element Thus the co-ordination number of boron, carbon and nitrogen is *four* in the series

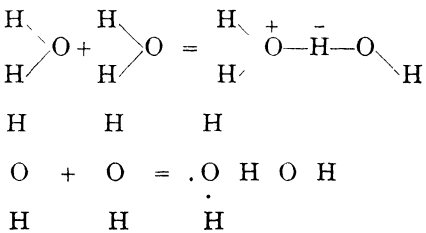



Borofluoride ion | Carbon tetrachloride | Methane | Ammonium ion

From the point of view of electronic theory, COORDINATION COMPOUNDS are formed when molecules or ions are coupled together by a dative bond Thus, in the actions cited above, the donors and acceptors are as follows




**Formation of molecular compounds. Association.**—The examples cited in the preceding paragraphs show that compounds can be formed by the union of integral molecules as well as of individual atoms The products are described as MOLECULAR COMPOUNDS, since they can often be reconverted into the molecules from which they were formed Thus the molecules of "hydrol," $H_2O$, in water-vapour unite with one another to form molecules of dihydrol $(H_2O)_2$, trihydrol $(H_2O)_3$, etc on liquefaction This process, when reversible, is described as ASSOCIATION On the assumption that the association depends on the formation of dative bonds (and not merely on the mutual attraction of dipoles, p 666), this process may be represented as follows




In this scheme, an oxygen atom as donor gives a half share of two electrons to a hydrogen atom, which acts as an acceptor

## CHAPTER VII

### FORMULAE AND EQUATIONS EQUIVALENTS OF COMPOUNDS

**Molecular and empirical formulae.**—When the molecular weight and the percentage composition of a volatile compound are known, it is possible, by a direct application of Avogadro's hypothesis, to deduce a MOLECULAR FORMULA, showing the number of atoms of each element in the molecule of the compound, as in the following example.

*Nitrobenzene*

Vapour density = 61 5, hence molecular weight = 123.

The percentage composition is

$$C = 58\,5\%; \quad H = 4\,1\%, \quad O = 26\,9\%, \quad N = 11\,4\%$$

Therefore in a molecule weighing 123 we have

$$C = 71\,9, \quad H = 5\,05, \quad O = 32, \quad N = 14,$$

or

$$C = 6 \times 12, \quad H = 5 \times 1, \quad O = 2 \times 16, \quad N = 1 \times 14,$$

and the formulae of nitrobenzene is $C_6H_5O_2N$

If the composition of the compound is known but not its molecular weight, the atomic weights deduced from Avogadro's hypothesis can still be used to express the composition of the compound by means of an EMPIRICAL FORMULA, showing the relative proportions of the atoms of each element, but not the actual number present in the molecule The method adopted in determining the empirical formula of a compound is as follows

(1) Divide the percentage of each element by its atomic weight. Thus in the case of nitrobenzene we have

| | C | H | O | N |
|---|---|---|---|---|
| Percentage composition | 58 5 | 4 1 | 26 0 | 11 4% |
| Atomic weights | 12 | 1 | 16 | 14 |
| Ratios | $\frac{58\,5}{12}$ | $\frac{4\,1}{1}$ | $\frac{26\,0}{16}$ | $\frac{11\,4}{14}$ |
| or | 4 875 | 4 1 | 1 625 | 0 814 |

(ii) Divide the smallest of these ratios into the others :

6·0 5 0 2 0 1

The quotients are the relative numbers of atoms of each element in the formula of the compound, which is therefore

$$C_6H_5O_2N$$

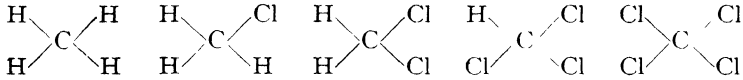
(iii) If fractions are present at this stage of the calculation they are converted into integers by multiplying the whole formula by a suitable factor, *e g* $C_2H_3O_{1\,5}$ would be written $C_4H_6O_3$

The molecular formula may be identical with the empirical formula or a multiple of it For instance, formaldehyde, acetic acid and grape-sugar have all the same composition and therefore the same empirical formula $CH_2O$, but the molecular formula of formaldehyde is identical with the empirical formula $CH_2O$, whilst the molecular formula of acetic acid is $(CH_2O)_2$, or $C_2H_4O_2$, and the molecular formula of grape-sugar is $(CH_2O)_6$ or $C_6H_{12}O_6$ Again, acetylene and benzene are both represented by the empirical formula CH, but the molecular formula of acetylene is $C_2H_2$, and that of benzene is $C_6H_6$

**Molecular weights of non-volatile compounds.**—Empirical formulae are used to express the composition of all compounds of which the molecular weight is unknown , and, even when the molecular weight can be determined, it is usual (i) to calculate an empirical formula to express the percentage composition, and then (ii) to find out by what factor it must be multiplied to give a molecular formula corresponding with the molecular weight of the compound Exact molecular weights, like exact atomic weights, are therefore generally determined in two stages, of which the second need not be based upon precise measurements, since it only requires a knowledge of an integral ratio For this reason, vapour densities are generally determined by comparatively rough methods, as described on pp 463 to 468 In the same way, the molecular weight of a dissolved substance can be deduced from observations of the boiling-point or freezing-point of its solution, as described on pp 519 to 529 , these methods also do not readily yield results of a high order of accuracy, but they suffice to deduce the integral ratio of the molecular to the empirical formula, and so enable us to determine the exact molecular weight of the compound

**Structural formulae.**—In addition to expressing the *proportions* of the different atoms in a chemical compound by means of an *empirical* formula, or the *numbers* of the different kinds of atoms in the molecule by means of a *molecular* formula, it is possible to express the *grouping* or *arrangement* of the atoms by means of a STRUCTURAL FORMULA For this purpose, however, it is essential to maintain the clear distinction which has been drawn in the preceding chapter between the two principal types of valency Thus the metal in the majority of salts must be shown as an ion, *e.g* $Na^+Cl^-$, since there is no evidence that the metal and non-metal are united by a covalent bond On the other hand, the compounds of carbon with hydrogen and with chlorine are represented with four bonds between the quadrivalent carbon and the

univalent hydrogen or chlorine atoms, since there is no evidence that these are present as ions



Methane | Methyl chloride | Methylene chloride | Chloroform | Carbon tetrachloride

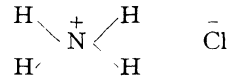
Moreover, the four bonds must be pictured as distributed equally in space, so that the univalent radicals are situated at the apices of a triangular pyramid or TETRAHEDRON (Fig 7, p 40), since, if they were placed at the corners of a square, we should expect to find two forms of methylene chloride, with the two chlorines *adjacent* or *opposite* to one another

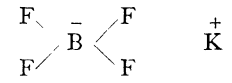
Structural formulae are often abbreviated so as to show only the way in which the multivalent atoms are linked together, *e g*

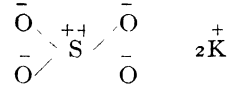
| | |
|---|---|
| Nitric acid | - - $NO_2$ OH |
| Sulphuric acid | - HO $SO_2$ OH |
| Alcohol - - | - $CH_3$ $CH_2$ OH |
| Acetic acid - | - $CH_3$ CO OH |

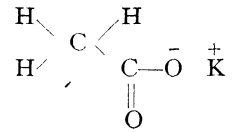
These abbreviations, in which the bonds between the radicals are often represented by dots instead of lines, are sometimes distinguished as CONSTITUTIONAL FORMULAE

The atoms of an organic compound can usually be represented as linked together throughout by a network of bonds, whilst a binary salt is shown as a mere aggregate of ions without any bonds at all There are, however, many examples, both of organic compounds and of mineral salts, in which the two types of union are present simultaneously, *e g*

*Ammonium chloride* $[NH_4]^+Cl^-$ or 

*Potassium borofluoride* $K^+[BF_4]^-$ or 

*Potassium sulphate* $K_2^{+\,+}[SO_4]^{-\,-}$ or 

*Potassium acetate* $[CH_3\ CO_2]^-K^+$ or 

In these compounds the radical shown in square brackets is held together by covalent bonds, but carries a positive or negative ionic charge by which it is linked to ions of opposite sign

Finally, it is possible to replace each bond of a structural formula by a pair of electrons, and thus to construct an ELECTRONIC FORMULA, in which the outer shell of valency electrons of each atom is represented by

a series of dots, so that the " lone pairs " of electrons as well as the " shared electrons " are indicated (compare p 39)

**Chemical equations.**—Lavoisier in 1789 made out a balance-sheet for the process of " vinous fermentation " He took 100 lbs of sugar, 400 lbs. of water and 10 lbs of yeast paste (containing 7 lbs of water), and obtained 460 lbs of liquor containing 409 lbs of water, 58 lbs of alcohol, 2 lbs of acetic acid, 4 lbs of unfermented sugar and 1 lb of dried yeast, whilst 35 lbs of " carbonic acid " escaped and carried with it 14 lbs of water Analysis, by combustion of the various components, showed that, both before and after fermentation, the material contained 70 lbs of hydrogen, 411 lbs of oxygen, and 29 lbs of carbon In this way he was able to establish the law of " Conservation of Mass " (p 3), and at the same time to illustrate the essential characteristics of a CHEMICAL EQUATION

The value of chemical equations became much more obvious when the various elements and compounds were represented by symbols, since the number of atoms of each element could then be balanced on the two sides of the equation and the quantities calculated from the atomic weights of the various elements Thus the equation,

$$2Na + Cl_2 = 2\overset{+}{N}a\overset{-}{Cl},$$

now implies that $2 \times 23$ grams of sodium combine with $2 \times 35\ 5$ grams of chlorine to form $2(23 + 35\ 5) = 2 \times 58\ 5$ grams of common salt

In the present chapter, the significance of chemical equations is illustrated in the special cases of

(i) Neutralisation of acids and bases

(ii) Oxidation and reduction

**Definitions of acids and bases** —Acids were first recognised by their sour taste, by their action on metals, alkalis and chalk, and by their ability to change the colour of indicators A more satisfactory definition was based on the part which they play in the formation of salts, thus

*An acid is a compound which contains one or more atoms of hydrogen which can be displaced by a metal to form a salt*

The development of physical chemistry led to the association of acidity in aqueous solutions with the presence of hydrogen ions, formed by a process of reversible ionisation, thus

$$HCl \rightleftharpoons \overset{+}{H} + \overset{-}{Cl}$$

Acidity was then defined and measured by the extent to which hydrogen ions were formed in aqueous solutions of an acid Since, however, the naked proton represented by the symbol, $H^+$, can only exist momentarily, *e g* as a positive ray in a vacuum tube, it is now recognised that acidity in aqueous solutions depends on the *transference* of a proton from the acidic hydride to the solvent, as represented, for instance, by the equations

$$\overset{+}{H} + H_2O = \overset{+}{H_3O},$$

$$H_2O + HCl = H_3\overset{+}{O} + \overset{-}{Cl}.$$

An acid is therefore now defined as a PROTON-DONOR Conversely, a base, which was formerly defined in terms of hydroxyl ions, *e.g.*

$$NaOH \rightleftharpoons \overset{+}{Na} + \overset{-}{OH},$$

is now defined in a more general way as a PROTON-ACCEPTOR We therefore use the following definitions

*An acid is a substance which will give up a proton to a base*
*A base is a substance which will accept a proton from an acid*

According to these definitions an acid must always be a hydride, which we can write as HA, but it need not be a neutral molecule Thus the oxonium ion $H_3O^+$ is an acid, since it can give its proton to some other substance, *e g* to an acetate ion, which then acts as a base by accepting a proton

$$\underset{\text{Acetate ion}}{CH_3\ CO\ \overset{-}{O}} + \underset{\substack{\text{Oxonium}\\\text{ion}}}{\overset{+}{O}H_3} \rightleftharpoons \underset{\text{Acetic acid}}{CH_3\ CO\ OH} + \underset{\text{Water}}{OH_2}$$

On the other hand, although the hydroxyl ion is a very strong base, it is not necessary that a base should be a hydroxide, since a molecule of ammonia can accept a proton in just the same way as a hydroxyl ion

$$\overset{-}{O}H + \overset{+}{O}H_3 = 2OH_2 \qquad NH_3 + HCl = \overset{+}{N}H_4 + \overset{-}{Cl}$$

We therefore write the acid as HA and the base as B, and represent the neutralisation of an acid and a base by the equation

$$B + HA \rightleftharpoons \overset{+}{B}H + \overset{-}{A}$$

**Equivalents of acids and bases.**—In accordance with the conceptions set out above, the equivalents of an acid and of a base are defined as follows

*The equivalent of an acid is that weight which contains one equivalent* (1 0078 *parts*) *of hydrogen which can be given to a base*
*The equivalent of a base is that weight which will accept one equivalent* (1 0078 *parts*) *of hydrogen from an acid*

The equivalents of hydrochloric, nitric, sulphuric and phosphoric acids in round numbers are therefore

$$HCl = 36\ 5, \quad HNO_3 = 63, \quad \tfrac{1}{2}H_2SO_4 = \tfrac{98}{2}, \quad \tfrac{1}{3}H_3PO_4 = \tfrac{98}{3},$$

but the equivalents of formic, acetic, permonosulphuric and hypophosphorous acids are

$$H_2CO_2 = 46, \quad H_4C_2O_2 = 60, \quad H_2SO_5 = 114, \quad H_3PO_2 = 66,$$

since each of the second group of acids contains only *one* atom of hydrogen which can be removed by a base Conversely, the equivalents of ammonia, sodium hydroxide, potassium hydroxide and calcium hydroxide are

$$NH_3 = 17, \quad NaOH = 40, \quad KOH = 56, \quad \tfrac{1}{2}Ca(OH)_2 = 37,$$

since each of these quantities will accept one atom of hydrogen from an acid in accordance with the following equations

$$NH_3 + HCl = NH_4Cl \qquad NaOH + HCl = NaCl + H_2O$$
$$KOH + HCl = KCl + H_2O \qquad Ca(OH)_2 + 2HCl = CaCl_2 + 2H_2O.$$

**Equivalents of oxidising and reducing agents.**—An OXIDISING AGENT is one which will give oxygen to, and a REDUCING AGENT is one which will take oxygen from, another substance Thus in the interaction between sulphurous acid and hydrogen peroxide,

$$H_2SO_3 + H_2O_2 = H_2SO_4 + H_2O,$$

hydrogen peroxide is an oxidising agent because it gives oxygen to the sulphurous acid, whilst sulphurous acid is a reducing agent because it takes oxygen from the hydrogen peroxide We therefore define the equivalents of oxidising and reducing agents as follows

*The equivalent of an oxidising agent is that weight which contains 8 grams of oxygen available for oxidation of other substances*

*The equivalent of a reducing agent is that weight which will remove 8 grams of oxygen from other substances*

In order to make use of this definition we must notice that the equivalent of oxygen is one half of its atomic weight, O = 16 (p 17) Since only half of the oxygen (1 atom or 2 equivalents) can be removed readily from hydrogen peroxide, the equivalent of this oxidising agent is .

$$\tfrac{1}{2}H_2O_2 = \tfrac{1}{2}(2 + 32) = 17.$$

Conversely, since a molecule of sulphurous acid requires one atom of oxygen to convert it into sulphuric acid, its equivalent is

$$\tfrac{1}{2}H_2SO_3 = 41$$

**Hydrogenation and dehydrogenation.**—An oxidising agent is often used, not to *add oxygen* to another substance, but to *remove hydrogen* from it Thus, when sulphuretted hydrogen is oxidised, either process may take place, giving rise to sulphuric acid or to elementary sulphur as a product

*Addition of oxygen* $H_2S + 2O_2 = H_2SO_4.$

*Removal of hydrogen* $H_2S + O = S + H_2O,$

*e g* $2H_2S + SO_2 = 2H_2O + 3S.$

Since reduction is the converse of oxidation, it is also customary to regard the *addition of hydrogen* as a form of reduction, *e g*

*Reduction of iodine and oxidation of sulphurous acid* $H_2SO_3 + H_2O + I_2 = H_2SO_4 + 2HI.$

Therefore when we are thinking of oxidation and reduction in terms of the removal and addition of hydrogen, we may use the following definitions.

*The equivalent of an oxidising agent is that quantity which will remove one equivalent (1·0078 parts) of hydrogen from another substance.*

*The equivalent of a reducing agent is that quantity which will give one equivalent (1·0078 parts) of hydrogen to some substance.*

On this basis the equivalent of iodine as an oxidising agent is $\frac{1}{2}I_2 = 127$, whilst that of hydrogen iodide as a reducing agent is $HI = 128$

Another interesting example of this type of oxidation and reduction is provided by hydriodic and iodic acids, which interact by transference of hydrogen from iodine to oxygen according to the equation

$$5HI + HIO_3 = 3I_2 + 3H_2O.$$

Since the salts of these two acids do not interact, this mixture can be used for the estimation of acids, each equivalent of which liberates one equivalent of iodine from the mixed salts

**Oxidation and reduction of metallic salts** —Many metals are capable of existing in several stages of oxidation and of forming salts derived from more than one basic oxide, *e g*

| | | | |
|---|---|---|---|
| $FeO + 2HCl = FeCl_2 + H_2O$ | | $Fe_2O_3 + 6HCl = 2FeCl_3 + 3H_2O$ | |
| Ferrous oxide | Ferrous chloride | Ferric oxide | Ferric chloride |
| $SnO + 2HCl = SnCl_2 + H_2O$ | | $SnO_2 + 4HCl = SnCl_4 + 2H_2O$ | |
| Stannous oxide | Stannous chloride | Stannic oxide | Stannic chloride |

The conversion of ferrous into ferric chloride and of stannous into stannic chloride are often described in terms of the corresponding oxides as processes of " oxidation," whilst the converse changes are described as " reduction " Thus, ferrous chloride is " oxidised " to ferric chloride by chlorine, whilst ferric chloride is " reduced " to ferrous chloride by the action of stannous chloride

$$2FeCl_2 + Cl_2 = 2FeCl_3 \qquad 2FeCl_3 + SnCl_2 = 2FeCl_2 + SnCl_4$$

In actions such as these, the equivalents of oxidising and reducing agents may be defined as follows

> *The equivalent of an oxidising agent is that weight which will add one equivalent of an acid radical to a metallic salt ,*

and

> *The equivalent of a reducing agent is that weight which will remove one equivalent of an acid radical from a metallic salt*

Thus the equivalent of ferric chloride as an oxidising agent is $FeCl_3 = 162{\cdot}5$, since only one equivalent of chlorine (35 5 parts) is liberated when the ferric salt is reduced to the ferrous state For the same reason, when a ferrous salt is used as a reducing agent, the equivalent is that quantity which contains one atomic proportion (56 parts) of iron, since each atom of iron takes up only one equivalent of chlorine Thus, the equivalent of ferrous ammonium sulphate, $FeSO_4$, $(NH_4)_2SO_4$, $6H_2O$ (which contains one-seventh of its weight of metallic iron), is $7 \times 56 = 392$

Finally, the process of *adding a metal* to an acid radical is described as reduction, whilst the process of *removing a metal* from an acid radical is

described as oxidation, *e g* iodine "oxidises" sodium thiosulphate to sodium tetrathionate, according to the equation:

$$2Na_2S_2O_3 + I_2 \rightarrow 2NaI + Na_2S_4O_6$$

Sodium thiosulphate — Sodium tetrathionate

The equivalent of sodium thiosulphate is $Na_2S_2O_3 = 158$, since each atom of iodine removes only one atom of sodium from a molecule of sodium thiosulphate and the atom of sodium is also its equivalent. Bromine, on the other hand, acts upon sodium thiosulphate according to the equation

$$Na_2S_2O_3 + 4Br_2 + 5H_2O = 2NaHSO_4 + 8HBr$$

In this reaction, therefore, the equivalent of the thiosulphate is only one-eighth of 158 or 19 75, since each molecule of this sulphate reduces eight equivalents of bromine.

In general, oxidation may be defined as *a process in which the ratio of negative or non-metallic to positive or metallic components is increased*, whilst reduction may be defined as a process in which this ratio is reduced

**Potassium dichromate and potassium permanganate as oxidising agents.**—Interesting examples of the use of salts as oxidising agents are provided by potassium dichromate, $K_2Cr_2O_7$, and potassium permanganate, $KMnO_4$ These two salts are derived from the higher *acidic* oxides of chromium and manganese, and therefore contain the metal as a part of the acid radical In presence of acids they are readily reduced to salts derived from the lower basic oxides These reductions correspond with the following changes in the oxidation of the metals

$$2CrO_3 \rightarrow Cr_2O_3 \qquad Mn_2O_7 \rightarrow 2MnO$$

They therefore provide *three* equivalents of oxygen for each atom of chromium and *five* equivalents of oxygen for each atom of manganese In the absence of acid, however, the reduction of potassium permanganate proceeds only as far as the neutral manganese dioxide, liberating only three equivalents of oxygen for each atom of manganese. The relevant equations are

$$K_2Cr_2O_7 + 4H_2SO_4 = K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3O.$$

Potassium dichromate — Chromic sulphate

$$2KMnO_4 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 3H_2O + 5O.$$

Potassium permanganate — Manganous sulphate

$$2KMnO_4 + H_2O = 2KOH + 2MnO_2 + 3O$$

Potassium permanganate — Manganese dioxide

The equivalents are therefore $\frac{1}{6}K_2Cr_2O_7 = 49$, $\frac{1}{5}KMnO_4 = 31\ 6$ in presence of acids, but $\frac{1}{3}KMnO_4 = 52\ 7$ for potassium permanganate in the absence of acids

The two former equations may be combined with the equation for reduction by ferrous sulphate in presence of sulphuric acid,

$$2FeSO_4 + H_2SO_4 + O = Fe_2(SO_4)_3 + H_2O,$$

as follows.

$$K_2Cr_2O_7 + 6FeSO_4 + 7H_2SO_4 = K_2SO_4 + Cr_2(SO_4)_3 + 3Fe_2(SO_4)_3 + 7H_2O,$$
$$2KMnO_4 + 10FeSO_4 + 8H_2SO_4 = K_2SO_4 + 2MnSO_4 + 5Fe_2(SO_4)_3 + 8H_2O$$

The first of these equations includes 59 atoms of oxygen of which 3 are used for oxidation and reduction, whilst the numbers for the second equation are 80 and 5

**Electronic theory of oxidation and reduction.**—The oxidation of ferrous chloride to ferric chloride and the reduction of ferric chloride to ferrous chloride in dilute aqueous solutions can be represented by the ionic equations,

$$\overset{++}{Fe} - e = \overset{+++}{Fe} \quad \text{and} \quad \overset{+++}{Fe} + e = \overset{++}{Fe},$$

where $e$ is a negatively charged electron It is therefore clear that in oxidations and reductions of this type

*Electrons are removed in the process of oxidation*
*Electrons are added in the process of reduction*

These definitions, however, are applicable over a much wider range Thus the use of chlorine as an oxidising agent, and of sodium as a reducing agent, is always accompanied by the conversion of the halogen into an anion and of the metal into a cation

$$Cl_2 + 2e = 2\overset{-}{Cl} \qquad Na - e = \overset{+}{Na}$$

In these operations, therefore, the molecule of chlorine is reduced by the addition of two electrons and is thus converted into two negatively charged chloride ions, whilst the atom of sodium is oxidised by losing an electron and is converted into a positively charged sodium ion

# CHAPTER VIII

## CLASSIFICATION OF THE ELEMENTS

**Properties of metals and non-metals.**—(*a*) *Electropositive and electro negative elements* —A METAL may be defined as *an element which readily loses electrons*, and a NON-METAL as *an element which readily accept electrons* The inert gases of the helium family are, however, classifiec as non-metals, because, although they cannot accept electrons, they ar too stable to hand over their electrons to another element The principa chemical property of a metal is therefore its ability to form a positivel charged *cation*, by giving electrons to a non-metal, whilst the principa chemical property of a non-metal is its ability to form a negativel charged *anion* by accepting electrons from a metal

The metals of the alkalis, which contain one more electron than a inert gas, are the elements which are most ready to give electrons t another element , they are therefore said to be the most ELECTROPOSITIV of the elements Conversely, the halogens, which contain one electro less than an inert gas, are the most strongly ELECTRONEGATIVE elements since they are the most ready to accept electrons from another element

(*b*) *Atomicity of vapours.*—Non-metals are very ready to undergo process of electron-sharing (p 38) The elements therefore often forn diatomic molecules, such as $H_2$, $Cl_2$, $N_2$, in which all the valencies of bot atoms are used up in binding the two atoms together by single, double, o triple bonds These molecules are " saturated " and have very little hol upon one another Many of the non-metals are therefore gases, o volatile liquids or solids, as in the series of halogens, where fluorine an chlorine are gases, bromine is a liquid and iodine a volatile solid Som non-metals, such as phosphorus and sulphur, however, form larger mole cules, $P_4$ and $S_8$, which are less volatile , and quadrivalent elements, suc as carbon (which cannot form saturated diatomic molecules, becaus quadruple bonds are not possible), give " giant molecules," *i e* a networ of atoms of indefinitely large area or volume, which boil at very hig temperatures, since the liberation of vapour involves the disruption c chemical bonds On the other hand, metallic vapours generally consis of single atoms, since metals do not readily share electrons Thus th vapours of mercury and of the alkali metals are predominantly monatomic

(*c*) *Thermal and electrical conductivities* —In the solid state, metal differ from non-metals in that the solid appears to consist of closely-packe cations held together by mobile electrons The METALLIC STATE is there fore characterised by (i) *metallic conductivity*, since the mobile electron can carry an electric current without any decomposition of the metal (ii) *thermal conductivity*, since the mobile electrons can also carry hea energy , (iii) *metallic lustre*, which depends on opacity and reflectin power These properties are developed to some extent in graphite, whic may be regarded as a quasi-metallic form of carbon, but not in diamond

In many metals, *e g* Al, Cu, Ag, Au, and iron above 796°, the crystal structure, shown in Fig 8, consists of layers of atoms which can easily slip over one another These metals are therefore malleable and ductile and form malleable and ductile alloys, which are often of great tensile strength, but these properties are not developed in metals, such as antimony and bismuth, which have a less favourable crystalline structure

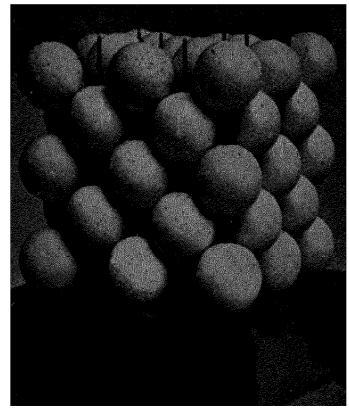


FIG 8 TYPICAL CRYSTAL-STRUCTURE OF MALLEABLE METALS AND ALLOYS

(*d*) *Density* —The density of an element depends largely on the magnitude of the positive charge by which the electrons are bound to the nucleus Since non-metals with very large nuclear charges are unknown, they do not give rise to very high densities, the maximum (4 95) being reached in iodine On the other hand, densities up to 20 are found amongst metals with large nuclear charges, although some of the alkali-metals are lighter than water

The properties of metals and non-metals are summarised in Table 2

TABLE 2 —PROPERTIES OF METALS AND NON-METALS

| METALS | NON-METALS |
|---|---|
| 1 Electropositive , form cations | 1 Electronegative , form anions |
| 2 Form metallic crystals, which exhibit metallic conductivity, thermal conductivity and metallic lustre , they often have useful mechanical properties, and may have high densities | 2 Form volatile diatomic molecules, *or* non-volatile giant molecules, giving rise to great hardness in diamond Graphite, arsenic and tellurium exhibit metallic properties , and iodine is lustrous because the crystals are opaque |
| 3 Halides generally form ionic aggregates and are non-volatile, but give conducting solutions in water Some halides, however, form covalent molecules, and thus resemble the non-metallic halides, *e g* $SnCl_4$ is a volatile liquid | 3 Halides form covalent molecules and are volatile Many of them are easily hydrolysed by water, *e g* $PCl_3$ |
| 4 Oxides are usually basic, but ZnO and $Al_2O_3$ are amphoteric, and some higher oxides, *e g* $CrO_3$, are acidic | 4 Oxides are usually acidic, but a few are neutral, *e g* CO, NO, $N_2O$, $H_2O$ |

**The electrochemical series.**—In discussing the properties of metals and non-metals (pp 51-52), it was pointed out that metals are *electropositive*, that is, they tend to lose electrons and form positive ions, whilst non-metals are *electronegative*, that is, they tend to acquire electrons and form negative ions This tendency can be measured quantitatively by finding the E M F that is produced when an element is placed in a normal solution of its ion Thus, when a plate of zinc is placed in a solution which is normal in respect to zinc ions, $Zn^{++}$, the metal sends more zinc ions into the solution (against the osmotic pressure of the zinc ions already in the solution) until there is an absolute potential difference of 1 034 volts between the metal and the solution By means of electrical measurements it is possible to arrange the elements in an ELECTROCHEMICAL SERIES, in which the metals are placed in descending order of electropositiveness, and the non-metals in ascending order of electronegativeness

| | |
|---|---|
| ELECTROPOSITIVE | K, Na, Ba, Sr, Ca, Mg, Al, Cr, Mn, Zn, Cd, Fe, Co, Ni, Sn, Pb, H, Sb, Bi, As, Cu, Hg, Ag, Pt, Au |
| ELECTRONEGATIVE | Si, C, B, N, P, S, I, Br, Cl, O, F |

This classification, which is based on electrical measurements, provides a useful guide to the properties of elements , for example

(i) *Displacement of hydrogen from water and acids* —The metals above hydrogen, with the exception of lead, displace this element from water and dilute acids Moreover, it is obvious that the higher the metal is in this series the more vigorous its action ought to be, since the E M F or driving force of the displacement

$$M + 2H^+ \rightarrow M^{++} + H_2$$

is clearly greater the higher the metal is above hydrogen Thus potassium and sodium, the most electropositive metals in the series, react violently with cold water, and explosively with dilute acids , barium, strontium and calcium react very vigorously with acids, but decompose water slowly and with decreasing vigour The metals from magnesium * to zinc decompose steam irreversibly,

$$Zn + H_2O \rightarrow ZnO + H_2,$$

but from iron downwards the reverse reaction becomes increasingly important,

$$3Fe + 4H_2O \rightleftharpoons Fe_3O_4 + 4H_2,$$

and the metals also dissolve in dilute acids with increasing difficulty Finally, lead and the metals below hydrogen are not sufficiently electropositive to displace this element directly from steam or dilute acids

(ii) *Combination with oxygen* —Since oxygen is an electronegative element it is not surprising to find that the stability of the metallic oxides increases with the electropositiveness of the metal Thus the oxides of

* Aluminium is not attacked by water or steam, unless the protective coating of oxide is loosened by amalgamation with mercury

aluminium and metals above it in the series are so stable that their reduction by carbon is either impossible or too difficult to be commercially profitable (magnesium excepted, p 114), hence these metals are manufactured by electrolytic methods (see pp 93, 105, 117, 129) The metals below aluminium are usually extracted by the reduction of their oxides with carbon, but it is instructive to note that, until iron is reached, the carbon is oxidised almost exclusively to carbon monoxide, *e g*

$$ZnO + C = Zn + CO$$

In the case of iron, however, a considerable amount of carbon dioxide is also produced, because iron oxide reacts reversibly with carbon monoxide (p 351)

$$FeO + CO \rightleftharpoons Fe + CO_2$$

The oxides of tin, lead and copper are so easily reduced that carbon dioxide is the main product of oxidation, whilst the oxides of mercury, silver and gold have such a low stability that they are readily decomposed by the action of heat alone

Finally, it is interesting to note (i) that the metals above magnesium are so reactive towards oxygen, water and acids, that they are kept in bottles like museum specimens, (ii) that magnesium can only be used for constructional purposes when it is alloyed with aluminium, and (iii) that the metals from copper downwards are so unreactive that they occur to an increasing extent in the native state, *e g* both platinum and gold are found almost exclusively in the metallic state

The affinity of the non-metals for oxygen does not follow quite the same sequence as that in the electrochemical series, *e g* the extreme inflammability of white phosphorus is in marked contrast to the inertness of nitrogen, which is only slightly oxidised even at 2000°, whilst the common oxides of chlorine are much more stable than the oxides of bromine

(iii) *Combination of metals with other non-metals and radicals* —The behaviour of metals towards oxygen is roughly paralleled by their behaviour towards the non-metals and non-metallic radicals, *i e* the more electropositive a metal is, the greater its affinity for a particular non-metal or radical For example, sodium will displace aluminium from aluminium chloride

$$3Na + AlCl_3 = 3NaCl + Al, \text{ or } 3Na + Al^{+++} = 3Na^{+} + Al$$

and zinc will precipitate copper from a solution of copper sulphate ,

$$Zn + CuSO_4 = ZnSO_4 + Cu, \text{ or } Zn + Cu^{++} = Zn^{++} + Cu$$

Conversely, a more electronegative non-metal will, in general, displace a less electronegative non-metal from combination with a metal, as when chlorine displaces bromine from potassium bromide,

$$2KBr + Cl_2 = 2KCl + Br_2, \text{ or } 2Br^{-} + Cl_2 = Br_2 + 2Cl^{-},$$

and bromine displaces iodine from potassium iodide

$$2KI + Br_2 = 2KBr + I_2, \text{ or } 2I^{-} + Br_2 = I_2 + 2Br^{-}.$$

**Triads, families and octaves of elements.**—(*a*) *Triads*.—Dobereiner in 1829 directed attention to the existence of TRIADS of similar elements, in each of which the atomic weight of the central element was the arithmetic mean of those of the other two. Thus, taking modern values for the atomic weights, we have in round numbers

| | | | |
|---|---|---|---|
| Cl = 35½ | Br = 80 | I = 127 | Mean of Cl and I = 81. |
| Ca = 40 | Sr = 88 | Ba = 137 | Mean of Ca and Ba = 88½. |

The chemical and physical properties of the central element are also approximately half-way between those of the other two elements.

(*b*) *Families*.—Dumas in 1859 developed Dobereiner's triads into FAMILIES or NATURAL SERIES of elements, *e g* by classifying fluorine with the triad of halogens and magnesium with the triad of metals of the alkaline earths, thus

F, Cl, Br, I, Mg, Ca, Sr, Ba.

The increments of atomic weight were then no longer uniform in a given family, but were often the same for two or more families.

(*c*) *Octaves*.—After Cannizzaro in 1857 had worked out a sound system of atomic weights, based upon Avogadro's hypothesis, Newlands in 1865 found that *when the elements were arranged in order of increasing atomic weights*, the members of a given family recurred at regular intervals, like octaves in music. Thus, the eighth element resembled the first, the ninth resembled the second, and so on. This relationship was known as the LAW OF OCTAVES. It proved satisfactory for the first seventeen elements, but broke down badly after the first two octaves, for reasons that are set out below.

**Mendeléeff's periodic classification of the elements.**—(*a*) *Long and short periods*.—Mendeléeff (1869, 1871) again arranged the elements in the order of their atomic weights, but adopted a more flexible form of the Law of Octaves. The principal features of his classification are reproduced in Table 3, with appropriate corrections of the atomic weights. In Mendeléeff's table the elements were arranged in SERIES corresponding with Newlands' "octaves," but hydrogen was placed by itself in Series 1. Series 2 and 3 correspond with Newlands' first two octaves and were described by Mendeléeff as SHORT PERIODS. These were followed by two LONG PERIODS of 17 elements, each composed of two octaves and an intermediate triad (Series 4-5 and 6-7). The octaves were arranged in seven vertical columns I to VII, each of which included a GROUP or FAMILY of elements. The intermediate triads were placed in an additional column VIII, together with the coinage metals, Cu, Ag, Au, which were shown in duplicate in the Table *. The number at the head of each column was

* Mendeléeff's method of dealing with the coinage metals is one of the most interesting features of his Table. The three elements, Cu, Ag, Au, were needed to fill the gaps in the odd series (5, 7, 11) of Column I, but they differ so widely from the corresponding elements K, Rb, Cs, of the even series (4, 6, 8), that Mendeléeff enclosed their symbols in brackets to show how little adapted these heavy inert metals were for classification with the light and intensely active metals of the alkalis. They were, however, completely in place when associated with the

identified with the valency of the principal oxide, although in column VIII this figure represents a maximum which is only reached in $RuO_4$ and $OsO_4$.

TABLE 3.—MENDELÉEFF'S PERIODIC CLASSIFICATION OF THE ELEMENTS (with atomic weights corrected and series 8-10 modified to show the rare earth elements).

| Series | Group I — $R_2O$ | II — RO | III — $R_2O_3$ | IV $RH_4$ $RO_2$ | V $RH_3$ $R_2O_5$ | VI $RH_2$ $RO_3$ | VII RH $R_2O_7$ | VIII — $RO_4$ |
|---|---|---|---|---|---|---|---|---|
| 1 | H = 1 | | | | | | | |
| 2 | Li = 7 | Be = 9 | B = 11 | C = 12 | N = 14 | O = 16 | F = 19 | |
| 3 | Na = 23 | Mg = 24 | Al = 27 | Si = 28 | P = 31 | S = 32 | Cl = 35.5 | |
| 4 | K = 39 | Ca = 40 | - = 44 | Ti = 48 | V = 51 | Cr = 52 | Mn = 55 | Fe = 56, Co = 59, Ni = 59, Cu = 63½ |
| 5 | (Cu = 63½) | Zn = 65 | - = 68 | - = 72 | As = 75 | Se = 79 | Br = 80 | |
| 6 | Rb = 85 | Sr = 87.6 | Yt = 89 | Zr = 91 | Nb = 93 | Mo = 96 | - = 100 | Ru = 102, Rh = 103, Pd = 107, Ag = 108 |
| 7 | (Ag = 108) | Cd = 112 | In = 115 | Sn = 119 | Sb = 122 | Te = 128 | I = 127 | |
| 8, 9, 10 | Cs = 133 | Ba = 137 | RARE EARTHS | ? = 180 | Ta = 181 | W = 184 | | Os = 191, Ir = 193, Pt = 195, Au = 197 |
| 11 | (Au = 197) | Hg = 200.6 | Tl = 204 | Pb = 207 | Bi = 209 | — | — | |
| 12 | — | — | — | Th = 232 | — | U = 238 | — | — |

Mendeléeff believed that his two long periods were followed by two more long periods of the same type. This is incorrect, since the range in question is occupied by a single very long period, which is expanded by

elements Ni, Pd, Pt, which precede them in column VIII, since the similarity between these elements is remarkably close. Later writers have ignored this feature of Mendeléeff's table and have therefore been obliged to exercise their imaginative powers in attempts to justify the classification of sodium and gold as members of the same family of elements.

the intrusion of a cluster of 15 tervalent elements of the RARE EARTHS, which all claim a place in Column III. Mendeléeff's classification therefore broke down after the two long periods, just as Newlands' classification had done after the first two octaves or short periods, and for a similar reason Since the non-existent period of Mendeléeff's table consisted mainly of blank spaces, it has been suppressed in Table 3

(*b*) *Odd and even series* —The seven elements of Series 2, which make up the FIRST SHORT PERIOD, show a striking resemblance to the elements of Series 3, which provide the SECOND SHORT PERIOD of Mendeléeff's table, thus

| | | I | II | III | IV | V | VI | VII |
|---|---|---|---|---|---|---|---|---|
| First Short Period | Series 2 | Li | Be | B | C | N | O | F |
| Second Short Period | Series 3 | Na | Mg | Al | Si | P | S | Cl |

On the other hand, the pairs of octaves (namely Series 4 and 5, or Series 6 and 7), which make up the two LONG PERIODS, differ widely from one another Mendeléeff therefore discriminated between the EVEN SERIES (*e g* Series 4, 6 and 8, which begin with the metals of the alkalis K, Rb, Cs) and the ODD SERIES (*e g* Series 5, 7 and 11, which begin with the coinage metals, Cu, Ag, Au) and directed attention to this difference by displacing the elements of the odd and even series to the right and left of its vertical columns This alternation, however, does not exist in the two short periods (Series 2 and 3), which both begin with an alkali metal It has therefore become customary to print the elements of the two short periods in the centre of the vertical columns, and to divide the elements of the long periods into (*a*) and (*b*) series, thus

| O | I | | II | | V | | VI | | VII | |
|---|---|---|---|---|---|---|---|---|---|---|
| He | Li | | Be | | N | | O | | F | |
| Ne | Na | | Mg | | P | | S | | Cl | |
| | (*a*) | (*b*) | (*a*) | (*b*) | (*a*) | (*b*) | (*a*) | (*b*) | (*a*) | (*b*) |
| A | K | Cu | Ca | Zn | V | As | Cr | Se | Mn | Br |
| Kr | Rb | Ag | Sr | Cd | Nb | Sb | Mo | Te | | I |
| Xe | Cs | Au | Ba | Hg | Ta | Bi | | | | |

The inert gases of the atmosphere were placed by Ramsay in an additional column O, corresponding with their zero valency, at the beginning of each period, as shown above , but they are now generally placed at the *ends* of the preceding periods

(*c*) *Typical and transitional elements* —The seven elements of the first short period (Series 2), together with hydrogen, were described by Mendeléeff as TYPICAL ELEMENTS Their properties are reproduced with more or less modification in the elements of the second short period, and by the elements which occupy the *ends* of the two long periods The elements which occupy the *middle* portions of the long periods, however, do not resemble the typical elements with which they are associated in the various vertical columns Thus the coinage metals of group I (*b*) do not resemble the alkali metals of group I (*a*), and manganese in group VII (*a*) is quite different from the halogens of group VII (*b*) These middle

elements, however, show a marked resemblance to one another Thus, as Mendeléeff pointed out, the last members of the even series, *e g* Cr and Mn, resemble the first members of the odd series, *e g* Cu and Zn, and so give rise, with the intermediate triad, to a TRANSITION SERIES as follows

$$Cr = 53,\ Mn = 55,\ Fe = 56,\ Co = 59,\ Ni = 59,\ Cu = 63\tfrac{1}{2},\ Zn = 65.$$

In these transition series, the vertical relationships of the typical elements are replaced by horizontal relationships

**Correction of atomic weights.**—Mendeléeff was able to use his periodic classification as a check upon certain doubtful atomic weights Thus beryllium, which had been regarded as a tervalent element like aluminium, could only be placed in group II, and must therefore be bivalent The atomic weight was therefore corrected from

$$4\,5 \times 3 = 13\,5 \quad \text{to} \quad 4\,5 \times 2 = 9\,0,$$

in spite of the fact that Dulong and Petit's law (p 21) indicated the higher value

**Prediction of new elements.**—Newlands' law of octaves broke down after the first 17 elements, because the eighteenth element was still unknown. Mendeléeff got over this difficulty by leaving blank spaces for this and other unknown elements, and even ventured to predict their properties from those of contiguous elements in his classification In particular, three elements, with atomic weights 44, 68 and 72, were required to occupy vacant places below boron, aluminium and silicon Within 15 years these were all discovered, with properties substantially as predicted, and renamed after their country of origin, thus

| | |
|---|---|
| Ekaboron, | Eb = 44, became Scandium, |
| | Sc = 44 1 (Nilson, 1879) |
| Ekaaluminium, | Ea = 68, became Gallium, |
| | Ga = 69 9 (Boisbaudron, 1875) |
| Ekasilicon, | Es = 72, became Germanium, |
| | Ge = 72 5 (Winkler, 1886) |

The verification of these predictions was an important factor in demonstrating the value of the periodic classification A few more of Mendeléeff's predictions have been verified in more recent years, but all his predictions in the range covered by the rare earths have been shown to be erroneous, and it was only after the development of Moseley's system of atomic numbers (p 29) that conclusive evidence as to the total number of vacant places could be given

**Periodicity of atomic volumes and of atomic heats at low temperatures.**—In 1869, Lothar Meyer stated the LAW OF PERIODICITY as follows "The properties of the elements are largely *periodic* functions of the atomic weight Identical or similar properties recur, if the atomic weight is increased by a definite amount, which is at first 16, then about 46, and finally 88 to 92 units" In particular, he drew attention to the fact that the atomic volumes of the elements are a periodic property of their atomic weights

The atomic volume of an element is defined by the equation:

specific volume × atomic weight = atomic volume

The SPECIFIC VOLUME is the volume occupied by 1 gram of the element, and the ATOMIC VOLUME is therefore the volume occupied by one gram-atom By plotting the atomic volumes of the elements against the atomic

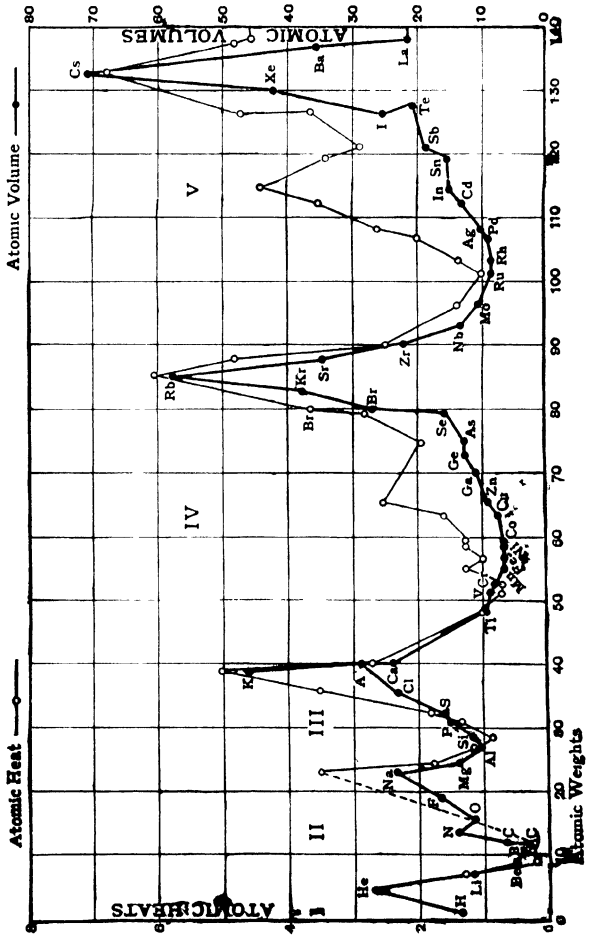



FIG 9 ATOMIC HEATS AND ATOMIC VOLUMES

weights, Meyer obtained a curve showing a series of waves, in which the short and long periods are clearly shown, with the light alkali metals at the crests and the heavy transition elements in the troughs of the waves. This curve expresses the law of periodicity even more clearly than Mendeleéff's second table (1871), since similar elements occupy similar positions on either side of the crests, but no trace whatever can be seen of

Mendeléeff's resolution of the long periods into odd and even series of octaves

A modern rendering of Meyer's curve is reproduced in Fig 9, where the black circles represent the atomic volumes of the elements and the hollow circles represent their atomic heats in the range from $-195°$ to $-253°$ It will be remembered (p 22) that Dulong and Petit found that at ordinary temperatures the atomic heats are nearly constant at about 6 3, and would therefore give a horizontal straight line in the diagram. Dewar showed that this is no longer the case at low temperatures, since the data then yield a curve which shows a remarkable similarity to Lothar Meyer's curve of atomic volumes

**Classification based upon atomic numbers.**—When the elements are classified in the order of their atomic weights, a few irregularities cannot be avoided Thus, cobalt, Co = 58 94, should obviously precede nickel, Ni = 58 69, in the transition series, since the former element shows the greater resemblance to iron which precedes them, and the latter to copper which follows them in the Series Fe, Co, Ni, Cu Even more obviously, tellurium, Te = 127 61, as a member of the oxygen family, must precede iodine, I = 126 92, in the group of halogens More recently, the inert gas argon, A = 39 944, has been placed before potassium, K = 39 096, and the radioactive element protactinium, Pa = 231, after thorium, Th = 232 12

These anomalies disappear when the elements are classified in the order of their ATOMIC NUMBERS (p 29) These are more fundamental than their atomic weights, since the latter depend on the proportions in which the isotopes of complex elements (p 29) are mixed, and may easily get "out of step" in two consecutive mixtures The success of Mendeléeff's classification therefore depended on the happy accident that the atomic weights generally increase with increasing atomic number, and only occasionally go astray

A classification based upon atomic numbers has the advantage that each element occupies a place in a series of integers Gaps caused by unknown elements can therefore be recognised immediately and allowance made for them in the table , and a claim that one of the missing elements has been found can be checked immediately by Moseley's method for the determination of atomic numbers (p 29)

In the following chapters the classification of the elements on the basis of their atomic numbers is used in its simplest possible form Thus in Part II, Mendeléeff's "typical elements" are described, together with those elements which most closely resemble them in structure and properties, whilst the "transitional elements" are described in Part III

The arrangement of the planetary electrons in the "typical" series of elements is shown in Table 4 It will be seen that the principal characteristic of each series of typical elements is the building up of an OCTET of eight electrons in the outer shell of the atom The *K*-shell, which is occupied by a *duplet* of electrons in helium, however, retains this number of electrons in all the atoms of higher atomic number Thus, in the first short period this kernel is surrounded by a progressively increasing number of electrons in the *L*-shell In this way it finally acquires a complete octet of electrons in neon and thus develops the characteristic stability

of an "inert gas" In the second short period the $K$- and $L$-shells remain filled with $2+8$ electrons, whilst the $M$-shell in its turn acquires an octet of electrons, which is completed in argon The outer shell of electrons has the same configuration in corresponding elements of the two short periods They therefore show a strong resemblance to one another, especially in valency, since the inner shells of electrons have relatively little influence on the chemical properties of the atom Nevertheless, there are rather wide differences between B and Al, C and Si, N and P, O and S, conversely, attention may be directed to the similarity (apart from valency) of the diagonally-related elements Be and Al, B and Si, etc

TABLE 4.—DISTRIBUTION OF PLANETARY ELECTRONS IN ELEMENTS OF THE TYPICAL SERIES

| | | $K$ |
|---|---|---|
| 1 | Hydrogen | 1 |
| 2 | Helium | 2 |

*First Short Period*

| | | $K$ | $L$ |
|---|---|---|---|
| 3 | Lithium | 2 | 1 |
| 4 | Beryllium | 2 | 2 |
| 5 | Boron | 2 | 3 |
| 6 | Carbon | 2 | 4 |
| 7 | Nitrogen | 2 | 5 |
| 8 | Oxygen | 2 | 6 |
| 9 | Fluorine | 2 | 7 |
| 10 | Neon | 2 | 8 |

*Second Short Period*

| | | $K$ | $L$ | $M$ |
|---|---|---|---|---|
| 11 | Sodium | 2 | 8 | 1 |
| 12 | Magnesium | 2 | 8 | 2 |
| 13 | Aluminium | 2 | 8 | 3 |
| 14 | Silicon | 2 | 8 | 4 |
| 15 | Phosphorus | 2 | 8 | 5 |
| 16 | Sulphur | 2 | 8 | 6 |
| 17 | Chlorine | 2 | 8 | 7 |
| 18 | Argon | 2 | 8 | 8 |

*First Long Period*

| | | $K$ | $L$ | $M$ | $N$ |
|---|---|---|---|---|---|
| 19 | Potassium | 2 | 8 | 8 | 1 |
| 20 | Calcium | 2 | 8 | 8 | 2 |
| | [Ten transitional elements] | | | | |
| 31 | Gallium | 2 | 8 | 18 | 3 |
| 32 | Germanium | 2 | 8 | 18 | 4 |
| 33 | Arsenic | 2 | 8 | 18 | 5 |
| 34 | Selenium | 2 | 8 | 18 | 6 |
| 35 | Bromine | 2 | 8 | 18 | 7 |
| 36 | Krypton | 2 | 8 | 18 | 8 |

*Second Long Period*

| | | $K$ | $L$ | $M$ | $N$ | $O$ |
|---|---|---|---|---|---|---|
| 37 | Rubidium | 2 | 8 | 18 | 8 | 1 |
| 38 | Strontium | 2 | 8 | 18 | 8 | 2 |
| | [Ten transitional elements] | | | | | |
| 49 | Indium | 2 | 8 | 18 | 18 | 3 |
| 50 | Tin | 2 | 8 | 18 | 18 | 4 |
| 51 | Antimony | 2 | 8 | 18 | 18 | 5 |
| 52 | Tellurium | 2 | 8 | 18 | 18 | 6 |
| 53 | Iodine | 2 | 8 | 18 | 18 | 7 |
| 54 | Xenon | 2 | 8 | 18 | 18 | 8 |

*Very Long Period*

| | | $K$ | $L$ | $M$ | $N$ | $O$ | $P$ |
|---|---|---|---|---|---|---|---|
| 55 | Caesium | 2 | 8 | 18 | 18 | 8 | 1 |
| 56 | Barium | 2 | 8 | 18 | 18 | 8 | 2 |
| | [Ten transitional elements, fourteen rare-earth elements] | | | | | | |
| 81 | Thallium | 2 | 8 | 18 | 32 | 18 | 3 |
| 82 | Lead | 2 | 8 | 18 | 32 | 18 | 4 |
| 83 | Bismuth | 2 | 8 | 18 | 32 | 18 | 5 |
| 84 | Polonium | 2 | 8 | 18 | 32 | 18 | 6 |
| 85 | ? | 2 | 8 | 18 | 32 | 18 | 7 |
| 86 | Radon | 2 | 8 | 18 | 32 | 18 | 8 |

*Radioactive Period*

| | | $K$ | $L$ | $M$ | $N$ | $O$ | $P$ | $Q$ |
|---|---|---|---|---|---|---|---|---|
| 87 | ? | 2 | 8 | 18 | 32 | 18 | 8 | 1 |
| 88 | Radium | 2 | 8 | 18 | 32 | 18 | 8 | 2 |
| | [Four (?) transitional elements.] | | | | | | | |

In the two long periods the same process of building up an octet of electrons again takes place in the outer *N*- or *O*-shell, and when completed gives rise to the inert gases krypton and xenon, but this process is interrupted (after calcium and strontium), when only two electrons have been added to the outer shell, in order that an inner shell of *M*- or *N*-electrons may satisfy its claim to expand from 8 to 18 electrons, before the rival claims of the outer shell to develop its octet are met. There is therefore a gap of 10 in the atomic numbers between

20 Calcium and 31 Gallium,

and between 38 Strontium and 49 Indium

This gap is occupied by elements of the transition series, which are described in Part III.

A similar interruption in the growth of the outer octet of *P*-electrons takes place after barium in the "very long period" which begins with caesium and ends with the radioactive gas, radon, but the gap in the atomic numbers now covers 24 elements, since the development of the outer octet is arrested whilst (i) the *O*-shell is developed from 8 to 18 electrons, and (ii) the *N*-shell is developed from 18 to 32 electrons. The development of the *O*-shell accounts for a third series of transition elements, which are again 10 in number, whilst the development of the *M*-shell provides for 14 additional tervalent elements of the rare-earth series, as described in Chapter XXII below.

# *PART II*

# TYPICAL ELEMENTS

## CHAPTER IX

### THE INERT GASES

**Position in periodic classification.**—Helium, neon, argon, krypton, xenon and radon are known as the INERT GASES, because of their reluctance to form chemical compounds When Mendeléeff put forward his periodic table they had not been discovered, and their existence could not have been predicted by means of his table They have therefore been placed in an additional Group O, where they serve to separate the electronegative halogens of Group VII from the electropositive alkali metals of Group I, The electronic theory, as we have already seen (p 36), attributes the chemical inertness of these elements to the fact that their atoms contain only stable groups or sub-groups of electrons and so have no tendency to lose or gain electrons

**The discovery of argon.**—Although all the inert gases except the radioactive emanations occur in the atmosphere, their existence was not suspected until the close of the nineteenth century, nearly a hundred years after the composition of the atmosphere had been, so it was thought, definitely established

The inactive gas, which is left after removing oxygen from the air, was described by Lavoisier as AZOTE (Greek, ἀ, not, ξωή, life), because it does not support life Cavendish in 1783 found that almost the whole of the azote could be converted into nitre by sparking over potash with an excess of oxygen, but there was a small residue (about 1/120 of the original volume) which would not dissolve, no matter how long the sparking was continued No importance was attached to this observation, although, if it had been followed up, the discovery of argon might have been advanced by more than a century In 1892, however, Rayleigh discovered that atmospheric nitrogen was about ½% heavier than chemical nitrogen Some of his results are given below

| 1. CHEMICAL NITROGEN from | Weight of gas in large globe |
|---|---|
| Reduction of nitric oxide by iron (4 experiments) | 2·30008 gram. |
| Reduction of nitrous oxide by iron (2 experiments) | 2 29904 ,, |
| Decomposition of ammonium nitrate (2 experiments) | 2 29869 ,, |

| 2 NITROGEN from air | Weight of gas in large globe |
|---|---|
| By means of red-hot copper | 2 31026 gram |
| By means of red-hot iron | 2 31003 ,, |
| By means of cold ferrous hydroxide | 2 31020 ,, |
| Mean value for chemical nitrogen | = 2 29927 ,, |
| Mean value for atmospheric nitrogen | = 2 31016 ,, |

The differences thus observed could not be attributed to experimental errors, and were evidently due to the presence of a *lighter* gas (*e g* hydrogen) in the " chemical nitrogen " or of a *heavier* gas in the " atmospheric nitrogen " No support could be found for the former hypothesis, whilst a search of the literature showed that the only evidence for the homogeneity of atmospheric nitrogen was that provided by Cavendish, and that Rayleigh's observations could be accounted for if Cavendish's " residue " were a heavy impurity with a density about twice as great as that of nitrogen This gas might have been a polymeric form of nitrogen, but spectroscopic observations showed that the residue left after sparking air with oxygen over potash gave a spectrum which differed from that of nitrogen, hydrogen, and all other known elements, thereby proving without a doubt that this residue contained a new element Rayleigh then prepared the new gas in larger quantities by Cavendish's sparking method (Fig 10), while Ramsay made use of red-hot magnesium (Fig 11) to absorb the nitrogen from air which had already been freed from moisture, carbon dioxide and oxygen

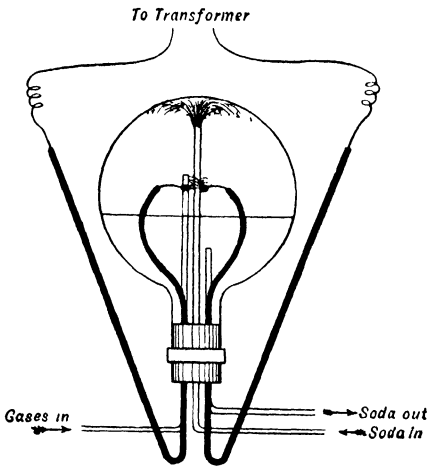



FIG 10 RAYLEIGH'S APPARATUS FOR SEPARATION OF ARGON FROM AIR BY SPARKING

Examination of the gas showed that it was not affected by reagents such as heated metals, copper oxide, potassium permanganate, phosphorus, etc , nor by sparking with hydrogen, chlorine or even fluorine On account of its great inertness, Ramsay called the gas ARGON (Greek, ἀ, not, ἔργον, work) Measurements of specific heat by Kundt's method showed that the gas was monatomic (p 460), and, since it was twenty times heavier than hydrogen, its atomic weight was about 40 This value for the atomic weight is greater than that of potassium, thus giving rise to an additional anomaly in the periodic classification of the elements (p 59), but its atomic number is intermediate between those of chlorine, $Z = 17$, and potassium, $Z = 19$, so that it fills a gap in the series of atomic numbers

**The discovery of helium.**—The isolation of argon suggested that a whole family of inert gases might exist, and this view was confirmed by the discovery of helium Hillebrand had stated that certain varieties of pitchblende evolved nitrogen when attacked by mineral acids Since this gas had been identified only by negative tests, Ramsay prepared some of it and purified it by sparking with oxygen over potash The residue gave a spectrum which included a yellow line (slightly more refrangible than the two D-lines of sodium), observed by Jansen and Lockyer (1868) in the solar spectrum This line was attributed by Lockyer to an unknown element, for which he proposed the name HELIUM (Greek, ἥλιος, the sun) It now appeared that helium was a real element which could be obtained as a gas from terrestrial sources

The occurrence of helium in radioactive minerals and in mineral springs is almost certainly due to radioactive disintegration Natural gas from petroleum wells, *e g* in Kansas, U S A , and Medicine Hat, Canada, may contain as much as one per cent by volume of helium As it has 92% of the lifting power of hydrogen and is non-inflammable, helium is now separated on a considerable scale from natural gas by fractional distillation, and is used for filling the gas bags of airships

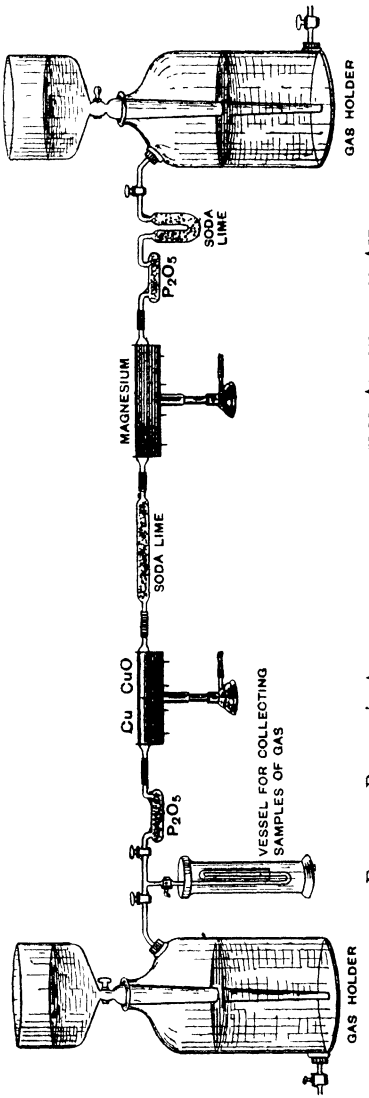



FIG 11 RAMSAY'S APPARATUS FOR SEPARATING ARGON FROM AIR

**Separation of inert gases from the atmosphere.**—About this time liquid air had been prepared on a considerable scale By fractionating the residue left after evaporating a large bulk of this liquid air, Ramsay was able to isolate two more gases, KRYPTON and XENON The inert gas NEON, which boils at a lower temperature than liquid air, was isolated by liquefying crude argon (prepared by the Ramsay method) and fractionating the liquid product It is now separated from liquid air and is used for filling the long glass tubes of neon-lamps for

luminous signs, whilst atmospheric argon is used in " gas-filled " electric filament lamps Finally the experiments of several chemists have established beyond doubt that the gaseous emanations, given off by radium and other radioactive bodies, represent the last member of the family of inert gases By these experiments a whole new family of elements was added to the periodic table within the ten years, 1894-1904 Their properties are summarised in Table 5

TABLE 5 —PROPERTIES OF THE INERT GASES

| Element | Atomic weight | Atomic number | Melting-point | Boiling-point | Ratio of specific heats | Volume in atmosphere |
|---|---|---|---|---|---|---|
| Helium - | 4 003 | 2 | - 272 2° | - 268 9° | 1 65 | 0 0005% |
| Neon - | 20 183 | 10 | - 248 67° | - 245 9° | 1 64 | 0 002% |
| Argon - | 39 944 | 18 | - 189 2° | - 185 7° | 1 65 | 0 94% |
| Krypton - | 83 7 | 36 | - 169° | - 152 9° | 1 69 | 0 000005% |
| Xenon - | 131 3 | 54 | - 140° | - 107 1° | 1 67 | 0 0000006% |
| Radon - | 222 | 86 | — | - 65° | — | — |

**Chemical combination of inert gases.**—Although the inert gases have no chemical activity of the ordinary kind, an atom of helium can interact with an atom which has been " activated " by sparking, giving rise to an activated molecule of $He_2$ Under similar conditions, helium appears to combine with mercury, and also to form a compound with tungsten, since, when helium is sparked with tungsten electrodes, a grey powder is produced, which, on treatment with potash gives helium, whilst tungsten, which is not ordinarily soluble in potash, goes into solution The separation of argon with six molecules of " water of crystallisation " should also be recorded under this heading

# CHAPTER X

## HYDROGEN, WATER AND HYDROGEN PEROXIDE

### 1 HYDROGEN H=1 0081

**Classification.**—Hydrogen is unique amongst the elements, since the hydrogen nucleus or PROTON is one of the fundamental materials from which all the other nuclei are built It also occupies a unique position in the Periodic Classification of the elements, as a member of the very short Period I, which contains only one other element, helium

(*a*) The neutral atom consists of a single proton and a single planetary electron Hydrogen therefore shows some similarity to the metals of the alkalis, which have a single loosely-bound electron outside the stable kernel of an inert gas The removal of this electron converts the hydrogen atom into a hydrogen ion, just as a sodium atom is converted into a univalent cation by the loss of its one loosely-bound " valency electron,"

$$H = \overset{+}{H} + e \quad \text{compare} \quad Na = \overset{+}{Na} + e$$

The relationship is expressed by saying that hydrogen has a *positive electrovalence* of one

The hydrogen ion, or PROTON, which is produced by the loss of an electron from a hydrogen atom, can be detected readily by the mass-spectrograph The free proton is, however, a tiny naked nucleus, the diameter of which is probably 1800 times less than that of an electron, and a million times less than that of an atom It therefore tends to bury itself in the electronic shell of another atom, so as to form covalent rather than electrovalent compounds Thus the " ionisation " of hydrogen chloride in water should be represented by the equation

$$H_2O + HCl \rightleftharpoons H_3\overset{+}{O} + \overset{-}{Cl} \quad \text{not} \quad HCl = \overset{+}{H} + \overset{-}{Cl},$$

and the ionisation of water itself by the equation,

$$2H_2O \rightleftharpoons H_3\overset{+}{O} + \overset{-}{O}H \quad \text{not} \quad H_2O = \overset{+}{H} + \overset{-}{O}H$$

In these ions, the hydrogen nucleus is no longer free, since it is bound to oxygen by a covalent bond, thus

$$\begin{matrix} H & & \\ & \overset{+}{O}\text{--}H & \text{or} \quad \overset{-}{O}\text{—}H \\ H & & \end{matrix}$$

Oxonium ion Hydroxyl ion

(*b*) On the other hand, the *addition* of a single electron suffices to give to hydrogen the stable electronic configuration of helium Hence hydrogen can gain an electron and form a negative ion, like the halogens

$$H + e = \bar{H} \quad \text{compare} \quad Cl + e = \bar{Cl}$$

This relationship is expressed by assigning to hydrogen a *negative electrovalence* of one The negatively charged hydrogen ion is much less stable than those of the halogens, since one positive charge is holding two electrons Salt-like hydrides, resembling the halides, are therefore formed only by metals which have a great tendency to part with electrons, such as the alkalis and alkaline earths

$$\overset{+}{Li}\ \overset{-}{H} \quad \text{compare} \quad \overset{+}{Li}\ \overset{-}{Cl}$$

$$\overset{-}{H}\ \overset{++}{Ca}\ \overset{-}{H} \quad \text{compare} \quad \overset{-}{Cl}\ \overset{++}{Ca}\ \overset{-}{Cl}$$

(*c*) It must be confessed that neither of these relationships expresses the real behaviour of hydrogen, since the element is neither a metal like sodium or potassium, nor an "oxidising agent" like chlorine It is, indeed, unreasonable to expect that a single element should exhibit simultaneously the strongly electropositive qualities (p 52) of an alkali metal, with its extreme reluctance to tolerate a surplus electron, and the strongly electronegative qualities of a halogen, with its intense electron-hunger Hydrogen therefore resembles these contrary elements only in the numerical value of its valency (+1 or −1), and in many respects shows a much closer similarity to *carbon*, which has a similar neutral character in virtue of its central position between the two inert gases, helium and neon Thus neither hydrogen nor carbon shows any readiness to form either positive or negative ions, but their covalent compounds are very important, and include the PARAFFINS (Latin, *parvum*, small, *affinitas*, affinity), $C_nH_{2n+2}$, which are only less stable than the inert gases Liquid hydrogen is therefore not a metal, as some people said it would be, since its electrons are not sufficiently mobile to give rise to metallic conductivity, on the contrary, its properties are those of a low-boiling petrol, and correspond precisely with those of the homologous series of paraffins, to which it is related by loss of $CH_2$ from methane as shown in the scheme

$$\underset{\text{Ethane}}{C_2H_6} \xrightarrow{-CH_2} \underset{\text{Methane}}{CH_4} \xrightarrow{-CH_2} H_2$$

The chemistry of hydrogen is therefore dominated, like that of carbon, by its covalency

**Properties of hydrogen.**—Table 6 contains a summary of the properties of hydrogen, in comparison and contrast with those of the alkali metals and the halogens

TABLE 6.—PROPERTIES OF HYDROGEN COMPARED WITH ALKALI METALS AND HALOGENS

| ALKALI METALS | HYDROGEN | HALOGENS |
|---|---|---|
| Solids, vapours are mainly monatomic | Diatomic gas | Gas, liquid or solid, vapours diatomic |
| Metals (electrons mobile) | Non-metal (electrons fixed) | Non-metals (electrons fixed) |
| Reducing agents (readily lose electrons) | Reducing agent | Oxidising agents (readily gain electrons) |
| Strongly electropositive, forming stable cations, $\overset{+}{Li}$, $\overset{+}{Na}$, $\overset{+}{K}$, $\overset{+}{Rb}$, $\overset{+}{Cs}$ | Feebly electropositive (H only found *in vacuo*) Feebly electronegative (H only found in $\overset{+}{Li}\overset{-}{H}$, $Ca\overset{+}{H}_2\overset{-}{H}$, etc) | Strongly electronegative, forming stable anions $\overset{-}{F}$, $\overset{-}{Cl}$, $\overset{-}{Br}$, $\overset{-}{I}$ |
| Compounds nearly all ionic, *e g* $\overset{+}{Li}\overset{-}{H}$, $\overset{+}{Na}\overset{-}{Cl}$, $\overset{+}{K}\overset{-}{NO_3}$, etc | Compounds generally covalent, *e g* H—Cl, H—S—H, etc | Compounds covalent or ionic, *e g* $\overset{+}{K}\overset{-}{Cl}$, Cl—S—Cl, etc |
| Burn in oxygen forming ionic oxides, *e g* $\overset{+}{Na}\overset{-}{O}\overset{-}{—}\overset{+}{O}\overset{+}{Na}$ | Burns in oxygen, forming covalent oxides, *e g* H—O—H | Form only unstable covalent oxides, *e g* $Cl_2O$, $ClO_2$ |
| Carbides probably ionic, *e g* $\overset{+}{Na}\overset{-}{C}\equiv\overset{-}{C}\overset{+}{Na}$ | Form covalent compounds with carbon, in which hydrogen and halogens can be interchanged without change of type, *e g* $CH_4$, $CH_3Cl$, $CH_2Cl_2$, $CHCl_3$, $CCl_4$ | |
| Form alloys with metals | Forms salt-like hydrides, with a few metals | Form salts (generally ionic) with metals |

**Occurrence of hydrogen.**—Traces of hydrogen (about 1 part per million) are found in a free state in the atmosphere and larger quantities in the gases from volcanoes In combination with oxygen, hydrogen forms one-ninth part by weight of water, of which 2% is present in the solid crust of the earth, whilst the ocean contains about 96½% of water Hydrogen is also found in combination with carbon in mineral oils (petroleum, etc) and is present, in combination with carbon, oxygen, and other elements, in almost all organic materials, including oils, fats, wood, peat, coal, etc The outer ten miles of the earth's crust, including the ocean and the atmosphere, contain about 1% of hydrogen, as contrasted with 50% of oxygen

**Preparation of hydrogen.**—(*a*) *By the action of acids on metals* —Hydrogen is usually prepared in the laboratory by the action of moderately dilute sulphuric acid (1 vol conc acid to 5 vols water) or hydrochloric acid (1 vol conc acid to 2 vols water) on granulated zinc in Kipp's apparatus (Fig 12)

$$Zn + H_2SO_4 = ZnSO_4 + H_2, \text{ or } Zn + 2H^+ = Zn^{++} + H_2,$$
$$Zn + 2HCl = ZnCl_2 + H_2, \text{ or } Zn + 2H^+ = Zn^{++} + H_2$$

Since pure zinc is only attacked very slowly by dilute acids, it is customary to add a little copper sulphate solution to the acid, when the following action occurs

$$CuSO_4 + Zn = Cu + ZnSO_4,$$
or $$Cu^{++} + Zn = Cu + Zn^{++}$$

The copper is deposited on the surface of the zinc and forms a zinc-copper couple which dissolves readily in the dilute acid.

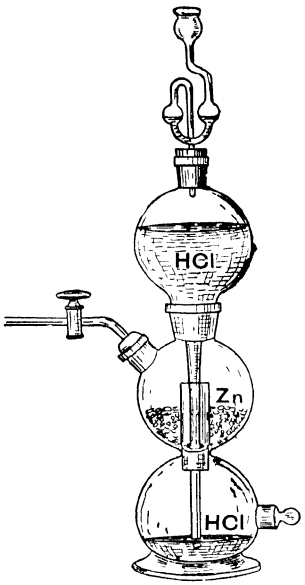



FIG 12 KIPP'S APPARATUS FOR THE PREPARATION OF HYDROGEN

The hydrogen obtained by the above method is rather impure since it contains traces of moisture, arsine, $AsH_3$, and hydrocarbons, in addition to acidic impurities such as hydrogen chloride from the hydrochloric acid, or sulphur dioxide and hydrogen sulphide from the reduction of the sulphuric acid. The presence of hydrocarbons and arsine is due to the action of the nascent hydrogen (p 74) on traces of carbon and arsenic in the granulated zinc

The gas can be purified by passing it (i) through a strong alkaline solution of potassium permanganate to remove the acid impurities and hydrocarbons, (ii) over red-hot copper to remove arsine and traces of oxygen, and (iii) over calcium chloride or phosphorus pentoxide to remove the moisture Sulphuric acid is not a suitable drying agent because it interacts slightly with hydrogen and gives up dissolved oxygen In spite of these precautions, which are tedious to carry out, the gas is not completely free from all impurities, and it is therefore customary to prepare very pure hydrogen by other methods as described under (*c*) p. 71 and (*e*) p. 72.

It is important to remember that all the metals above lead in the electrochemical series, p 53, can liberate hydrogen from non-oxidising acids, and that, in general, the higher the metal is in the series the more vigorous the displacement Thus in the following examples the metals are placed in descending order of both electropositiveness and reactivity

$$Mg + 2HCl = MgCl_2 + H_2, \quad \text{or } Mg + 2H^{++} = Mg^{++} + H_2,$$
$$2Al + 6HCl = 2AlCl_3 + 3H_2, \text{ or } 2Al + 6H^{+} = 2Al^{+++} + 3H_2,$$
$$Fe + 2HCl = FeCl_2 + H_2, \quad \text{or } Fe + 2H^{+} = Fe^{++} + H_2,$$
$$Sn + 2HCl = SnCl_2 + H_2, \quad \text{or } Sn + 2H^{+} = Sn^{++} + H_2.$$

It should be noted in the last two equations that ferrous and stannous chlorides are formed and not the corresponding ferric and stannic salts.

When an acid is also a powerful oxidising agent, the nascent hydrogen is oxidised to water, and gaseous products other than hydrogen are liberated Thus concentrated sulphuric acid attacks the above metals to give sulphur dioxide as the principal gaseous product, *e g.*.

$$Mg + 2H_2SO_4 = MgSO_4 + SO_2 + 2H_2O,$$

whilst nitric acid gives oxides of nitrogen (see p 200), unless it is very dilute and the metal is magnesium

$$Mg + 2HNO_3 = Mg(NO_3)_2 + H_2, \text{ or } Mg + 2H^+ = Mg^{++} + H_2$$

(*b*) *By the action of metals on alkalis* —A solution of caustic soda or potash dissolves aluminium readily with evolution of hydrogen, zinc also dissolves with liberation of hydrogen, but the action is much slower and requires heat

$$2Al + 2NaOH + 2H_2O = \underset{\text{Sodium aluminate}}{2NaAlO_2} + 3H_2.$$

$$Zn + 2NaOH = \underset{\text{Sodium zincate}}{Na_2ZnO_2} + H_2$$

(*c*) *By the action of metals on water* —The action of metals on water has already been discussed on p 53, but there are two reactions which require further consideration

(i) The action of steam on sodium is sometimes used in the laboratory as a method of obtaining very pure hydrogen

$$2Na + 2H_2O = 2NaOH + H_2$$

Alternatively, an amalgam of sodium and mercury can be added to cold water, when a gentle effervescence takes place

$$2NaHg_2 + 2H_2O = 2NaOH + 4Hg + H_2$$

The direct addition of sodium to water is not recommended because the action is very violent and liable to be dangerous

(ii) In LANE'S PROCESS, which is now nearly obsolete, hydrogen is manufactured by passing steam over finely divided iron (in the form of a briquette with clay) heated to 650-800° C in iron retorts

$$3Fe + 4H_2O \rightleftharpoons Fe_3O_4 + 4H_2$$

The reversed arrows indicate that the reaction is reversible, and as the formation of hydrogen takes place with the liberation of heat, it follows from Le Chatelier's theorem, p 558, that the proportion of steam reduced to hydrogen falls as the temperature is raised, *i e* the reverse reaction becomes increasingly important The relatively high temperature range of 650-800° C has to be employed, however, since at lower temperatures the rate of reaction is too slow

The triferric tetroxide, $Fe_3O_4$, is reduced back to iron by passing water gas ($CO + H_2$, p 151) over it, so that the iron can be used over again

$$Fe_3O_4 + 4H_2 = 3Fe + 4H_2O,$$
$$Fe_3O_4 + 4CO = 3Fe + 4CO_2$$

(*d*) *By the action of carbon on steam* —Enormous quantities of hydrogen are manufactured by passing steam over white hot coke, when a mixture known as WATER-GAS is obtained

$$C + H_2O = CO + H_2$$

The carbon monoxide is converted almost completely into carbon dioxide by adding more steam and passing the mixture at about 500° over a suitable catalyst, such as iron oxide with aluminium oxide as promoter

$$CO + H_2O = CO_2 + H_2$$

The resulting carbon dioxide is largely removed by washing the product with water under pressure, and, if necessary, the residual oxides of carbon (CO and $CO_2$) can be eliminated by washing the gas with an ammoniacal solution of cuprous salts

(*e*) *By electrolysis* —Very pure hydrogen and oxygen are prepared in the laboratory by electrolysing a warm solution of barium hydroxide in a hard glass U-tube fitted with nickel electrodes The barium hydroxide helps in the conductance of the electric current, but remains chemically unchanged, and hence the electrolysis merely results in the decomposition of the water

$$2H_2O = \underset{\text{Cathode}}{2H_2} + \underset{\text{Anode}}{O_2}$$

A little oxygen dissolves in the electrolyte and diffuses round to the cathode, so it is necessary to pass the hydrogen over heated platinised asbestos to convert the traces of oxygen into water Moisture is then removed by drying the gas with phosphorus pentoxide

On the industrial scale hydrogen is obtained as by-product in the manufacture of caustic soda by the electrolysis of brine, p 96 A large amount of hydrogen is also manufactured by the electrolysis of a 20% solution of caustic soda using an iron cathode and a nickel-plated anode, which resists anodic oxidation

**Uses of hydrogen** —Hydrogen is used on a large scale in the manufacture of ammonia (p 180), methyl alcohol (p 677) and synthetic petrol It is also used to harden oils and soft fats, which unite with hydrogen in presence of a nickel catalyst, forming solid fats, which are used in the manufacture of margarine (p 718)

**Physical properties of hydrogen.**—Hydrogen is a colourless, odourless gas. It is almost insoluble in water, only 2 volumes dissolving in 100 volumes of water at 8° (*cf* $N_2$, 2 vols , $O_2$, 4 vols ) It is the lightest gas known , one litre at 0° and 760 mm weighs 0 0899 grs At −253° it condenses to a colourless liquid of density 0 076, which is the lightest liquid known When evaporated very rapidly under reduced pressure, liquid hydrogen freezes to a colourless crystalline solid, which melts at −259° and does not exhibit metallic properties

Hydrogen possesses the property of dissolving in solid metals Thus palladium will dissolve 900 times its own volume of hydrogen at atmospheric temperatures, but releases it again when heated (p 84) , this fact is made use of in the purification of hydrogen As a consequence of its solubility in metals, hydrogen can diffuse very rapidly through a membrane of palladium, and less rapidly through one of platinum

Ordinary hydrogen is a mixture of two allotropes, ORTHO-HYDROGEN 75% and PARA-HYDROGEN 25% In the molecule of ortho-hydrogen the nuclei of both atoms are spinning in the same direction, ↑ H H ↑ , whilst the spins are in opposite directions in the molecule of para-hydrogen, ↓ H H ↑ These allotropes are chemically similar, since their electronic configurations are identical, but they have different specific heats At low temperatures the equilibrium is increasingly in favour of the para form

Hydrogen is also interesting because it contains traces (1 part in 5000) of an isotope with an atomic weight of two When acidulated water is electrolysed, the HEAVY HYDROGEN is concentrated in the residue and can be isolated The HEAVY WATER thus prepared has a density, 1 1056 at 25°, which reaches a maximum at 11 6° instead of at 4° It boils at 101 42° and freezes at 3 82° Similar differences are observed in the physical properties of other derivatives, and marked differences have already been recorded in the velocity of reactions in which this isotope of hydrogen is involved In accordance with the definition of an element which has been suggested on p 51, heavy hydrogen has been described as DEUTERIUM and represented by the symbol D, as if it were a new element and not a mere isotope of H

**Chemical properties of hydrogen.**—Hydrogen combines with a few of the most strongly electropositive metals to form solid salt-like hydrides, *e g* $Li^+H^-$, and with some of the least electropositive metals to form gaseous hydrides, *e g* $SnH_4$, $BiH_3$, $SbH_3$, $AsH_3$ The remaining metals do not form chemical compounds with hydrogen, although the gas is freely soluble in palladium On the other hand, all the non-metals (except the inert gases) form gaseous or volatile hydrides Thus hydrogen ignites in air at about 580° and burns to form water

$$2H_2 + O_2 = 2H_2O$$

This combination is catalysed by finely-divided platinum and palladium, but can be arrested by drying the gases, *e g* when a mixture of pure hydrogen and oxygen is dried with phosphoric oxide in a clean tube of hard glass, a silver wire can be melted in it at a temperature of 960° without causing it to explode Hydrogen will also burn in chlorine, with which it forms an explosive mixture , and it combines explosively with fluorine even at − 250°

$$H_2 + Cl_2 = 2HCl \qquad H_2 + F_2 = 2HF$$

Hydrogen combines less readily with sulphur to form sulphuretted hydrogen, $H_2S$ (p 249), and with nitrogen to form ammonia, $NH_3$ (p 180) , but arsenic and antimony unite only with " nascent hydrogen " to form arsine, $AsH_3$ and stibine, $SbH_3$

The hydrides of the more electronegative non-metals readily part with a proton and are therefore acidic in character , but this property is only developed in presence of water (or some similar " proton-acceptor," p 46), since the hydrides themselves are covalent compounds

**Hydrogen as a reducing agent.**—Hydrogen will remove oxygen from many metallic oxides, *e g* (1) $CuO + H_2 = Cu + H_2O$

This reduction was used by Dumas in determining the composition of water, and is employed in the combustion of organic compounds

(ii) $Fe_3O_4 + 4H_2 \rightleftharpoons 3Fe + 4H_2O$

This action is the converse of the decomposition of steam by iron as described above

(iii) The oxides of magnesium and sodium are not reduced by hydrogen, but on the contrary these metals are able to liberate hydrogen from steam

The metals and their oxides can thus be divided into three groups as follows

| | |
|---|---|
| *Reduction of oxide by hydrogen,* | $CuO + H_2 \rightarrow Cu + H_2O$ |
| *Reduction of oxide and oxidation of metal,* | $Fe_3O_4 + 4H_2 \rightleftharpoons 3Fe + 4H_2O$ |
| *Oxidation of metal by steam,* | $MgO + H_2 \leftarrow Mg + H_2O$ |

In the first group the action proceeds from left to right only and in the third group from right to left only, in the case of iron the action is reversible

**Nascent hydrogen** —Many agents which liberate hydrogen are able to effect reductions which cannot be brought about by hydrogen itself Thus, ferric chloride is not reduced by gaseous hydrogen, but, if added to a mixture of zinc and sulphuric acid, which is evolving hydrogen, the ferric salt is rapidly reduced to the ferrous state

$$FeCl_3 + H = FeCl_2 + HCl$$

Again, arsenic is converted into arsine when hydrogen is liberated in contact with solutions containing arsenic, but not by bubbling gaseous hydrogen through the solution,

$$As + 3H = AsH_3$$

These reductions were formerly attributed to a special form of hydrogen which was described as NASCENT HYDROGEN, *i e* hydrogen at the moment of its birth It was generally supposed to consist of atoms of hydrogen which had not yet settled down into stable molecules, but this simple explanation cannot be maintained, in view of the fact that "nascent hydrogen" from different sources has different powers of reduction Thus a solution of potassium chlorate is reduced to potassium chloride by zinc and sulphuric acid, but is unaffected by the hydrogen from sodium amalgam and water These differences can be explained if we recognise that chemical changes which liberate hydrogen proceed with the liberation of different amounts of energy The energy available from the oxidation of hydrogen from a given source may or may not, therefore, be sufficient to bring about a difficult reduction, when the oxidising and reducing actions are coupled together into a single process

Zenghelis has shown, however, that the chemical activity of ordinary hydrogen gas may be much increased by bringing the gas in very minute bubbles into contact with solutions Thus ordinary hydrogen gas, when forced through paper cartridges immersed in a solution of potassium chlorate at 80°, brought about the reduction of the latter to potassium chloride From this it must be concluded that the fineness of subdivision of the hydrogen also affects its reducing powers

## WATER

**Occurrence.**—Water is found in the combined state as "water of crystallisation" in minerals such as GYPSUM, $CaSO_4$, $2H_2O$ MICA, in igneous rocks which have crystallised under pressure, and KAOLIN, or clay, in sedimentary deposits, contain hydrogen silicates, which can also be formulated as hydrates In the free state, natural waters occur in the following forms

(*a*) *Rain-water* —The water vapour of the atmosphere condenses on cooling as RAIN, HAIL, or SNOW RAIN-WATER is the purest of natural waters, containing as a rule only gaseous impurities, such as dissolved oxygen, nitrogen and carbon dioxide, together with sulphurous and sulphuric acids formed by the burning of coal containing iron pyrites Carbon dioxide imparts to the water a solvent power which enables it to attack both igneous and sedimentary rocks Rain-water also carries down combined nitrogen, mainly in the form of ammonium nitrate, to the extent of about 4 lb of nitrogen per acre per annum, providing the original source for most of the fixed nitrogen (cf p 177) of the soil and of vegetable and animal products There is also an extensive circulation of salt spray from the sea, which is carried back again by rain

(*b*) *River-water* contains additional impurities dissolved out from the soil and rocks, *e g* chlorides, sulphates, carbonates and bicarbonates of sodium and potassium, calcium, magnesium and iron Thus the soluble bicarbonates of calcium and magnesium are formed by the action of dissolved carbon dioxide on insoluble carbonates or silicates, *e g*

$$\underset{\text{Calcium carbonate}}{CaCO_3} + H_2O + CO_2 \rightarrow \underset{\text{Calcium bicarbonate}}{Ca(HCO_3)_2}$$

Colloidal solids are also held in suspension and are precipitated by mineral salts (p 646) where the river flows into the sea, giving rise sometimes to the formation of deltas

The amount of oxygen dissolved in river water is reduced by the presence of organic matter, *e g* in sewage, and may fall to a point at which fishes are unable to live in it Thus the ratio of oxygen to nitrogen in Thames water at various places is given below

| | | | |
|---|---|---|---|
| Kingston, | 1 2 | Hammersmith, | 1 3 7. |
| Greenwich, | 1 60 | Woolwich, | 1 52 |

(*c*) *Spring-water and deep-well water* differ from river water owing to filtration through porous strata, which removes nearly all the suspended material and increases the mineral content

(*d*) *Sea-water* contains 2 6% of common salt, and about 1% of other salts (p 105) The high ratio of sodium to potassium is accounted for in part by the fact that the soil preferentially retains potassium salts

(*e*) *Mineral waters* contain substances such as sulphuretted hydrogen and ferrous bicarbonate, to which medicinal properties are attributed. Special value is assigned to traces of radium emanation in the mineral waters of Bath and Buxton.

**Hardness of water.** —Water which produces a lather only with difficulty is described as HARD WATER This effect is due to the presence of calcium, magnesium and iron * salts, which convert soluble ordinary soaps † into an insoluble curd, *e g*

$$2C_{15}H_{31}\,CO\,ONa + Ca(HCO_3)_2 = (C_{15}H_{31}\cdot CO\,O)_2Ca + 2NaHCO_3$$

Sodium palmitate (soluble soap) — Calcium bicarbonate — Calcium palmitate (insoluble curd) — Sodium bicarbonate

A lather can only be formed when the calcium and magnesium salts have been removed This may waste a lot of soap in addition to producing a slimy deposit There are two types of hardness

(*a*) *Temporary hardness* —Hardness which is caused by the bicarbonates of calcium, magnesium and iron is called TEMPORARY HARDNESS, because it can be removed by boiling, when the soluble bicarbonates are converted into the much less soluble carbonates

$$Ca(HCO_3)_2 \rightarrow CaCO_3 + CO_2 + H_2O$$

Calcium bicarbonate (soluble) — Calcium carbonate (insoluble)

On a large scale, temporary hardness is generally removed by adding the correct amount of lime to convert the bicarbonate into carbonate

$$Ca(HCO_3)_2 + Ca(OH)_2 \rightarrow 2CaCO_3 + 2H_2O$$

The precipitate is allowed to settle and the water may also be filtered through beds of coke or sand

If magnesium bicarbonate is present, double the amount of lime must be added so as to precipitate magnesium hydroxide,

$$Mg(HCO_3)_2 + 2Ca(OH)_2 \rightarrow Mg(OH)_2 + 2CaCO_3 + 2H_2O,$$

since magnesium carbonate, although much less soluble than the bicarbonate, is appreciably soluble in water (0 1 grams per litre of water, as compared with 0 013 grams of calcium carbonate), while the hydroxide is much less soluble (only 0 01 grams per litre)

(*b*) *Permanent hardness* —The chlorides and sulphates of calcium and magnesium, which cannot be removed by boiling, give rise to PERMANENT HARDNESS This form of hardness is much more troublesome, since, when the water is evaporated in a steam-boiler, it deposits a hard scale of gypsum, $CaSO_4$, $2H_2O$, which seriously impedes the transmission of heat This scale must be removed by scraping or chipping, whereas chalk is precipitated only as a soft mud Permanent and temporary hardness can be removed by adding sodium carbonate to the water, *e g*

$$CaSO_4 + Na_2CO_3 = CaCO_3 + Na_2SO_4$$

* Any metal, other than an alkali metal, behaves similarly if present in water

† Ordinary soaps consist of the sodium and potassium salts of palmitic acid, $C_{15}H_{31}$ CO OH, stearic acid, $C_{17}H_{35}$ CO OH, and oleic acid, $C_{17}H_{33}$ CO OH (p 717) These form insoluble calcium and magnesium salts , but some modern detergents, *e g* cetyl sodium sulphate, $C_{16}H_{33}O\,SO_2\,ONa$, form soluble salts of these metals and are therefore equally efficient in hard and soft water

Hard water can also be softened by passing it over **PERMUTITE**, a hydrated sodium aluminium silicate, which readily exchanges its sodium for calcium or magnesium, *e g*

$$2NaAlSi_2O_6 + CaSO_4 \rightleftharpoons Ca(AlSi_2O_6)_2 + Na_2SO_4$$

The permutite is revived by soaking in a strong solution of brine, when the calcium and magnesium are replaced by sodium and are carried away as soluble chlorides in the subsequent washing

Sticks of tri-sodium phosphate are now frequently placed in household water tanks, as they dissolve slowly and precipitate calcium, magnesium and iron as phosphate The advantages of this method over the permutite method are that no special apparatus is required and there is no wastage of water

**Estimation of hardness.**— The total hardness of water may be estimated by finding what volume of a standard soap solution is required to produce a lather lasting for three minutes (p 433)

Temporary hardness can be estimated by titration against a standard acid using methyl-orange as an indicator Permanent hardness can be estimated in a similar way by adding an excess of standard alkali (sodium carbonate with a little hydroxide), filtering off the chalk (after boiling, if magnesium is present), and titrating back with a standard acid (p 434)

**Drinking water.**—Pure water has a " flat " vapid taste, on account of the absence of dissolved salts and of carbon dioxide, which imparts a " fresh " taste to the water In the presence of oxygen, soft water acts on lead pipes, giving rise to lead hydroxide, $Pb(OH)_2$, which is appreciably soluble and acts as a cumulative poison Hard water, on the other hand, produces a coherent coating of insoluble lead carbonate in the pipes, so that no lead gets into the water For this reason soft moorland water is sometimes made very slightly hard by the addition of lime

**Physical properties of water.**—Although water is often selected as a typical liquid and is used as a standard in measurements of temperature, density and heat capacity, its properties are perhaps more anomalous than those of any other liquid Thus, its boiling-point is 133° higher than that of ammonia (b -pt $-33°$) and 260° higher than that of methane (b -pt $-160°$) It also boils at a higher temperature than the hydrides of sulphur and selenium, instead of having the lowest boiling-point in this family of compounds

| | | B -pt | Mol wt |
|---|---|---|---|
| Water - - - | $H_2O$ | 100° | 18 |
| Hydrogen sulphide - | $H_2S$ | $-61.8°$ | 34 |
| Hydrogen selenide - | $H_2Se$ | $-41°$ | 81 |

The specific heat of water is also abnormally high, whilst its latent heats of fusion and of evaporation are higher than those of any other common liquid

These anomalies are attributed to a reversible polymerisation, whereby the simple molecules of " monohydrol," $H_2O$, which are the principal constituent of steam, become associated into more complex molecules when cooled, *e g* $(H_2O)_2$, $(H_2O)_3$, etc (p 41),

**Water as a solvent.**—The solvent properties of water are of supreme importance both in mineral chemistry and in the complex processes of vegetable and animal life It is unique in the readiness with which it dissolves metallic salts, giving rise to solutions which are good electrolytic conductors It is also an excellent IONISING SOLVENT for acids and bases Finally, its power of association enables it to break up the aggregates of other compounds , thus acetic acid in benzene forms double molecules $(CH_3 CO OH)_2$, while in water it is mainly in the form of single molecules $(CH_3 \cdot CO OH)$

**Chemical properties of water.**—(*a*) *Decomposition by heat* —When water is heated above 1200°, it begins to decompose into hydrogen atoms and hydroxyl radicals

$$H_2O \rightleftharpoons H + OH - 115{,}000 \text{ calories}$$

These recombine to form water , but they may also unite with one another to form molecules of hydrogen, $H_2$, and of hydrogen peroxide, $H_2O_2$ The latter in its turn may decompose into water and oxygen, giving rise to the reversible reaction

$$2H_2 + O_2 \rightleftharpoons 2H_2O$$

Since this decomposition takes place with the absorption of heat it is favoured by increasing the temperature (Le Chatelier, p 558), and although it amounts only to some 2% at 2000°, it can be shown by means of the following experiment

EXPT 9 **Decomposition of water by sparking**

Steam is generated in a large flask *A* and passes to a wide tube *B* in which it is subjected to sparking Under these conditions the molecules of water which have been decomposed by the heat of the spark are quenched immediately by the surrounding vapour, and this cooling is so rapid that the hydrogen and oxygen have not time to recombine before they are swept forward in the current of steam The products of decomposition are therefore obtained as an explosive mixture when the steam is condensed in the tube *C*

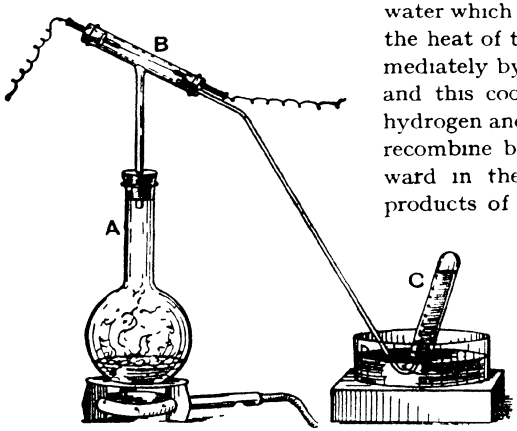



FIG 13 APPARATUS FOR THE DECOMPOSITION OF STEAM BY ELECTRIC SPARKS

The thermal decomposition of water vapour can also be brought about by plunging white hot platinum under the surface of the liquid, when bubbles of inflammable gas are formed and can be collected. This thermal decomposition of water was the first chemical change to which the term DISSOCIATION was applied, but this expression is now used to

cover all cases of *reversible decomposition* (*e g* ammonium chloride, p 185, nitrogen peroxide, pp 194 and 560, phosphorus pentachloride, pp. 217, and 561).

(*b*) *Decomposition by electrolysis* —Unlike steam, which dissociates into *neutral radicals*, liquid water dissociates into hydrogen and hydroxyl ions *

$$H_2O \rightleftharpoons H^+ + OH^-.$$

This dissociation, however, only affects about one molecule in 550 million Water is therefore a very bad conductor, and is never used alone as an electrolyte Dilute sulphuric acid, however, is a good electrolyte, and on electrolysis yields hydrogen and oxygen, exactly as if pure water were being used. The course of the action is as follows (see also p. 596).

*At the cathode,* $2H^+ \rightarrow 2H \rightarrow H_2$,
*At the anode,* $4OH^- \rightarrow 4OH \rightarrow O_2 + 2H_2O$

If dilute sulphuric acid and a low current density are used, quantitative yields of hydrogen and oxygen are obtained Under these conditions, therefore, a Hofmann voltameter (Fig 14) can be used to show that two volumes of hydrogen are evolved at the cathode for every volume of oxygen at the anode If, however, the current density is high, *e g* because the electrodes are small, other substances may be formed at the anode, such as persulphuric acid, $H_2S_2O_8$, hydrogen peroxide, $H_2O_2$, and ozone, $O_3$ The volume of oxygen liberated at the anode may then be much less than one-half of the volume of the hydrogen

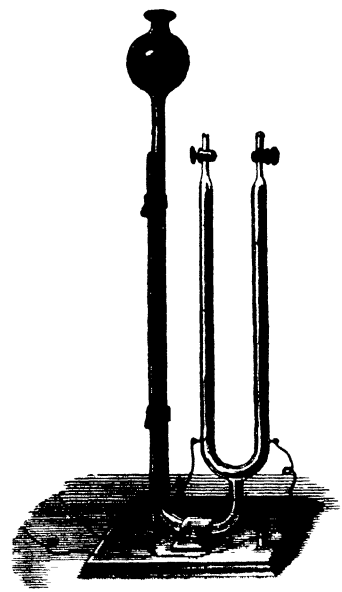


FIG 14 VOLTAMETER FOR ELECTROLYSIS OF AQUEOUS SOLUTIONS

(*c*) *Decomposition by metals* —Many metals decompose water either in the cold (*e g* sodium, potassium, magnesium amalgam) or when heated (magnesium, iron) as described on p 53

(*d*) *Decomposition by chlorine* — Under the influence of sunlight, water is decomposed by chlorine (p 280)

$$2Cl_2 + 2H_2O \rightleftharpoons 4HCl + O_2$$

Oxygen is liberated, but the action is reversible, since strong hydrochloric acid liberates chlorine when exposed to air and sunshine

**Water as a catalyst.**—Water is very active as a catalyst in bringing about certain chemical changes which do not take place when the material

* The hydrogen ions are really hydrated, namely, $H_3O^+$, as explained on page 45 but for simplicity it is customary to ignore this fact, especially in formulatin

are perfectly dry Thus, sodium can be melted in dry chlorine without any interaction taking place, although ordinary moist chlorine acts vigorously on sodium in the cold Carbon monoxide will not burn in dry oxygen (cf p 142), and silver can be melted in a dry mixture of hydrogen and oxygen without an explosion taking place

Many similar examples of the effects of intense drying have been given in the literature, but some of them are open to doubt in view of recent work Thus Baker measured the vapour-density of dry ammonium chloride by the Victor Meyer method, and concluded from his measurements that the ordinary thermal dissociation, $NH_4Cl \rightleftharpoons NH_3 + HCl$, had not taken place Recent experiments, however, indicate that dry ammonium chloride does dissociate on vaporisation, and that Baker possibly obtained erroneous results because he did not allow sufficient time for the rather slow vaporisation of the dried salt

The physical properties of substances are also affected in an extraordinary way by the removal of traces of moisture Thus Baker found that benzene which had been dried by phosphoric oxide for eight years boiled at 106°, instead of at 80°

Intense drying has been applied to other liquids with similar effects on the boiling-points, but compounds containing oxygen seem to revert much more quickly to their normal state when exposed to moist air The following table gives some of the results obtained

| | Years of drying | Original boiling-point | New boiling-point | Rise |
|---|---|---|---|---|
| Mercury - - | 9 | 358° | 420-425° | 62° |
| Carbon disulphide - | 28 | 49·5° | 80° | 30° |
| Ethyl ether - - | 9 | 35° | 83° | 48° |
| Bromine - - | 8 | 63° | 118° | 55° |

**Composition of water.**—Until 1781, water was always regarded as an element About that time, however, Priestley noticed the formation of dew after exploding a mixture of common air and inflammable air (or hydrogen) by means of an electric spark in a closed glass vessel No importance was attached to the observation, because it was well known that moisture could be thrown out of air by cooling, but in 1781 Cavendish repeated Priestley's experiment, in order to determine whether any change in weight took place He also burnt large volumes of the gases, in order to determine the nature of the dew, and collected 135 grams of water A complete solution of the problem of the composition of water was delayed because, when the experiment was repeated with oxygen instead of air, the water was found to contain nitric acid ! This he afterwards recognised as an oxidation product of atmospheric nitrogen present as an impurity in the gases. In the meanwhile, Lavoisier, having heard of his results, burnt inflammable air with oxygen in a bell jar over mercury and collected half an ounce of water. He then announced that

water was a compound of inflammable air and oxygen, a conclusion which Cavendish had already reached, but had not published Lavoisier therefore gave to inflammable air the name of "hydrogen," from the Greek words ὕδωρ, water, and γεννάω, I beget In a later experiment Lavoisier obtained hydrogen from water by passing steam through a red-hot gun barrel, an oxide of iron was also produced, thereby confirming the composition of water

**Volumetric analysis of water.**—The composition of water was determined in 1781 by Cavendish, who found the ratio,

$$hydrogen \quad oxygen = 201 \quad 100 \text{ by volume.}$$

Exact volumetric analyses were made in 1893 by Scott, who purified his gases until the residue left after explosion was usually less than 1 part in 100,000 and found the ratio,

$$hydrogen \quad oxygen = 200\,285 \cdot 100.$$

This result is in close agreement with those of Morley (1895),

$$hydrogen \quad oxygen = 200{\cdot}269 \quad 100,$$

and of Burt and Edgar (1915),

$$hydrogen \quad oxygen = 200\,288 \cdot 100$$

Scott prepared hydrogen by the action of steam on sodium, thus avoiding all the common impurities which are present in hydrogen made by the action of zinc on sulphuric acid, *e g* $AsH_3$ and $SH_2$ Oxygen was prepared by heating silver oxide, containing a little potash to prevent contamination by carbon dioxide (derived from silver carbonate in the silver oxide) Errors due to oxidation of grease in the stopcocks of the eudiometer were finally eliminated by lubricating them with syrupy phosphoric acid

Morley prepared a mixture of hydrogen and oxygen, by passing an electric current through ice-cold dilute potash, and collected the gas in three large glass globes of known capacity The density of this mixture was then calculated from the loss in weight of the electrolytic apparatus, and its composition deduced from the known densities of hydrogen and oxygen These were determined (i) by expelling about 4 grams of hydrogen from a weighed bulb of palladium (Fig 16) and measuring the pressure produced in three 14-litre globes immersed in ice, (ii) by weighing oxygen in a 20-litre globe, suspended against a counterpoise in a desiccator cupboard below the balance The "electrolytic gas" contained a small surplus of hydrogen, which was measured by noting the residual volume after explosion, so that the true volumetric ratio of hydrogen to oxygen could be deduced

| | | |
|---|---|---|
| Composition of electrolytic gas - - - | 2 00357 | 1 |
| Surplus of hydrogen after explosion - - | 0 00088 | 1 |
| Composition of water - - - - | 2 00269 | 1 |

Scott combined his measurements of combining volumes with Rayleigh's measurements of density and deduced the gravimetric ratio

$$oxygen \quad hydrogen = 7\,931 : 1.$$

In the same way, Morley,, by using his own measurements of density deduced the gravimetric ratio

$$oxygen : hydrogen = 7\,9395 : 1.$$

**Gravimetric experiments on the composition of water.**—Gravimetri experiments on the composition of water were made by Berzelius an

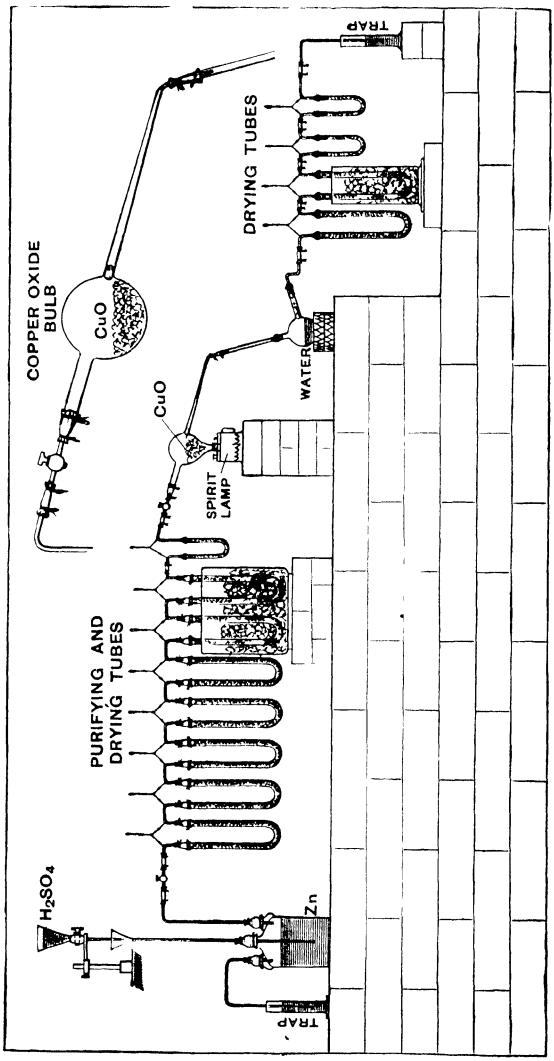



FIG 15 DUMAS' APPARATUS FOR DETERMINING THE COMPOSITION OF WATER

Dulong in 1820 Instead of combining the two gases directly, they passe hydrogen over copper oxide, thereby producing water and metallic copper

$$H_2 + CuO = H_2O + Cu$$

No attempt was made to weigh the gases directly, but the water wa

weighed, and the weight of oxygen which it contained was calculated from the loss of weight of the copper oxide The difference between the weights of the water and of the oxygen gave the weight of the hydrogen

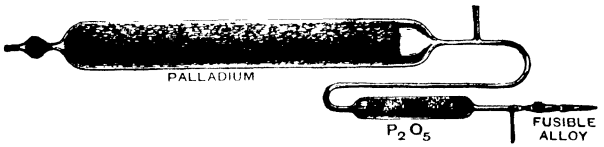



FIG 16 MORLEY'S PALLADIUM-TUBE FOR WEIGHING HYDROGEN
The bulb contained 600 grams of palladium, with a tube of phosphoric oxide to dry the gas and a seal of fusible metal

These experiments were repeated on a large scale by Dumas in 1842 The hydrogen, prepared by the action of zinc on dilute sulphuric acid, was purified and dried by passing it through seven U-tubes each about a metre in height (Fig 15) these contained lead nitrate solution to remove *sulphuretted hydrogen*, silver nitrate solution to remove *arseniuretted hydrogen*, potash to remove *acid vapours*, and oil of vitriol cooled in ice, or phosphoric oxide, to remove *water vapour* The copper oxide and copper were weighed in a large vacuous bulb provided with a beak 1 metre in length , during the reduction, the bulb was heated by a large spirit lamp The water was condensed in a glass bulb and the vapour absorbed in U-tubes similar to those used for drying the hydrogen In nineteen experiments Dumas prepared one kilogram of water and found the ratio

$$oxygen \quad hydrogen = 7\,98 : 1$$

Dumas' determinations are subject to errors from at least three sources (i) *Oxygen*, dissolved in the sulphuric acid, and reduced to water without producing a corresponding loss of weight in the copper oxide tube (ii) *Hydrogen*, occluded by the reduced copper when cooled in the gas (iii) *Sulphur dioxide*, produced by reduction of sulphuric acid in the drying tubes and converted finally into copper sulphide and water These sources of error all tend to reduce the loss in weight of the copper oxide tube, and so to reduce the proportion of oxygen Since the proportion found by Dumas was too high, instead of being too low, it is obvious that this list of errors must be incomplete

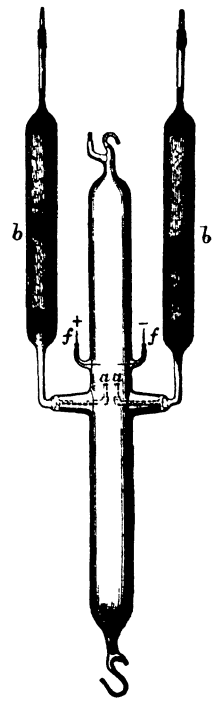



FIG 17 MORLEY'S COMBUSTION-TUBE

**Morley's experiments** (1895) —The most exact experiments on the gravimetric composition of water are those of Morley, who used very pure hydrogen and oxygen, and found the weight of each gas as well as the weight of the water formed by their combination

The hydrogen was absorbed in palladium in a bulb (Fig. 16) which was weighed before and after the hydrogen had been expelled by heating The oxygen required for combustion was drawn from glass globes, which were weighed before and after the experiment The gases were led through drying tubes *bb* (Fig 17) to a combustion vessel provided with two jets, *aa*, and a pair of wires, *ff*, for a spark to ignite the gas During the combustion the upper part of the tubes was surrounded with cold water and the lower part with a freezing mixture The water formed by the burning of the oxygen and hydrogen at the jets was thereby condensed and collected in the lower part of the tube The tube was exhausted and weighed before and after the experiment and the weight of water was found by subtraction The drying tubes, *bb*, packed with phosphoric oxide prevented loss of water vapour on exhaustion The residual gases in the tube were estimated, so that the actual weight of hydrogen and oxygen burnt was obtained In a typical experiment the weights were as follows

| | | |
|---|---|---|
| Wt of hydrogen passed into the apparatus | = 3 8223 | grs |
| Wt of residual hydrogen | = 0 0012 | ,, |
| Hydrogen burnt | = 3 8211 | ,, |
| Wt of oxygen passed into the apparatus | = 30 3775 | ,, |
| Wt of residual oxygen | − 0 0346 | ,, |
| Wt of oxygen burnt | = 30 3429 | ,, |
| Wt of hydrogen + wt of oxygen | = 34 1640 | ,, |
| Wt of water produced | = 34 1559 | ,, |
| Experimental error | = 0 0081 | ,, |

Oxygen to hydrogen = 7 941 1

Water to hydrogen = 8 939 1

The mean of twelve experiments, in which a total of over 400 grams of water were produced, gave the following ratio

oxygen to hydrogen = 7·9394 1

This value, which agrees closely with the ratio deduced from volumetric analysis and densities (p 81), namely,

oxygen to hydrogen = 7 9395 1,

was formerly accepted as a basis for the atomic weight of hydrogen (O = 16), but the latter has now been determined with even greater accuracy by means of the mass spectrograph This new value for the atomic weight of hydrogen, namely,

**1 0081,**

means that the ratio of oxygen to hydrogen in water is

**8 .1 0081 or 7 9357 . 1.**

## Hydrogen Peroxide

**History and occurrence.**—Hydrogen peroxide was discovered in 1818 by Thenard, who prepared it by the action of dilute acids on barium peroxide It occurs only in traces in the free state, since it decomposes very readily into oxygen and water

**Preparation.**—The peroxides of the alkalis and alkaline earths yield solutions of hydrogen peroxide on acidification Thus sodium peroxide, $Na_2O_2$, and barium peroxide, $BaO_2$, interact with sulphuric acid and with sodium dihydrogen phosphate as follows

(i) $BaO_2 + H_2SO_4 = H_2O_2 + BaSO_4$,

(ii) $Na_2O_2 + H_2SO_4 = H_2O_2 + Na_2SO_4$,

(iii) $Na_2O_2 + 2NaH_2PO_4 = H_2O_2 + 2Na_2HPO_4$

(i) Hydrogen peroxide is prepared commercially from barium peroxide (p 123) A thin paste of barium peroxide is added gradually to a well-cooled dilute solution of sulphuric acid The mixture is stirred vigorously for some time in order to bring the peroxide, which is coated with a layer of sulphate, into contact with the acid The solution is filtered from the barium sulphate and usually stabilised by adding some preservative such as glycerol

In another method, carbon dioxide is blown through a fine suspension of the peroxide in water, when barium carbonate is precipitated and can be filtered off If a thin paste of the peroxide is added to water through which carbon dioxide is being blown, so that the carbon dioxide is in excess, an insoluble barium percarbonate, $BaCO_4$, is formed

$$BaO_2 + H_2O + CO_2 \rightarrow \begin{cases} BaCO_3 + H_2O_2 \\ BaCO_4 + H_2O \end{cases}$$

(ii) A 30% solution of hydrogen peroxide can be prepared by the action of fairly dilute sulphuric acid on sodium peroxide (Merck's method), the sodium sulphate being frozen out as decahydrate $Na_2SO_4,10H_2O$

(iii) A strong solution of hydrogen peroxide can be prepared in the laboratory by adding the calculated quantity of sodium peroxide to a saturated solution of sodium dihydrogen phosphate cooled in ice, when the phosphate separates as $Na_2HPO_4,12H_2O$, and some of the water as ice

Expt 10 **Preparation of hydrogen peroxide**

Caustic soda (40 grams) is dissolved in water (250 grams) and added to syrupy (90%) phosphoric acid (110 grams) The solution, which contains $NaH_2PO_4$, is cooled in ice, and sodium peroxide (39 grams) is added slowly, the temperature being kept as low as possible The sodium peroxide is just insufficient to make the product alkaline, since hydrogen peroxide is very unstable in the presence of alkalis The nearly solid mass is drained in a Buchner funnel The filtrate is then placed in a mixture of ice and salt at $-18°$ in order to freeze out the remaining phosphate and some ice

The 20% hydrogen peroxide obtained by this method can be concentrated by fractional distillation under reduced pressure Extraction with

ether, in which water is almost insoluble, is not recommended, as ethyl peroxide may be formed, and this sometimes shatters the apparatus by causing an explosion

(iv) Hydrogen peroxide is now often manufactured by methods which involve the intermediate preparation of perdisulphuric acid, $H_2S_2O_8$ (p 264), or its salts Thus, in one process, 40% sulphuric acid is electrolysed under a high current density with platinum electrodes The resulting perdisulphuric acid is hydrolysed with dilute sulphuric acid,

$$H_2S_2O_8 + 2H_2O = 2H_2SO_4 + H_2O_2,$$

and the hydrogen peroxide is distilled off under reduced pressure

**Uses of hydrogen peroxide.**—Hydrogen peroxide is used as a bleaching agent for delicate materials, such as wool, ostrich feathers, silk, bone, ivory, cotton, teeth and hair It has valuable disinfecting properties and is used as a mouth-wash or gargle Its bleaching and disinfecting properties are due to the ease with which it loses oxygen

**Physical properties.**—Anhydrous hydrogen peroxide is a colourless liquid of density 1 46, but it is blue in bulk, like water It boils at 84° under a pressure of 68 mm and freezes at −1 7°

**Chemical properties of hydrogen peroxide.**—(*a*) *Decomposition and dissociation* —Hydrogen peroxide is an exothermic compound,

$$H_2(\text{gas}) + O_2(\text{gas}) = H_2O_2(\text{soln}) + 45{,}300 \text{ cal}$$

It is, however, less exothermic than water, and a considerable amount of heat is, therefore, set free when it decomposes into water and oxygen

$$\underset{2 \times 45{,}300}{2H_2O_2} = \underset{2 \times 68{,}360}{2H_2O} + O_2 + 2 \times 23{,}060 \text{ cal}$$

At atmospheric temperatures hydrogen peroxide decomposes slowly, but completely, according to the above equation The decomposition is accelerated by alkalis, by contact with finely divided or colloidal metals such as platinum and manganese, and by certain solids such as manganese dioxide Thus a solution of colloidal manganese dioxide, containing 5 mg per litre, has a pronounced catalytic effect on the decomposition Aqueous solutions of hydrogen peroxide are sometimes kept in bottles lined with paraffin wax in order to prevent the catalytic effect of the alkali of the glass Certain substances such as calcium chloride, glycerol, acetanilide (p 798), etc , retard the decomposition, *i e* they act as negative catalysts (p 590), and are therefore often added as preservatives to commercial solutions

**Hydrogen peroxide as an oxidising agent.**—Hydrogen peroxide is a powerful oxidising agent, thus

(i) Iodine is liberated quantitatively from solutions of acidified *potassium iodide*

$$H_2O_2 + 2HCl + 2KI = 2KCl + I_2 + 2H_2O$$

This reaction may be used for the estimation of hydrogen peroxide In the absence of acids, potassium hypoiodite is formed instead of free iodine

$$H_2O_2 + KI = KIO + H_2O.$$

(ii) *Ferrous salts* are oxidised to ferric salts in acid solutions

$$2FeSO_4 + H_2SO_4 + H_2O_2 = Fe_2(SO_4)_3 + 2H_2O$$

A mixture of ferrous sulphate and hydrogen peroxide is used as an oxidising agent in organic chemistry and is known as Fenton's reagent

(iii) *Lead sulphide* is oxidised to lead sulphate

$$PbS + 4H_2O_2 = PbSO_4 + 4H_2O$$

The black lead sulphide, which is formed by the action of atmospheric hydrogen sulphide on "white lead" paints (containing the basic carbonate $2PbCO_3,Pb(OH)_2$) can be bleached, and discoloured pictures can be "restored" permanently, by the action of hydrogen peroxide, since the white lead sulphate is not attacked by sulphuretted hydrogen

(iv) *Sulphurous acid* is oxidised to sulphuric acid, and hydrogen sulphide to sulphur and water

$$H_2SO_3 + H_2O_2 = H_2SO_4 + H_2O,$$
$$H_2S + H_2O_2 = S + 2H_2O$$

(v) *Chromic acid* ($K_2Cr_2O_7$ + dil $H_2SO_4$) is oxidised to an unstable blue **perchromic acid**, possibly $HCrO_5$ Thus, a blue ethereal layer is formed when hydrogen peroxide is added to an acidified chromate solution covered by ether, and serves as a good laboratory test for hydrogen peroxide

**Hydrogen peroxide as a reducing agent.**—Hydrogen peroxide can also act as a reducing agent

(i) *Silver oxide* is reduced to silver

$$Ag_2O + H_2O_2 = 2Ag + H_2O + O_2$$

(ii) *Acid ferrocyanide* is oxidised by hydrogen peroxide to ferricyanide, but reduction takes place when hydrogen peroxide is added to *alkaline ferricyanide*

$$2K_4Fe(CN)_6 + 2HCl + H_2O_2 = 2K_3Fe(CN)_6 + 2KCl + 2H_2O,$$
$$2K_3Fe(CN)_6 + 2KOH + H_2O_2 = 2K_4Fe(CN)_6 + 2H_2O + O_2$$

(iii) *Permanganate* in acid solution is rapidly reduced as follows

$$2KMnO_4 + 3H_2SO_4 + 5H_2O_2 = 8H_2O + K_2SO_4 + 2MnSO_4 + 5O_2$$

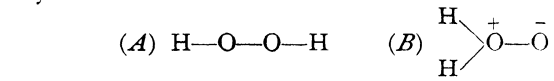
The reaction takes place quantitatively and may be used for the estimation of hydrogen peroxide (p 427) Potassium iodide must be used, however, if organic material is also present, since the latter may reduce some of the permanganate

**Acid properties.**—Hydrogen peroxide has acidic properties Thus, it turns blue litmus red and reacts with baryta to give a crystalline precipitate of barium peroxide, $BaO_2,8H_2O$

$$Ba(OH)_2 + H_2O_2 = BaO_2 + 2H_2O$$

This reaction can be used to prepare pure barium peroxide and hydrogen peroxide from commercial barium peroxide.

**Structure of hydrogen peroxide**.—Hydrogen peroxide can be represented by two structural formulae



Formula *A* contains univalent hydrogen and bivalent oxygen, exactly as in water itself, it represents hydrogen peroxide as a combination of two *hydroxyl radicals*. Formula *B* contains one singly-bound and one triply-bound atom of oxygen, carrying respectively a single negative and a single positive charge, both types are already known, *e g* in the ions $\bar{O}H$ and $\overset{+}{O}H_3$, so that the formula is a reasonable one.

Formula *A* is supported by the relationship of hydrogen peroxide to the metallic peroxides from which it is prepared. Thus, sodium peroxide must be formulated as containing a peroxide ion, $\overset{+}{Na}\ \bar{O}—\bar{O}\ \overset{+}{Na}$, corresponding with the disulphide ion in iron pyrites, $\overset{++}{Fe}\ \bar{S}—\bar{S}$. On the addition of acid, the peroxide ion, $\bar{O}—\bar{O}$, would be likely to attract one proton to each oxygen, rather than two protons to one oxygen, thus giving rise to a symmetrical molecule, $\overset{+}{H} + \bar{O}—\bar{O} + H = H—O—O—H$.

Derivatives of type *A* can be prepared by the action of chlorosulphonic acid Cl $SO_2$ OH, on hydrogen peroxide

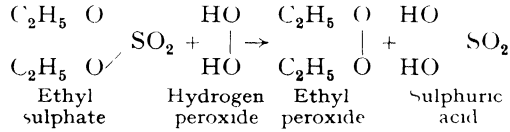
$$HO\ SO_2\ Cl + HO\ OH = HO\ SO_2\ O\ OH + HCl,$$

Per*mono*sulphuric acid

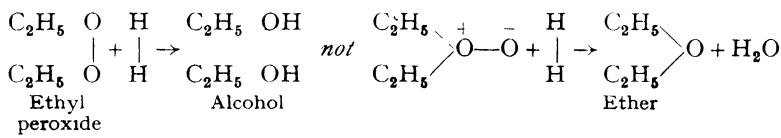
$$HO\ SO_2\ O\ OH + Cl\ SO_2\ OH = HO\ SO_2\ O\ O\ SO_2\ OH + HCl$$

Per*di*sulphuric acid

Further, when diethyl sulphate is treated with hydrogen peroxide, diethyl peroxide is formed

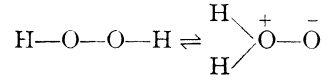



This compound can be reduced to alcohol, whereas, if it were a derivative of *B*, ether should be formed instead




On the other hand, Formula *B* has the merit of representing hydrogen peroxide as containing a molecule of water loosely bound to an additional

atom of oxygen, and so explains its ready reduction and its powerful oxidising properties. A compound, to which this formula was assigned, has been prepared by the action of atomic hydrogen on molecular oxygen at $-180°$. On warming to $-80°$ it changes to ordinary hydrogen peroxide. It is therefore possible that *both* formulae are right, and that hydrogen peroxide may be an equilibrium mixture of two isomers (p 248)



**Estimation of hydrogen peroxide.**—In commerce, the strength of a solution of hydrogen peroxide is stated in terms of the number of *volumes* of oxygen which can be obtained by the catalytic decomposition of unit volume of the solution Thus one litre of hydrogen peroxide of TWENTY VOLUMES strength will yield 20 litres of oxygen, when treated with a catalyst such as colloidal platinum This method of measuring the strength of a solution of hydrogen peroxide is too tedious for ordinary laboratory work, so that it is usual to determine the strength by titrating a measured portion of the solution against standard potassium permanganate, in the presence of dilute sulphuric acid (p 427)

$$2KMnO_4 + 5H_2O_2 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 8H_2O + 5O_2$$

Commercial hydrogen peroxide usually contains an organic preservative which may be attacked by the permanganate, so that it is safer to add an excess of potassium iodide and dilute sulphuric acid to the peroxide, and then to estimate the iodine with standard thiosulphate in the usual way (p 421)

$$2KI + H_2SO_4 + H_2O_2 = K_2SO_4 + 2H_2O + I_2,$$

$$2Na_2S_2O_3 + I_2 = 2NaI + Na_2S_4O_6$$

The disadvantage of this method is that the liberation of iodine is rather slow, although it can be accelerated by using a large excess of dilute acid and potassium iodide

# CHAPTER XI

## THE ALKALI METALS

| Atomic number | Element | Symbol | Atomic weight | Density | Melting-point | Boiling-point |
|---|---|---|---|---|---|---|
| 3 | LITHIUM | Li | = 6 940 | 0 53 | 186° | > 1200° |
| 11 | SODIUM | Na | = 22 997 | 0 97 | 97 5° | 877° |
| 19 | POTASSIUM | K | = 39 096 | 0 86 | 62 3° | 757° |
| 37 | RUBIDIUM | Rb | = 85 44 | 1 52 | 38 5° | 696° |
| 55 | CAESIUM | Cs | = 132 91 | 1 87 | 28° | 670° |

**Classification.**—The five alkali-metals follow immediately after the inert gases in the periodic classification of the elements, thus

2 Helium 10 Neon 18 Argon 36 Krypton 54 Xenon
3 Lithium 11 Sodium 19 Potassium 37 Rubidium 55 Caesium

Each atom therefore contains *one* loosely-bound electron, which is of dominant importance in determining the properties of the element Thus the elements are all *univalent metals*, and their compounds are formed in almost every case by the conversion of neutral atoms into *univalent cations*, $Li^+$, $Na^+$, $K^+$ These ions are extremely stable, since they possess the electronic configuration of an inert gas, and higher valencies are therefore impossible Compounds such as sodium peroxide, $Na_2O_2$, potassium peroxide, $K_2O_4$, and potassium triodide, $KI_3$, are only apparent exceptions to this rule, since the cation is univalent and the anion complex, as represented by the formulae

$$\overset{+}{Na}\ \overset{-}{O}—\overset{-}{O}\ \overset{+}{Na} \qquad \overset{+}{K}\ \overset{-}{O}—O—O—\overset{-}{O}\ \overset{+}{K} \qquad \overset{+}{K}\ \overset{-}{I}—I—I$$

Covalent links are present, however, in the diatomic molecules which form a substantial proportion of the vapour at temperatures above 800°

Na—Na K—K compare H—H

**Chemical properties of the alkali metals.**—(*a*) *Reduction* —The alkali metals are powerful reducing agents Thus metallic sodium was formerly used to separate aluminium from its chloride:

$$3Na + AlCl_3 = 3NaCl + Al$$

This reduction involves the conversion of the neutral atoms of metallic sodium into the sodium ions of sodium chloride by loss of electrons (p 50) The readiness with which this is done is a measure of the electro-positiveness of the metal (p 52) In general a more electropositive

element will hand over its electrons to a less electropositive metal, so that sodium will replace aluminium from its salts, aluminium will replace iron, etc The most electropositive metal is caesium, whilst gold and platinum are among the least electropositive metals

(*b*) *Combination with non-metals* —The alkali metals are even more ready to hand over their spare electrons to non-metals, to form binary salts, such as

Sodium chloride, $2Na + Cl_2 = 2\overset{+}{N}a\overset{-}{C}l$

Sodium sulphide, $2Na + S = \overset{++}{Na_2}\overset{--}{S}$

These salts are freely soluble in water, and this is a general property of the salts of all the alkali metals

(*c*) *Combination with oxygen* —The alkali metals combine very readily with oxygen, in which they burn to oxides and peroxides They also displace hydrogen from water, forming hydroxides, *e g*

$$2Na + 2H_2O = 2\overset{+}{N}a\overset{-}{O}H + H_2$$

These hydroxides have an ionic structure like the salts, and are therefore strong bases The violence of the action on water and the strength of the bases increase with increasing atomic weight of the metal

(*d*) *Combination with hydrogen* —The alkali metals combine with hydrogen, forming hydrides which are salt-like in character and probably contain a negative hydride ion, *e g* $Li^+H^-$

**Properties of lithium, rubidium and caesium** —The characteristic properties of the common alkali metals, sodium and potassium, are modified substantially in lithium, as is often the case in the first member of a family of elements, and to a lesser degree in the higher homologues, rubidium and caesium In particular, the properties of lithium tend to approach those of the alkaline earths of the next family, thus

(i) The metal burns with a dazzling flame like magnesium.

(ii) It decomposes water only slowly, like calcium

(iii) It burns in hydrogen to form LiH, compare $CaH_2$, which is decomposed by water with liberation of hydrogen

$$LiH + H_2O = LiOH + H_2$$

(iv) It differs from all the alkali metals, and resembles magnesium and calcium, in combining vigorously with nitrogen to form a stable nitride, $Li_3N$, which is decomposed by water with liberation of ammonia

$$Li_3N + 3H_2O = 3LiOH + NH_3.$$

(v) Lithium hydroxide is a caustic alkali, but dissolves only in eight times its weight of water, whereas sodium and potassium hydroxides dissolve in roughly their own weight of water This deviation is in the direction of the alkaline earths, although calcium hydroxide dissolves only in 800 parts and barium hydroxide in 25 parts of water

(vi) Lithium carbonate also approximates to the carbonates of the alkaline earths in that it is anhydrous and sparingly soluble in water

(1 4%), whilst the unstable bicarbonate, which is only known in solution, is much more soluble (5 5%)

(vii) Lithium chloride is deliquescent, like calcium chloride, it dissolves in its own weight of water and separates with 1, 2 or 3 molecules of water of crystallisation, whereas the chlorides of the alkali metals are anhydrous, except for the dihydrate, $NaCl,2H_2O$, which is only stable below the freezing-point of water

(viii) On the other hand, lithium fluoride, LiF, is sparingly soluble (calcium fluoride is insoluble) in water, and lithium phosphate, $Li_3PO_4,\frac{1}{2}H_2O$, like calcium phosphate, is almost insoluble in water

Rubidium and caesium are more electropositive than sodium and potassium, and the hydroxides are stronger bases, but the most conspicuous contrast is found in the greater readiness of the higher homologues to form crystalline polyhalides Thus sodium does not form a polyiodide, but potassium gives $KI_3$ Rubidium and caesium, however, form polyhalides also with chlorine and bromine, *e g*

$$CsBr_3,\ CsBrCl_2,\ CsICl_2 \text{ and } CsICl_4$$

Reference may also be made to the low density (0 53) of lithium and relatively high density of caesium (1 87), and to the very low melting-point (28°) of caesium and relatively high melting-point (186°) of lithium. The red, reddish violet, and blue flame spectra of lithium, rubidium and caesium are also of interest, since Bunsen discovered the two latter elements in 1860-1 with the help of a spectroscope

## 11 SODIUM Na = 23 00

**Occurrence of sodium.**—Sodium is one of six common metals, which, with silicon and oxygen, make up about 97% of the outer surface of the earth, but, on account of the great readiness with which it interacts both with oxygen and with water, it is never found in the free state The more important naturally-occurring compounds of sodium are

(*a*) *Sodium chloride*.—This is present to the extent of 2 8 % in sea water, and can be extracted from it in the form of SEA SALT by evaporation It is also found as ROCK SALT in extensive mineral deposits, formed by the evaporation of prehistoric seas Thus the salt bed at Wielitzka in Galicia is said to be 500 miles long, 20 miles broad and 1200 feet thick In England, important beds occur at Northwich (Cheshire), Droitwich (Worcestershire) and Middlesborough (Yorkshire), but these deposits are mainly under water, the salt is then pumped up in the form of brine and recovered by evaporation

(*b*) *Felspar*.—Sodium occurs in igneous rocks in the form of alumino silicates, such as FELSPAR, $NaAlSi_3O_8$, in which a part of the silicon of quartz has been replaced by the group NaAl

(*c*) *Soda*.—In the weathering of rocks, minerals such as felspar are decomposed by the carbon dioxide of the air to give sodium carbonate and clay

$$2NaAlSi_3O_8 + 2H_2O + CO_2 = Na_2CO_3 + H_4Al_2Si_2O_9 + 4SiO_2$$

Felspar — Clay

The sodium carbonate is dissolved by rain and accumulates in inland seas or salt lakes, such as Lake Magadi in East Africa, and the Great Salt Lake of Utah These deposits consist largely of **sodium sesquicarbonate,**

$$Na_2CO_3,NaHCO_3,2H_2O,$$

and may also contain **borax,** $Na_2B_4O_7,10H_2O$, which is of use for laundering, etc (p 129)

(*d*) *Chile saltpetre* —The deserts on the borders of Chile and Peru contain extensive deposits of **sodium nitrate,** $NaNO_3$, in the form of CALICHE or CHILE SALTPETRE, which are of value mainly on account of the "fixed nitrogen" (p 177) which they contain These deposits also contain borax, and iodine in the form of **sodium iodate,** $NaIO_3$, but they

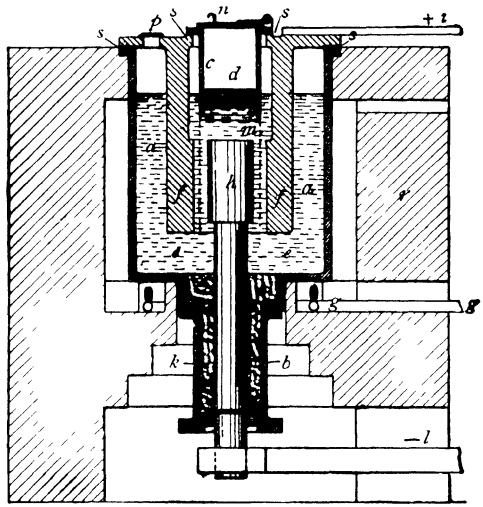



FIG 18 CASTNER'S APPARATUS FOR THE PREPARATION OF SODIUM

are usually free from bromides and phosphates and cannot therefore have come from sea-water or from guano The nitrogen is probably of organic origin, and may represent an extraction and concentration by occasional tropical floods of the fixed nitrogen from fertile soils

**Preparation of metallic sodium.**—Davy first isolated sodium in 1807 by the electrolysis of fused sodium hydroxide

$$NaOH \rightarrow \begin{cases} Na^{+} \xrightarrow{\text{cathode}} Na \\ OH^{-} \xrightarrow{\text{anode}} OH, \ 4OH = 2H_2O + O_2 \end{cases}$$

This process was abandoned for a time in favour of reduction by carbon, $2NaOH + 2C = 2Na + 2CO + H_2$, but it is now used again for the commercial preparation of the metal because of the cheapness of electricity

In the CASTNER PROCESS (Fig 18), sodium hydroxide, *a*, in an iron bath is melted initially by gas burners at *g*, but is afterwards kept in a molten condition by the heating effect of the current used for electrolysis The

steel cathodes, *h*, are led into the bath from below through pipes, *b*, from which they are insulated by solidified sodium hydroxide, *k*, they are surrounded by iron gauze, *m*, suspended from an iron cylinder, *c*, in which metallic sodium collects, as at *d*. The anodes, *f*, are of nickel to resist oxidation, they surround the cathodes and form part of the cover, being insulated by asbestos, *ss*, from the iron bath and from the iron cylinders, *c*. The oxygen set free at the anode is a valuable by-product and is collected and stored in cylinders, whilst the hydrogen set free at the cathode escapes round the edges of the cover, *n*. This cover is lifted from time to time, and the sodium removed by a ladle of nickel gauze, in which the metal is retained on account of its high surface tension, whilst the hydroxide flows back into the bath. The bath holds about 100 kg. of sodium hydroxide and uses a current of 1200 amperes at 5 volts. To ensure a good yield the temperature should be kept within 20° of the melting-point of sodium hydroxide at 318°.

The principal disadvantages of the above process are that the raw material, sodium hydroxide, is relatively expensive and the efficiency of the method is lowered by the formation of water at the anode, since some of this diffuses across to the cathode and attacks the sodium. In the DOWNS PROCESS, which will eventually displace the Castner Process because it does not suffer from these disadvantages, fused sodium chloride, containing sufficient calcium chloride to lower the melting-point of the salt from about 800° C. to 650° C., is electrolysed in an iron vessel lined with fire bricks. Chlorine is liberated at the graphite anode in the centre of the cell and is led away by an iron hood which is placed above the anode. The sodium which is set free at the circular iron cathode (surrounding the anode) is caught and separated in a tube as it rises to the surface of the electrolyte.

**Physical properties of sodium.**—Sodium is a light, soft, silvery metal, which can be squeezed through a die in the form of SODIUM WIRE. It is a good conductor of heat and of electricity, its conductivity being almost one-third of that of silver. It melts at 98°, boils at 877° and has a density of 0·97.

**Chemical properties of sodium.**—(*a*) *Oxidation.*—Sodium tarnishes quickly in damp air owing to oxidation. It is therefore stored under paraffin, but on a commercial scale is sent out in small ingots enclosed in soldered tins. It burns in air with a bright yellow flame, giving a mixture of $Na_2O$ and $Na_2O_2$.

(*b*) *Displacement of hydrogen by sodium.*—Sodium floats upon water, which it attacks violently, liberating hydrogen and forming sodium hydroxide:

$$2Na + 2H_2O = 2NaOH + H_2.$$

If allowed to move freely, the metal does not ignite, but it bursts into flame if stopped, and large pieces are liable to cause an explosion.

Sodium dissolves quietly in alcohol, displacing hydrogen and forming sodium ethoxide (p. 681):

$$2C_2H_5{\cdot}OH + 2Na = 2C_2H_5{\cdot}ONa + H_2$$

The action is analogous to the decomposition of water by sodium, but the

heat evolved is much less. Since sodium ethoxide is decomposed by water, as shown in the equation,

$$C_2H_5{\cdot}ONa + H_2O = C_2H_5{\cdot}OH + NaOH,$$

standard solutions of sodium hydroxide can be prepared conveniently (p 415) by dissolving a known weight of sodium in alcohol and diluting with water to a definite volume

Sodium will also displace hydrogen from many other compounds which are not acids, and do not form salts even with caustic alkalis, the products, which are usually decomposed by water, are described as SODIUM DERIVATIVES. Thus, when dry ammonia is passed over heated sodium, at 300° to 400°, hydrogen is displaced and **sodamide** is formed

$$2Na + 2NH_3 = 2NaNH_2 + H_2$$

Sodamide is violently decomposed by water, giving ammonia and sodium hydroxide It is used in many synthetical operations, often as a substitute for sodium

(*c*) *Combination with hydrogen* —By heating sodium in a current of dry hydrogen in an iron vessel at 360° to 430°, **sodium hydride**, NaH, is obtained in the form of slender, transparent needles It is decomposed by water, giving hydrogen and sodium hydroxide, while carbon dioxide in the presence of a trace of water combines with it to produce sodium formate

$$NaH + CO_2 = H \cdot CO \cdot ONa$$

(*d*) *Chlorination* —Sodium is not attacked by dry chlorine, but in damp chlorine it burns to sodium chloride, NaCl This is also formed when sodium is used as a reducing agent to liberate metals, such as magnesium and aluminium, from their chlorides

$$MgCl_2 + 2Na = Mg + 2NaCl$$

These two methods of preparation are now obsolete, but metallic sodium is still used in the laboratory for the preparation of the more refractory elements from their chlorides, *e g* cerium from cerium chloride, $CeCl_3$.

(*e*) *Amalgamation* —Sodium dissolves in mercury to form a liquid, SODIUM AMALGAM, but it also forms solid compounds, including $NaHg_2$, melting at 360°

**Uses of sodium.**—Metallic sodium was formerly used in the manufacture of aluminium and magnesium, but these are now prepared by electrolysis. At the present time sodium is used for the preparation of sodamide and sodium peroxide, and also for a variety of reductions and syntheses in organic chemistry

## COMPOUNDS OF SODIUM.

**Sodium oxide**, $Na_2O$, is formed by heating sodium peroxide with sodium, or by partially oxidising sodium in pure oxygen, and then distilling off the unchanged metal It is a white crystalline solid and dissolves violently in water, with the liberation of much heat, giving **sodium hydroxide**, or CAUSTIC SODA, NaOH

$$Na_2O + H_2O = 2NaOH$$

**Sodium peroxide**, $Na_2O_2$, is manufactured by passing dry air, purified from carbon dioxide, over sodium at 300° in aluminium trays in an iron tunnel So much heat is evolved that the trays, which are carried on iron trucks, are moved in the opposite direction to the current of air to moderate the reaction, otherwise the aluminium would be melted The product is a yellowish solid which dissolves in cold water with hydrolysis

$$Na_2O_2 + 2H_2O \rightleftharpoons 2NaOH + H_2O_2.$$

On warming, the hydrogen peroxide (which is very unstable in alkaline solution) decomposes into water and oxygen The peroxide is used for bleaching (after acidification) and for oxygenating the air in submarines

$$2Na_2O_2 + 2CO_2 \rightarrow 2Na_2CO_3 + O_2$$

**Preparation of sodium hydroxide**, NaOH —(*a*) *From sodium carbonate* —Sodium carbonate precipitates chalk from lime water and is thereby converted into sodium hydroxide or " caustic soda " according to the equation

$$Na_2CO_3 + Ca(OH)_2 \rightleftharpoons 2NaOH + CaCO_3$$

In concentrated solutions this action is incomplete, since calcium hydroxide is only sparingly soluble in strong solutions of sodium hydroxide, and can be precipitated from lime water by the addition of concentrated sodium hydroxide Caustic soda is therefore made from soda ash (p 100) by the action of lumps of lime on a 10% solution of sodium carbonate, in an iron vessel, into the contents of which steam is blown A sludge containing chalk and an excess of lime is allowed to settle The clear caustic liquid is run off and concentrated in vacuum pans, when unchanged sodium carbonate separates and is removed The remaining water is removed by heating the concentrate in iron pans, and the molten caustic soda is poured into iron drums, in which it solidifies The sludge is washed on a filter to recover the soda which it contains, and the washings are used to dissolve further quantities of soda ash

(*b*) *From sodium chloride by electrolysis* —Sodium hydroxide is also made directly from salt by electrolysis The essential actions are

At the cathode, $\overset{+}{Na} \rightarrow Na$, $2Na + 2H_2O = 2NaOH + H_2$.

At the anode, $\overset{-}{Cl} \rightarrow Cl$, $2Cl = Cl_2$

Sodium hydroxide and hydrogen are thus produced at the cathode and chlorine at the anode The output of sodium hydroxide by this process is insufficient to supply the market, since it is limited by the demand for chlorine. This essential product of the process may be condensed to a liquid, burnt with hydrogen from the process to form hydrogen chloride (p 281), combined with lime to form bleaching powder (p 285) or with acetylene to form **acetylene tetrachloride**, $C_2H_2Cl_4$ (p 675), or it may be used for the preparation of carbon tetrachloride or other chlorinated products

The products formed at the anode and cathode must be kept separate, in order to prevent the formation of hypochlorites and chlorates (p 285),

and of explosive mixtures of hydrogen and chlorine This separation may be effected (i) by the use of mercury, (ii) with the help of diaphragms

(i) *Electrolysis with a mercury cathode* —In the CASTNER-KELLNER PROCESS (compare Fig 19) a stream of brine is electrolysed between graphite anodes and a thin layer of mercury which forms the cathode. Sodium, liberated at the cathode, unites with the mercury to form a dilute liquid amalgam This is circulated continuously, the sodium being removed from the amalgam in a secondary cell in which it forms the anode, with a cathode of metallic iron Since this cell is usually short-circuited, the action can be regarded as a simple decomposition of

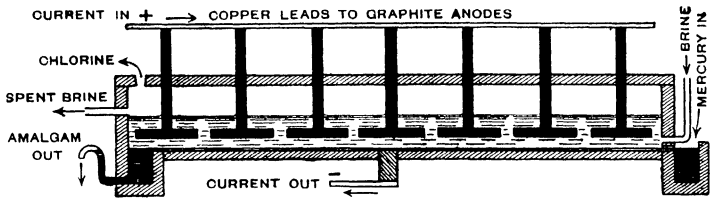



FIG 19 DIAGRAM TO ILLUSTRATE THE ELECTROLYSIS OF BRINE WITH A MERCURY CATHODE

sodium amalgam by water to produce caustic soda at concentrations up to 40% The ultimate actions are

$$\text{In the primary cell,} \quad 2\overset{+}{\text{Na}}\ \overset{-}{\text{Cl}} + 2x\text{Hg} = 2\text{NaHg}_x + \text{Cl}_2.$$

$$\text{In the secondary cell,} \quad 2\text{NaHg}_x + 2\text{H}_2\text{O} = 2\overset{+}{\text{Na}}\overset{-}{\text{OH}} + \text{H}_2 + 2x\text{Hg}$$

This method is more expensive than the other electrolytic processes, as a large amount of mercury has to be used for each cell and a small fraction of it is lost per annum , but it produces the purest form of caustic soda in solutions of relatively high concentration

In the ACKER PROCESS molten salt was electrolysed with a cathode of molten lead instead of mercury The lead-sodium alloy was then decomposed by steam, and anhydrous caustic soda was thus produced without evaporation

(ii) *With diaphragms.*—Several forms of apparatus have been devised in which the alkali formed at the cathode and the chlorine set free at the anode are kept apart by means of a porous partition or diaphragm It is essential that the diaphragm shall not offer too great a resistance to the current, but it must not allow the contents of the anode and cathode compartments to mix, nor must it be attacked by the alkali or by the chlorine Such diaphragms are almost invariably made from asbestos, often impregnated with barium sulphate or other inactive material

In the BILLITER PROCESS (Fig 20), purified brine is allowed to soak through a horizontal partition, *D*, at the bottom of the anode compartment Chlorine is set free at the graphite anodes, *AAA*, and is driven out from the solution with the help of steam coils, *SS*, whilst sodium hydroxide and hydrogen are formed at a cathode of wire gauze in contact with the lower

surface of the partition The space *R* below the partition is empty, ar any excessive flow of brine into it is checked by adding barium sulpha to the liquid above the partition The chlorine and hydrogen escape at and *W* respectively The caustic soda is drawn off through a syphon, l and concentrated, when the unchanged sodium chloride crystallises ou the fused soda is then poured off and cast into drums or sticks

**Purification of sodium hydroxide.**—Sodium hydroxide may be purifi by dissolving it in alcohol (in which the chloride, carbonate and sulpha are only sparingly soluble) and evaporating the solution in a silver dis the product is known as sodium hydroxide " pure by alcohol "

Sodium hydroxide free from non-metallic impurities can be prepar by the action of water or of water vapour upon metallic sodium , but, as t sodium hydroxide prepared by the Castner-Kellner process is actual

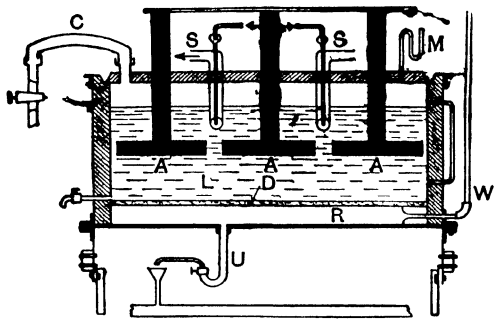



FIG. 20 BILLITER CELL FOR THE ELECTROLYSIS OF BRINE

made from sodium amalgam, this method of preparation is no long needed, unless complete freedom from carbonates is required

**Properties of sodium hydroxide.**—Sodium hydroxide is a white cryst line solid which melts at 318° It is very soluble in water, 100 grams which dissolve 42 grams NaOH even at 0° It is deliquescent and readi absorbs carbon dioxide from the air It is a very stable compound a cannot be converted directly into the oxide by heating, but when strong heated with carbon it gives sodium, hydrogen and carbon monoxide

$$2NaOH + 2C = 2Na + 2CO + H_2$$

It is a very strong base, and will precipitate the hydroxide or oxide heavy metals from solutions of their salts, and liberate ammonia fr ammonium salts

$$CuSO_4 + 2NaOH = Cu(OH)_2 + Na_2SO_4$$
$$NH_4Cl + NaOH = NH_3 + NaCl + H_2O.$$

Aqueous sodium hydroxide attacks glass, the silica being dissolved sodium silicate It also dissolves amphoteric metallic oxides, such as al minium oxide and zinc oxide, since these are weakly acidic, as well as ba (p 233) :

$$Al_2O_3 + 2NaOH = H_2O + 2NaAlO_2 \text{ (Sodium aluminate),}$$
$$ZnO + 2NaOH = H_2O + Na_2ZnO_2 \text{ (Sodium zincate).}$$

This property is used for the purification of bauxite in the manufacture of aluminium Aqueous sodium hydroxide also dissolves metallic boron, silicon, aluminium and zinc, liberating hydrogen, and forming a sodium salt of the oxide

$$2B + 2NaOH + 2H_2O = 3H_2 + 2NaBO_2 \text{ (Sodium borate)}$$
$$Si + 2NaOH + H_2O = 2H_2 + Na_2SiO_3 \text{ (Sodium silicate)}$$
$$2Al + 2NaOH + 2H_2O = 3H_2 + 2NaAlO_2 \text{ (Sodium aluminate)}$$
$$Zn + 2NaOH = H_2 + Na_2ZnO_2 \text{ (Sodium zincate)}$$

Other metals are attacked by fusion with sodium hydroxide in presence of air, but nickel and the noble metals, silver, gold and platinum are almost unaffected Some of the non-metals are also dissolved, as oxy-salts, by aqueous sodium hydroxide, but with simultaneous formation of a hydride (or a salt of the hydride) instead of free hydrogen

$$P_4 + 3NaOH + 3H_2O = PH_3 + 3NaH_2PO_2$$
$$4S + 6NaOH = 2Na_2S + Na_2S_2O_3 + 3H_2O$$
$$Cl_2 + 2NaOH = NaCl + NaOCl + H_2O$$
$$3Cl_2 + 6NaOH = 5NaCl + NaClO_3 + 3H_2O$$

On account of its power of emulsifying oils and grease, sodium hydroxide is a very powerful cleansing agent for machines, metal sheets, etc It is too caustic for use in washing , but the cleansing power of washing soda and of borax may be attributed to the liberation of traces of sodium hydroxide by the hydrolysis of these salts

**Uses of sodium hydroxide.**—Caustic soda is used to convert fats into hard soap (potassium hydroxide gives " soft soap ") It is also used in the manufacture of sodium and of alkaline bleaching solutions, in the purification of bauxite (p 129), and as a reagent in the treatment of organic materials, *e g* in the manufacture of paper, artificial silk, dyes, etc

**Sodium carbonate**, $Na_2CO_3$.—The manufacture of sodium carbonate from salt is one of the largest chemical industries Early in the nineteenth century the manufacture of soda from the ash of sea-weed was superseded by the Leblanc Process, but at the present time the Solvay Process is the only method of making sodium carbonate that is operated on a large scale

The essential features of the LEBLANC PROCESS were as follows

(*a*) Sodium chloride was converted into sodium sulphate by the action of sulphuric acid

$$NaCl + H_2SO_4 = NaHSO_4 + HCl \text{ (in an iron pan)}$$
$$NaHSO_4 + NaCl = Na_2SO_4 + HCl \text{ (on the hearth of a furnace)}$$

Crude sodium sulphate or SALT CAKE is still made by this process for use in the manufacture of glass, and hydrochloric acid is a valuable by-product of the process (p 281 )

(*b*) Sodium sulphate was reduced to sulphide and (in the same operation) converted into carbonate by double decomposition with calcium carbonate

$$Na_2SO_4 + 4C = Na_2S + 4CO,$$
$$Na_2S + CaCO_3 = CaS + Na_2CO_3.$$

For this purpose salt cake was mixed with limestone and powdered coal and heated to 700-1000° in a rotary furnace The crude mixture of sodium carbonate and calcium sulphide (with CaO, $CaCO_3$, NaCl, $Na_2SO_4$, coal and other impurities) was known as BLACK ASH

(*c*) The sodium carbonate was extracted with water and the solution was either (i) converted into caustic soda by the action of lime (p 96), or (ii) freed from caustic by contact with carbon dioxide from lime-kilns or furnace gases and crystallised out as WASHING SODA or SODA CRYSTALS, $Na_2CO_3,10H_2O$ containing 60% of water (Evaporation at the boiling-point gives the monohydrate, $Na_2CO_3,H_2O$, containing only 15% of water) The ALKALI WASTE, left behind after extracting the soda, contained most of the sulphur of the sulphuric acid in the form of calcium sulphide It was at first an obnoxious by-product, but methods were soon developed for recovering sulphur from it, and it finally became of value as a raw material for the manufacture of thiosulphates and other sulphur-compounds

**Manufacture of soda by the Solvay ammonia process** —The AMMONIA-SODA PROCESS is based on the fact that, when excess of carbon dioxide is passed into a solution of common salt containing ammonia, the ammonium bicarbonate, which is first formed, interacts with the sodium chloride to give a precipitate of sodium bicarbonate, since this salt is only sparingly soluble in brine

$$NH_3 + H_2O + CO_2 = (NH_4)HCO_3,$$

$$NH_4HCO_3 + NaCl = NH_4Cl + NaHCO_3 \text{ (ppt)}$$

Sodium carbonate is then easily prepared from the bicarbonate by heating

The process is carried out in the following stages

(*a*) *Preparation of ammoniacal brine* —Brine, pumped from a flooded salt mine, flows down a tower, fitted with numerous partitions, up which a stream of ammonia gas is passed The brine becomes saturated with ammonia and at the same time calcium and magnesium are precipitated as carbonates (since mother liquors containing bicarbonates are added to the brine) and are allowed to settle out

(*b*) *Carbonation* —The carbonation is effected in a Solvay tower (Fig 21), consisting of a large number of superposed cylindrical compartments or drums The bottom of each compartment has a large circular hole covered with a perforated sieve, the object of which is to break up the carbon dioxide into small bubbles and so to obtain as perfect absorption as possible The carbon dioxide is pumped in at the bottom of the towers, whilst the ammoniacal brine is admitted at the top in such a way as to fill the tower almost completely The absorption of carbon dioxide by the ammoniacal solution, forming ammonium carbonate $(NH_4)_2CO_3$ and then ammonium bicarbonate $(NH_4)HCO_3$, liberates considerable heat, which is removed by cold-water coils in the lower sections only During the action the temperature is kept at 30-40°, but when nearing completion the temperature is reduced to about 15°, so as to bring about a maximum separation of sodium bicarbonate The carbon dioxide is obtained by ignition of the sodium bicarbonate (see below) and by heating calcium carbonate in special kilns

(*c*) *Filtration* —The solid sodium bicarbonate is filtered off, washed with

a little water, dried, and heated in ovens, in such a way that the carbon dioxide generated can be used again

$$2NaHCO_3 = Na_2CO_3 + H_2O + CO_2$$

When the sodium carbonate is required in a heavy form for export, it is again calcined at a high temperature and subsequently ground to a powder

(*d*) *Recovery of ammonia* —As ammonia is much more costly than sodium carbonate, great care has to be taken to recover as much of it as possible The liquid from the filters contains nearly all the ammonia as chloride and carbonate, together with a certain amount of sodium carbonate, bicarbonate and chloride The free ammonia is distilled off in steam , lime from the carbon dioxide plant is then added, and steam again blown in so that all the ammonia is liberated for use in (*a*)

$$Ca(OH)_2 + 2NH_4Cl = CaCl_2 + 2NH_3 + 2H_2O,$$

$$(NH_4)_2CO_3 + Ca(OH)_2 = CaCO_3 + 2NH_3 + 2H_2O$$

In practice, a little ammonia is always lost and a few pounds have to be replaced for every ton of sodium carbonate manufactured

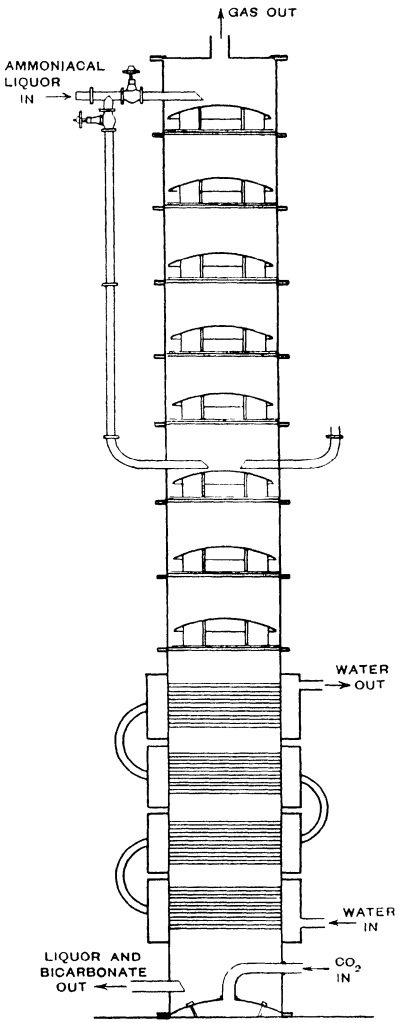



FIG 21 SOLVAY TOWER

**Advantages of the Solvay process** — The Solvay process has ousted the Leblanc process for the manufacture of soda owing to the following advantages

(i) The materials are much less costly, since brine at a cost of a few pence per ton of salt is used instead of rock salt, and no sulphuric acid is required

(ii) The consumption of fuel is very much less, since there are no solutions to be evaporated

(iii) No noxious by-products are produced

(iv) A purer product is obtained

(v) The process is continuous, and the soda is not handled until it is packed for delivery

(vi) The efficiency ratio is higher , thus 97% of the carbon dioxide in the limestone is converted into sodium carbonate

The disadvantages of the Solvay process are

(i) The high cost of ammonia for replacing losses

(ii) The fact that the whole of the chlorine of the salt is lost as calcium chloride, since no adequate market has yet been found for this by-product

**Properties of sodium carbonate.**—Anhydrous sodium carbonate is a white powder, which readily dissolves in water and forms a series of hydrates The principal hydrates and their range of stability in water are set out in Table 7 (compare also Fig 136, p 504)

TABLE 7.—HYDRATES OF SODIUM CARBONATE

| Formula of hydrate | Name of hydrate | Commercial name | Range of stability |
|---|---|---|---|
| $Na_2CO_3$ | — | Soda-ash | — |
| $Na_2CO_3, H_2O$ | Monohydrate | Crystal carbonate | Above 35 4° |
| $Na_2CO_3, 7H_2O$ | Heptahydrate | — | 32 0° to 35 4° |
| $Na_2CO_3, 10H_2O$ | Decahydrate | Washing soda or soda crystals | 2 1° to 32 0° |

Anhydrous sodium carbonate absorbs water from the air and forms the monohydrate, $Na_2CO_3,H_2O$, this salt is also formed when the decahydrate is exposed to dry air Aqueous solutions of the carbonate are alkaline owing to hydrolysis

$$Na_2CO_3 + H_2O \rightleftharpoons NaOH + NaHCO_3$$

On exposure to the air they absorb carbon dioxide and form the bicarbonate

$$Na_2CO_3 + CO_2 + H_2O = 2NaHCO_3$$

**Uses of sodium carbonate** —Sodium carbonate is used in the manufacture of glass, in the washing and bleaching of textile fabrics, for the preparation of other sodium salts, and for softening water (p 76)

**Sodium bicarbonate.**—Sodium bicarbonate is the first product of the Solvay process It can be prepared in the laboratory by passing carbon dioxide into a saturated solution of washing soda, $Na_2CO_3,10H_2O$, when the much less soluble bicarbonate is precipitated as an anhydrous crystalline powder Thus 100 grams of water at 15° dissolve 63 grams of $Na_2CO_3, 10H_2O$ or 16 grams of $Na_2CO_3$, but only 9 grams of $NaHCO_3$

Solutions of sodium bicarbonate are very slightly alkaline When boiled they give the normal carbonate as a result of the removal of carbon dioxide from the balanced action

$$2NaHCO_3 \rightleftharpoons Na_2CO_3 + H_2O + CO_2$$

Solid sodium bicarbonate begins to dissociate below 100° When heated between 250° and 300° it is converted into pure anhydrous sodium carbonate, which can be used for the standardisation of acids (p 415), but care must be taken not to heat too strongly, otherwise some caustic alkali may be produced.

**Sodium chloride.**—Common salt is prepared from brine by evaporation Crude brine from salt wells usually contains calcium and magnesium salts, as well as sulphates and bicarbonates These impurities may be eliminated by a preliminary electrolysis, when sodium hydroxide is formed and interacts with dissolved carbon dioxide to give sodium carbonate, which precipitates the calcium and magnesium salts, thus

$$Na_2CO_3 + CaSO_4 = CaCO_3 + Na_2SO_4$$

In the laboratory, pure sodium chloride can be prepared by passing hydrochloric acid gas into a saturated solution of impure salt, when pure salt is precipitated (see p 638 for explanation), and the impurities, such as magnesium salts, are left in solution

Common salt is the principal source for the preparation of chlorine and sodium and their compounds It is an essential constituent of the food of man and other animals, and is largely manufactured for this purpose, it is also used for preserving fish, meat and other food

**Sodium nitrate.**—Immense deposits of impure sodium nitrate occur in Chile and are the source of the sodium nitrate of commerce The crude "caliche" contains up to 65% of sodium nitrate, together with potassium nitrate (2 to 15 %), sodium chloride (up to 20%), sodium iodate, sodium chlorate and perchlorate, and gypsum, $CaSO_4,2H_2O$ It is purified by solution in water and recrystallisation, and then contains about 95% of sodium nitrate, together with sodium chloride (1 to 2%) and smaller amounts of other impurities The mother liquor contains sodium iodate, which is an important source of iodine (p 295)

Sodium nitrate is a white deliquescent crystalline solid which is very soluble in water It loses oxygen when strongly heated and is converted into the nitrite, but traces of oxides of nitrogen are also lost

$$2NaNO_3 = 2NaNO_2 + O_2.$$

Sodium nitrate is exported from Chile for use as a fertiliser in agriculture It is also used for the manufacture of nitric acid, of sodium nitrite, and of potassium nitrate for the preparation of gunpowder, since sodium nitrate itself is too hygroscopic to be used for this purpose

**Sodium nitrite**, $NaNO_2$, can be obtained in the laboratory by adding pieces of lead to fused sodium nitrate The fused mass is added gradually to water, and the resulting solution of sodium nitrite is filtered from the litharge formed by oxidation of the lead

$$NaNO_3 + Pb = PbO + NaNO_2$$

The filtrate is neutralised with nitric acid to remove traces of sodium hydroxide formed during the action, it is then evaporated and allowed to crystallise

The above method was formerly used on the commercial scale but has been abandoned in favour of the process described on p. 203, since about three tons of lead had to be used for the production of one ton of the nitrite, to say nothing of the lead poisoning that occurred among the workmen engaged in the industry

Sodium nitrite is very soluble in water but under ordinary conditions is not deliquescent Its chemical properties are considered with those of nitrous acid (p 203)

**Sodium hydrosulphide**, NaHS, is formed when a solution of sodium hydroxide is saturated with hydrogen sulphide On evaporating the solution in a current of hydrogen sulphide, crystals of the **dihydrate**, $NaHS,2H_2O$ are obtained

**Sodium sulphide**, $Na_2S$, is formed when an equivalent quantity of sodium hydroxide is added to a solution of the hydrosulphide On evaporation, crystals of the **nonahydrate**, $Na_2S,9H_2O$, separate out It is prepared commercially by heating sodium sulphate with coal at 1000°

$$Na_2SO_4 + 4C = Na_2S + 4CO$$

The mass is extracted with water, and the solution evaporated to give crystals of $Na_2S,9H_2O$ It is used in the textile industries, in the manufacture of dyes and in the extraction of silver

**Sodium sulphate**, $Na_2SO_4$, is manufactured by the Leblanc process (p 99) and used in making glass Below 32° it crystallises from water as the **decahydrate**, $Na_2SO_4,10H_2O$, commonly called GLAUBER'S SALT and used as a purgative in medicine, but above 32° the anhydrous salt separates and becomes less soluble as the temperature is raised (Fig 136, p 504) A **heptahydrate**, $Na_2SO_4,7H_2O$, is also known, but is less stable than the decahydrate below 32°, or than the anhydrous salt above this "transition temperature" (p 536) Sodium sulphate also provides the most familiar example of supersaturated solutions (p 504)

**Sodium bisulphate**, $NaHSO_4$, is produced, under the name of NITRE CAKE, as a by-product of the manufacture of nitric acid from sodium nitrate

$$NaNO_3 + H_2SO_4 = NaHSO_4 + HNO_3$$

It crystallises from water as the monohydrate and has a pronounced acid reaction When it is heated, **sodium pyrosulphate**, $Na_2S_2O_7$, is formed, and this is converted on further heating into sodium sulphate and sulphur trioxide

$$2NaHSO_4 = Na_2S_2O_7 + H_2O, \qquad Na_2S_2O_7 = Na_2SO_4 + SO_3$$

The bisulphate can be used to prepare hydrochloric acid (p 280) and as a substitute for sulphuric acid in the cleansing of sheet iron before the latter is tinned

## 19 POTASSIUM K = 39 096

**Occurrence of potassium.**—(*a*) *Silicates* —Potassium and sodium are equally abundant in igneous rocks, which contain about 2 5% of each of these metals **Potassium aluminotrisilicate**, $KAlSi_3O_8$ (compare $NaAlSi_3O_8$), or POTASH FELSPAR, is a principal constituent of granite

(*b*) *Sea water* —Sea water contains less than 0 1% of potassium salts in contrast to nearly 3% of sodium salts This is due to the fact that potassium salts are preferentially absorbed by soil and also to the precipitation of **potassium ferrisilicate**, $KFeSi_2O_6$, from the ocean in the form of GLAUCONITE.

(*c*) *Salt deposits.*—The upper layers of the salt beds at Stassfurt in North Germany contain large quantities of CARNALLITE, $KCl, MgCl_2, 6H_2O$, with KAINITE, a mixture of potassium and magnesium sulphates with potassium and sodium chlorides, and SYLVINE or **potassium chloride,** KCl These salt beds have probably been formed by the evaporation of sea water, from which gypsum and sodium chloride are first deposited, after which the mother liquors yield potassium and magnesium sulphates and chlorides

(*d*) *Organic compounds* —All plants contain a certain proportion of potassium which cannot be replaced by sodium Thus grape-juice deposits **potassium hydrogen tartrate,** $KHC_4H_4O_6$, as CREAM OF TARTAR (p 754) and sorrel contains **potassium hydrogen oxalate,** $KHC_2O_4$ (p 750) The presence of potassium is shown by the fact that the ashes of land plants consist largely of **potassium carbonate,** $K_2CO_3$, which was formerly extracted by lixiviation and sold as POT-ASH Potassium is therefore an essential constituent of fertile soils and is of great value as a fertiliser Potassium salts can be recovered from the uncrystallised mother liquors produced in the manufacture of sugar from beet-root, from wool-washings, and from the dust deposited from blast furnace gases

**Metallic potassium.**—(*a*) *Preparation* —Potassium was formerly prepared by heating potassium carbonate with wood charcoal at a white heat,

$$K_2CO_3 + 2C = 2K + 3CO,$$

but the method was dangerous, owing to the formation of an explosive **potassium carbonyl,** $(KCO)_6$ Potassium is now prepared by the electrolysis of potassium hydroxide in a cell similar to that used in the manufacture of sodium (p 93)

(*b*) *Physical properties* —Potassium is a light, soft, lustrous metal, but tarnishes quickly on exposure to air It melts at 62 3°, boils at 757°, and its density is 0 86 The eutectic alloy (p 541) of 23% of sodium with 77% of potassium melts at − 12 5°

(*c*) *Chemical properties* —Potassium resembles sodium very closely, but is rather more active Thus, if a piece of potassium be thrown into water, it decomposes it, forming potassium hydroxide and hydrogen, and evolves so much heat that the hydrogen burns and the potassium bursts into flame and produces an explosion

$$2K + 2H_2O = 2KOH + H_2$$

(*d*) *Combination with hydrogen* —When hydrogen is passed over potassium at 360°, **potassium hydride,** KH, is formed in slender white needles It liberates hydrogen when exposed to moist air, and is also decomposed into its constituents when heated to a red heat It combines with carbon dioxide in the cold to form potassium formate (p 715)

$$CO_2 + KH = H \quad CO \quad OK$$

(*e*) *Action on Ammonia* —Potassium, like sodium, dissolves in anhydrous liquid ammonia, forming a blue solution When heated in a current of ammonia, it gives **potassamide,** $KNH_2$, a compound which resembles sodamide.

**Compounds of potassium.**—Potassium salts are more expensive than the corresponding salts of sodium, but they are generally less soluble. They are therefore used to separate the more costly acid radicals, *e g*

| | |
|---|---|
| Potassium bromide, KBr | Potassium chromate, $K_2CrO_4$ |
| Potassium iodide, KI | Potassium permanganate, $KMnO_4$ |
| Potassium chlorate, $KClO_3$ | Potassium ferrocyanide, $K_4FeC_6N_6$ |

In the same way, potassium nitrate is used for making gunpowder, because it is much less soluble and therefore less hygroscopic than sodium nitrate and is thus less liable to make the powder damp Potassium hydroxide and potassium carbonate, however, are more soluble than the sodium compounds

**Potassium tetroxide**, $K_2O_4$, is formed when the metal burns in oxygen It is a yellow powder, which is decomposed by cold water according to the equation

$$K_2O_4 + 2H_2O = 2KOH + O_2 + H_2O_2$$

If the temperature is allowed to rise, the hydrogen peroxide is rapidly decomposed into water and oxygen

**Potassium monoxide**, $K_2O$, is said to be formed when potassium is heated with potassium nitrate in the proportions shown by the equation

$$2KNO_3 + 10K = 6K_2O + N_2$$

It dissolves in water with great evolution of heat to give the hydroxide

**Potassium hydroxide**, KOH, resembles sodium hydroxide, but is a stronger base and even more readily soluble in water It is made, like sodium hydroxide, by electrolysis of the chloride

**Potassium carbonate**, $K_2CO_3$, was formerly prepared, under the name of POT-ASH, by extracting wood-ashes with water and evaporating the solution in earthenware pots , it was also made by calcining "tartar" and is still made in this way from beet-sugar residues and from wool-washings It can be made from potassium chloride by a modification of the Leblanc process, but it cannot be prepared by the Solvay process owing to the fact that the bicarbonate is too soluble

Potassium carbonate is now manufactured from the chloride by the MAGNESIA PROCESS This depends on the fact that, when carbon dioxide is passed into a solution of potassium chloride in presence of hydrated magnesium carbonate at a temperature of 20°, an insoluble **potassium hydrogen magnesium carbonate,**

$$MgCO_3,KHCO_3,4H_2O \quad \text{or} \quad Mg(CO_3H)(CO_3K),4H_2O,$$

is precipitated

$$2KCl + 3(MgCO_3,3H_2O) + CO_2 = MgCl_2 + 2(MgCO_3,KHCO_3,4H_2O)$$

The sparingly soluble double salt is separated and decomposed by warming with water, or preferably by the action of magnesium oxide at a temperature below 20°

$$2(MgCO_3,KHCO_3,4H_2O) + MgO = 3(MgCO_3,3H_2O) + K_2CO_3$$

A solution of potassium carbonate is thus obtained, and hydrated magnesium carbonate is precipitated, ready for use with a fresh quantity of

potassium chloride By filtering and evaporating the solution, a potassium carbonate is obtained which is free from sodium salts, since sodium chloride is not precipitated by the magnesium carbonate in this process

Pure anhydrous potassium carbonate is obtained by igniting potassium hydrogen tartrate (cream of tartar), or pure potassium bicarbonate

$$2KHCO_3 = K_2CO_3 + CO_2 + H_2O$$

Potassium carbonate is a white granular powder which is very soluble in water and deliquesces on exposure to moist air It separates from solution as the **dihydrate**, $K_2CO_3,2H_2O$, in contrast to sodium carbonate, which separates as the decahydrate In its chemical properties, potassium carbonate resembles the sodium compound, but is more alkaline, and is converted into bicarbonate on exposure to air It is used in the manufacture of glass and in dyeing

**Potassium bicarbonate**, $KHCO_3$, is prepared by passing carbon dioxide into a solution of the carbonate It resembles sodium bicarbonate but is much more soluble , thus at 20° water dissolves one-third of its weight of $KHCO_3$, but only one-tenth of its weight of $NaHCO_3$

**Potassium chloride**,* KCl, is found in the Stassfurt salt beds as SYLVINE, KCl, and in larger quantities as CARNALLITE, $MgCl_2,KCl,6H_2O$ or $KMgCl_3,6H_2O$ It can be separated from carnallite by treatment with hot water, when the potassium salt crystallises out on cooling, whilst the more soluble magnesium salt remains in solution

Potassium chloride has a cooling saline taste, which is quite distinct from that of common salt, and, unlike sodium chloride, it is much more soluble in hot than in cold water, so that it can be recrystallised in the ordinary way from hot water

Large quantities are used in agriculture, in the manufacture of caustic potash, and in the preparation of other potassium salts

**Potassium bromide**, KBr, can be prepared by the action of bromine on a warm solution of potassium hydroxide

$$6KOH + 3Br_2 = 5KBr + KBrO_3 + 3H_2O$$

The solution contains bromate as well as bromide , to convert this bromate into bromide, the solution is evaporated to dryness, a little charcoal added, and the mixture heated

$$2KBrO_3 + 3C = 2KBr + 3CO_2.$$

On a large scale, the bromide is generally manufactured by the action of bromine and water on iron filings, which produces a bromide of iron , the iron is precipitated by the addition of potassium carbonate and the solution, after filtering from the precipitate of iron oxide, gives crystals of potassium bromide on evaporation

$$Fe_3Br_8 + 4K_2CO_3 = 8KBr + Fe_3O_4 + 4CO_2.$$

Potassium bromide forms colourless cubic crystals which are very soluble

* The potassium salts of the oxy-acids of the halogens, *e g* potassium chlorate, $KClO_3$, are described in Chapter XXI

in water. It is used for the preparation of photographic plates and papers (p 326) and as a sedative in medicine

**Potassium iodide**, KI, is prepared from iodine by similar methods to those described in the case of the bromide, and resembles it in properties A solution of potassium iodide dissolves iodine by a reversible reaction, forming **potassium tri-iodide**, $KI_3$, which has been isolated in the form of black needle-shaped crystals

$$KI + I_2 \rightleftharpoons KI_3$$

Solutions of potassium iodide dissolve several other iodides which are insoluble in water Thus insoluble mercuric iodide forms a soluble **potassium mercuri-iodide**, $K_2HgI_4$, which is used as a test for traces of ammonia under the name of NESSLER'S SOLUTION (p 340)

**Potassium nitrate**, $KNO_3$ —(*a*) *Occurrence* —This salt, commonly known as NITRE or SALTPETRE, occurs in the soil of hot countries In India, it is obtained by the lixiviation of certain rocks which contain 2 5 to 8% of $KNO_3$ (whence the name sal-petrae), and of soils enriched with nitrogenous excrements It is formed by the decay of nitrogenous organic matter, in contact with alkali, under the influence of a nitrifying organism which oxidises ammoniacal nitrogen to nitric acid This process is known as NITRIFICATION and was formerly brought about artificially in "nitre plantations" Brushwood was interlaid with manure, strewn with wood ashes and lime, and left exposed to the air for long periods, being watered from time to time with urine or stable drainage The fermentation of the organic matter produces ammonia, which is oxidised by the nitrifying organisms, utilising atmospheric oxygen, first to nitrite then to nitrate On extracting with water, a solution of calcium nitrate is obtained, from which the addition of wood-ashes (potassium carbonate) precipitates calcium carbonate, leaving a solution of potassium nitrate

$$Ca(NO_3)_2 + K_2CO_3 = CaCO_3 + 2KNO_3$$

This solution on evaporation yields crude nitre, which can be purified by recrystallisation

(*b*) *Manufacture from sodium nitrate* —Saltpetre is also manufactured from sodium nitrate and potassium chloride by the so-called "conversion-process"

$$NaNO_3 + KCl = KNO_3 + NaCl$$

A saturated solution of sodium nitrate is mixed with a molecular proportion of potassium chloride and concentrated to density 1 50, when nearly all the sodium separates as chloride, since sodium chloride is far less soluble in the hot solution than any of the other salts On cooling, the clear solution deposits nearly pure potassium nitrate, because potassium nitrate is less soluble in the cold than any of the other salts The solubilities of the different salts which determine this result are shown in Fig 22

(*c*) *Properties* —Potassium nitrate resembles sodium nitrate, but is less soluble and is not deliquescent It is therefore used in preference to sodium nitrate in the manufacture of GUNPOWDER This consists of a mixture of about 75% of potassium nitrate, 10% of sulphur and 15% of

charcoal, intimately incorporated by grinding under heavy rollers Potassium nitrate is rich in oxygen, and gunpowder depends for its effect on the sudden oxidation of the carbon and sulphur by the oxygen of the nitre, giving rise to a large volume of gaseous products Experiments have shown that more than half the products of the explosion of gunpowder are solid compounds, principally potassium carbonate, thiosulphate, and sulphide, which form a dense white smoke, whilst the principal gases are carbon dioxide and nitrogen Gunpowder as a propellant has now been superseded by SMOKELESS POWDERS, made from guncotton or from mixtures of guncotton with nitroglycerine (p 736) which give only gaseous products, and therefore little or no smoke.

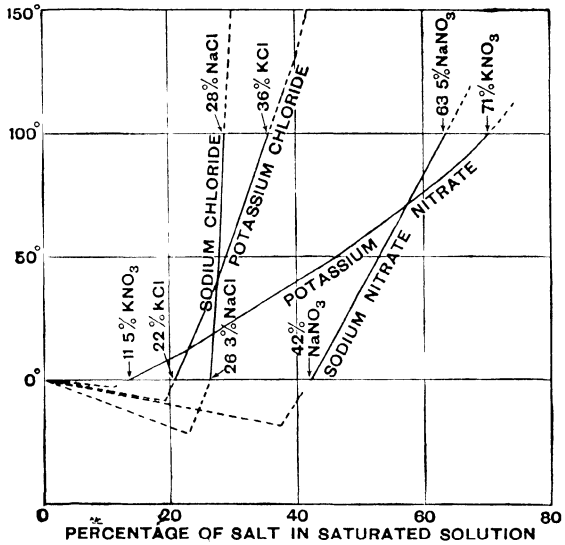



FIG 22 SOLUBILITY OF SODIUM AND POTASSIUM CHLORIDES AND NITRATES

**Potassium nitrite**, $KNO_2$, is obtained by similar methods to those used in making sodium nitrite, and forms white, deliquescent crystals

**Potassium sulphate**, $K_2SO_4$, is manufactured from minerals such as SCHONITE, $Mg(SO_4K)_2,6H_2O$, by a process of crystallisation It separates from water in anhydrous crystals, in marked contrast to the sodium salt, which comes out as the decahydrate, $Na_2SO_4 10H_2O$ , it is also much less soluble than the sodium compound Enormous quantities are used as a fertilizer, particularly for cornfields, as the quality of the straw is greatly improved

**Summary.**—From the foregoing paragraphs it will be seen that sodium and potassium and their compounds are very similar The main differences are

(1) Metallic potassium is more active than sodium

(ii) Potassium salts are less soluble, except the hydroxide, carbonate and bicarbonate

(iii) Potassium salts are not so hygroscopic as sodium salts, and do not form hydrates to the same extent, thus potassium sulphate crystallises out of solution as the anhydrous salt, while sodium sulphate comes out as the decahydrate, $Na_2SO_4,10H_2O$

**Estimation of potassium.**—For quantitative work potassium is precipitated from aqueous solutions as **potassium platinichloride**, $K_2PtCl_6$, or as **potasssium perchlorate**, $KClO_4$, in the presence of alcohol which reduces its solubility In qualitative analysis it may be precipitated as **potassium cobaltinitrite**, $K_3Co(NO_2)_6$

# CHAPTER XII

## METALS OF THE ALKALINE EARTHS

| Atomic number | Element | Symbol | Atomic weight | Density | Melting-point | Boiling-point |
|---|---|---|---|---|---|---|
| 4 | BERYLLIUM | Be | 9 02 | 1 8 | 1350° | 1500°? |
| 12 | MAGNESIUM | Mg | 24 32 | 1 74 | 651° | 1110° |
| 20 | CALCIUM | Ca | 40 08 | 1 55 | 810° | 1170° |
| 38 | STRONTIUM | Sr | 87 63 | 2 55 | About 800° | 1150° |
| 56 | BARIUM | Ba | 137 36 | 3 78 | 850° | 1140° |
| 88 | RADIUM | Ra | 225 97 | — | — | — |

**Classification.**—The metals of the alkaline earths follow those of the alkalis in the periodic classification of the elements Their atomic numbers are therefore two units greater than those of the inert gases of the helium family, and they carry two more planetary electrons These two "valency electrons" form a tiny sub-group outside the electronic shell of an inert gas They are very easily lost, giving rise to bivalent ions,

$$Be^{++},\ Mg^{++},\ Ca^{++},\ Sr^{++},\ Ba^{++},\ Ra^{++},$$

with the electronic configuration of an inert gas, so that ions of higher valency are not known On the other hand, univalent ions are not formed, since the second valency electron is removed more easily than the first The bivalency of these elements is therefore just as rigid as the univalency of the metals of the alkalis.

The salts derived from these bivalent ions are colourless, like those of the alkalis, unless the anion is coloured, but they are often much less soluble in water Thus $CaF_2$, $CaCO_3$ and $BaSO_4$ are insoluble in water, whereas NaF, $Na_2CO_3$ and $Na_2SO_4$ are freely soluble The valency, however, is not the only factor which determines solubility, since the univalent silver salts are even less soluble in water

**Properties.**—The elements are all metals, since the valency electrons are sufficiently mobile to give rise to metallic conductivity They are "light metals," but (unlike lithium, sodium and potassium), they are all denser than water Their melting-points and boiling-points are also much higher than those of the alkali metals

The metals are strongly electropositive, and this property increases, as in the alkali metals, with increasing atomic weight

(*a*) *Calcium, strontium and barium*.—The backbone of the group is formed by the "triad,"

20 Calcium, 38 Strontium, 56 Barium,

in which the rule of the arithmetic mean is obeyed somewhat closely. These strongly electropositive metals are converted into hydroxides by cold water, liberating hydrogen, although much less vigorously than sodium or potassium. They are therefore to be regarded as chemical reagents rather than as possible components of alloys. Thus calcium resembles lithium in combining both with oxygen and with nitrogen, and is added to steel as a reagent for eliminating gases. The oxides, lime, strontia and baryta, are strongly basic, and fully deserve the name of ALKALINE EARTHS, since their solutions are only less powerfully alkaline than those of the alkalis themselves.

(*b*) *Magnesium*.—The boiling-point of magnesium (1110°) is almost identical with those of calcium, strontium and barium, but its melting-point (651°) and density (1·74) are intermediate between those of calcium and zinc (with both of which elements it is associated in Mendeléeff's table), and many of its chemical properties are more like those of zinc than of calcium. Thus calcium tarnishes readily in air and decomposes cold water, whereas magnesium and zinc decompose water only at higher temperatures and are sufficiently stable in air to be used in metallurgy. Again, magnesium and zinc do not form hydrides, whereas calcium unites directly with hydrogen to form a salt-like hydride.

Many of the chemical properties of magnesium can be explained by the similarity of ionic radii in the series

| | | | |
|---|---|---|---|
| | $Mg^{++}$ 0·78 | $Zn^{++}$ 0·83 | $Fe^{++}$ 0·83 A U |
| contrast | $Ca^{++}$ 1·06 | $Sr^{++}$ 1·27 | $Ba^{++}$ 1·43 A U |

Thus the sulphates and double sulphates of magnesium and zinc are alike in appearance and in solubility

| | | |
|---|---|---|
| | $MgSO_4,7H_2O$ | $K_2SO_4,MgSO_4,6H_2O$ |
| | $ZnSO_4,7H_2O$ | $K_2SO_4,ZnSO_4,6H_2O$ |
| contrast | $CaSO_4,2H_2O$. | — |

Similarity of properties can also be noted in the ready hydrolysis of the chlorides of magnesium and zinc, and in the behaviour of the carbonates and basic carbonates. For the same reasons, magnesium and ferrous iron occur together in FERROMAGNESIAN MINERALS, such as OLIVINE $[MgFe]_2SiO_4$, whereas the more strongly basic lime is more often found (like sodium and potassium) as a constituent of FELSPAR.

Table 8 summarises some of the principal properties of calcium, magnesium and zinc.

TABLE 8.—PROPERTIES OF CALCIUM, MAGNESIUM AND ZINC

| | CALCIUM | MAGNESIUM | ZINC |
|---|---|---|---|
| **Physical properties** | | | |
| Lustre | Grey-white | Grey-white | Grey-white |
| Density | 1 55 | 1 74 | 7 1 |
| Melting-point | 810° | 651° | 419° |
| Boiling-point | 1100° | 1110° | 907° |
| Conduction of heat and electricity | Good | Good | Good |
| **Valency** | 2 | 2 | 2 |
| **Preparation** | Electrolysis of fused chlorides | | Reduction of oxide by carbon |
| **Chemical properties** | Readily tarnishes in air, burns to CaO and $Ca_3N_2$, decomposes cold water | Slowly tarnishes in air, burns to MgO and $Mg_3N_2$, when heated decomposes steam | Slowly tarnishes in air, burns to ZnO, when heated decomposes steam |
| | All three elements dissolve in dilute acids with the liberation of hydrogen | | |
| **Compounds.** | | | |
| Hydride | Stable salt-like solid, $CaH_2$ | Probably none | Probably none |
| Chloride | Deliquescent solid, forming many hydrates, *e g* $CaCl_2$, $6H_2O$, which are only slightly hydrolysed on ignition | Deliquescent solid, forming many hydrates, *e g* $MgCl_2$, $6H_2O$, which are hydrolysed to MgO on ignition | Deliquescent solid, forms a monohydrate which is hydrolysed to ZnO on ignition |
| Cyanide | $Ca(CN)_2$ soluble | $Mg(CN)_2$ soluble | $Zn(CN)_2$ insoluble, but soluble in KCN, forming $K_2Zn(CN)_4$ |
| Oxide | Very stable, cannot be reduced to metal by C or H, a strong base, dissolves in 400 parts of water | Very stable, cannot be reduced by C or H, rather weak base, dissolves in 50,000 parts of water | Very stable, but can be reduced by carbon, amphoteric oxide, dissolves in 250,000 parts of water |
| Carbonate | Normal carbonate precipitated by $Na_2CO_3$ solution, dissolves in carbonic acid to form unstable bicarbonate | Basic carbonates are precipitated by $Na_2CO_3$ solution, showing weaker basicity of MgO and ZnO Normal carbonates are precipitated by $NaHCO_3$, and dissolve (slightly in case of Zn) in carbonic acid to form very unstable bicarbonates | |
| Sulphate | Dissolves in 400 parts of water, and crystallises as $CaSO_4$, $2H_2O$, does not form double sulphates like Mg and Zn | Dissolve in 4 parts and 0 75 parts of water respectively Crystallise as isomorphous vitriols, $MgSO_4$, $7H_2O$ and $ZnSO_4$, $7H_2O$, form double salts of the type $(NH_4)_2SO_4$, $MgSO_4$, $6H_2O$ | |
| Nitrate | Deliquescent crystals of $Ca(NO_3)_2$, $4H_2O$, separate from solution Decomposed to CaO by heat | Deliquescent crystals of $Mg(NO_3)_2$, $6H_2O$ and $Zn(NO_3)_2$, $6H_2O$, separate from solution Decomposed by heat to MgO and ZnO | |

(*c*) *Beryllium* —Beryllium is even less electropositive than magnesium. Thus, like magnesium, but in contrast to lithium and calcium, it is not sufficiently positive to form a salt-like hydride It is also stable in air and does not decompose water even at 1000°, so that it is a safe component to add to metallic alloys Moreover, its oxide is so feebly basic that it dissolves in alkalis, like aluminium oxide, and may therefore be regarded as an " earth " rather than as an " alkaline earth " Finally, the chloride is volatile and fumes in moist air, just like aluminium chloride

$$BeCl_2 + H_2O = 2HCl + BeO$$

Beryllium, therefore, resembles aluminium even more closely than lithium resembles calcium Indeed, an erroneous atomic weight was at first assigned to beryllium, because it was assumed that the similarity between the two elements must be accompanied by equality of valency, whereas it is more probably due to the smallness of their ionic radii,

$$\overset{++}{Be}\ 0\,34, \quad \overset{+++}{Al}\ 0\,57, \quad \overset{+++}{Fe}\ 0\,67, \quad \overset{+}{Li}\ 0\,78, \text{ A U.}$$

## 12 MAGNESIUM Mg = 24 32

**Occurrence of magnesium** —Magnesium is never found in the free state , but its oxide, as a constituent of rocks, is only less abundant than silica, alumina and oxides of iron In igneous rocks, it occurs as a silicate with isomorphous ferrous iron in OLIVINE, $[MgFe]_2SiO_4$, and in hornblende, serpentine and asbestos In sedimentary rocks the carbonate occurs as MAGNESITE, $MgCO_3$, and forms mountainous masses in combination with calcium carbonate as DOLOMITE, $MgCa(CO_3)_2$ Soluble compounds, including EPSOM SALTS, $MgSO_4,7H_2O$, are found in mineral springs and in hard waters, whilst the mother liquors of oceanic salt deposits, in the upper layers of the salt beds at Stassfurt and elsewhere, yield soluble salts such as KIESERITE, $MgSO_4,H_2O$, SCHONITE, $K_2SO_4,MgSO_4,6H_2O$, KAINITE, $MgSO_4,KCl,3H_2O$ and CARNALLITE, $MgCl_2,KCl,6H_2O$

**Manufacture of magnesium.** Magnesium oxide is so stable that it is only recently that the metal has been manufactured by the reduction of its oxide with carbon above 2000°

$$MgO + C \rightleftharpoons Mg + CO.$$

This reaction is markedly reversible below 2000°, so that the magnesium vapour has to be condensed rapidly in hydrogen gas to prevent reoxidation.

Magnesium is, however, still largely manufactured by the electrolysis of fused magnesium chloride, which is mixed with sodium or potassium chlorides to lower the melting-point and improve the conductivity The electrolysis is carried out in a rectangular steel tank which acts as the cathode, whilst the anode consists of graphite rods which are surrounded by porcelain tubes to lead off the chlorine The temperature of the fused mixture is above the melting-point of magnesium and its density is higher, so that liquid metal floats to the surface and is run off Since magnesium readily combines with oxygen and nitrogen, the air in the apparatus is displaced by an inert gas, such as coal gas.

**Properties of magnesium.**—(i) Magnesium is a brilliant white metal which can be drawn into wire and rolled into ribbon Owing to its low density it is used with aluminium in the production of light alloys for aircraft, etc , but it is too easily corroded to be used alone

(ii) The metal is a powerful reducing agent, and is sometimes used to liberate elements such as silicon from their oxides

$$2Mg + SiO_2 = 2MgO + Si$$

(iii) When heated in air or oxygen, magnesium catches fire and burns with a brilliant flame, which is rich in actinic rays It is therefore used in the manufacture of star shells for military and naval service, and is mixed with potassium chlorate for use as a " flashlight " in photography Its affinity for oxygen is so great that it will continue to burn in carbon dioxide

$$2Mg + CO_2 = 2MgO + C$$

(iv) When burnt in air, magnesium combines with nitrogen as well as oxygen, forming the nitride, $Mg_3N_2$ This nitride is readily formed by passing nitrogen over heated magnesium, and is decomposed by water, giving ammonia

$$Mg_3N_2 + 3H_2O = 3MgO + 2NH_3$$

(v) At atmospheric temperatures magnesium is not affected by dry air, nor by water from which all carbon dioxide has been expelled , but, when this gas is present, the metal is corroded by moist air, and is attacked rapidly by water Hydrogen is evolved in this action, and the magnesium passes into solution as **magnesium hydroxycarbonate**, $Mg(OH)CO_3H$

$$Mg + H_2CO_3 + H_2O = Mg(OH)CO_3H + H_2$$

(vi) Magnesium decomposes boiling water slowly, but burns when heated in steam

$$Mg + H_2O = MgO + H_2$$

It also liberates hydrogen from dilute acids, including dilute nitric acid but unlike zinc it is not dissolved by caustic alkalis

(vii) Metallic magnesium dissolves in dry ethereal solutions of methyl iodide and organic halides of similar type, forming " Grignard compounds " (p 726) which are of great importance in organic syntheses

$$CH_3I + Mg = CH_3MgI \quad \text{(Grignard compound)}$$

## Compounds of Magnesium

**Magnesium oxide**, MgO, is formed when the metal is burnt in oxygen It is manufactured by igniting magnesite, $MgCO_3$

$$MgCO_3 = MgO + CO_2$$

This action proceeds readily under a very gentle heat, and affords a convenient method of generating small quantities of pure carbon dioxide, *e g* for use in analysis Unlike lime, the product does not slake It is almost insoluble in water, but imparts to it an alkaline reaction Magnesium, like calcium oxide, is a remarkably stable and refractory material, its melting-point being about 2800° , it is therefore used in constructing

furnaces for metallurgical operations, and in the manufacture of crucibles and cupels

**Magnesium hydroxide**, $Mg(OH)_2$, is precipitated as a gelatinous mass on adding a solution of potassium, sodium or ammonium hydroxide to a solution of a magnesium salt, but is easily converted into the oxide by heating it Ammonium hydroxide, to which ammonium chloride has been added to reduce the alkalinity of the solution (p 637), does not precipitate the hydroxide Conversely, magnesium hydroxide will dissolve when an excess of ammonium chloride solution is added to it , but, unlike zinc hydroxide, it will not dissolve in excess of alkali

**Magnesium carbonate**, $MgCO_3$, occurs naturally as MAGNESITE It may be precipitated by the addition of sodium bicarbonate to an aqueous solution of a magnesium salt , but (like zinc and unlike calcium) a basic carbonate of variable composition, $xMgCO_3,yMg(OH)_2,zH_2O$, is precipitated by the addition of sodium carbonate The normal carbonate is converted into a soluble bicarbonate by aqueous carbon dioxide, but is reprecipitated from the solution by boiling

$$MgCO_3 + CO_2 + H_2O \rightleftharpoons Mg(CO_3H)_2$$

Magnesium carbonate also dissolves in excess of alkali carbonates, giving solutions from which double carbonates, *e g* $Mg(CO_3Na)_2$, can be crystallised out For similar reasons it is soluble in solutions of ammonium salts, with which it forms a double carbonate, and is therefore not precipitated with the other alkaline earths in Group 5 in the qualitative analysis of metals (p 383)

**Magnesium chloride**, $MgCl_2$, can be prepared by the action of dilute hydrochloric acid on the carbonate On evaporating the resulting solution, the **hexahydrate**, $MgCl_2,6H_2O$, crystallises out When heated, it loses hydrogen chloride as well as water

$$MgCl_2 + H_2O = MgO + 2HCl$$

The anhydrous salt can be prepared, however, by heating the hydrate in a stream of dry hydrogen chloride, or by igniting ammonium magnesium chloride

$$NH_4Cl,MgCl_2,6H_2O = MgCl_2 + NH_4Cl + 6H_2O$$

Magnesium chloride is hydrolysed in solution, especially at higher temperatures

$$MgCl_2 + 2H_2O \rightleftharpoons Mg(OH)_2 + 2HCl$$

It has therefore a strong corrosive action upon iron, since the trace of acid set free by hydrolysis is replaced as fast as it is used up by the iron The corrosive action of sea water in marine boilers is attributed to the magnesium salts which it contains

**Magnesium sulphate**, $MgSO_4$, is found in mineral springs , it can also be separated from the mother liquors of sea water as the **heptahydrate**, $MgSO_4,7H_2O$ This has long been known and used as a purgative under the name of EPSOM SALTS The **monohydrate**, $MgSO_4,H_2O$, is found in the Stassfurt salt beds as KIESERITE It is almost insoluble in water, but is slowly converted into the soluble heptahydrate

Magnesium sulphate is manufactured by recrystallisation of kieserite, but it can also be prepared in the laboratory by dissolving the oxide or carbonate in dilute sulphuric acid and evaporating the solution, when the heptahydrate crystallises out The anhydrous salt is obtained by igniting the hydrate, since the trace of sulphuric acid, produced by hydrolysis, is not sufficiently volatile to be driven off like hydrogen chloride

**Estimation of magnesium.**—The gravimetric estimation of magnesium depends upon the fact that it can be precipitated quantitatively from solution as magnesium ammonium phosphate ·

$$MgSO_4 + NH_4OH + Na_2HPO_4 = MgNH_4PO_4 + Na_2SO_4 + H_2O$$

If other metals are present, they are first removed by successive treatment with hydrogen sulphide in acid solution, ammonium sulphide, and ammonium carbonate

## 20 CALCIUM Ca = 40 07

**Occurrence of calcium.**—Metallic calcium is not found in nature, but its oxide, which forms nearly 5% of the solid crust of the earth, is only less abundant than silica, alumina, and the oxides of iron The chief mineral is the carbonate, which occurs in two crystalline forms as ARAGONITE and as CALCITE or ICELAND SPAR, and in more massive forms as MARBLE, CHALK and LIMESTONE The double carbonate, DOLOMITE, $MgCO_3,CaCO_3$, is the chief constituent of some mountain ranges Other important minerals are GYPSUM, $CaSO_4,2H_2O$, FLUORSPAR, $CaF_2$, APATITE, $3Ca_3(PO_4)_2,CaF_2$, DIOPSIDE, $CaMg(SiO_3)_2$ and LIME-FELSPAR, $CaAl_2Si_2O_8$

**Preparation of metallic calcium** —Metallic calcium is now manufactured by electrolysing a fused mixture of calcium chloride and calcium fluoride at a temperature of about 700° The product contains about 99% of calcium, the remaining 1% being made up of silicon, aluminium and iron

The anode is of carbon, and the cathode is an iron rod, which is drawn up as the calcium is deposited upon it, in order to prevent the calcium from melting in the bath The metal is isolated in the solid state because the liquid is not light enough to float satisfactorily on molten calcium chloride Calcium fluoride (m.p 1378°) is added to the calcium chloride (m p 774°) in order to lower its freezing-point, which would otherwise be too near to that of the metal (m p 800°) to allow of easy electrolysis of the molten salt without also melting the metal The eutectic mixture of the two salts freezes at 644°, and thus gives a range of about 150° for the temperature of electrolysis

**Properties of metallic calcium.**—Calcium is a grey-white malleable metal and is about as hard as tin It burns in air, forming the oxide and a little **calcium nitride**, $Ca_3N_2$ When heated in hydrogen it rapidly forms **calcium hydride** $CaH_2$ It combines with carbon, forming **calcium carbide**, $CaC_2$, so that the metal cannot be prepared from the oxide by reduction with carbon It tarnishes gradually in moist air and decomposes water in the cold, with evolution of hydrogen

$$Ca + 2H_2O = Ca(OH)_2 + H_2$$

Since, when heated, it absorbs all the gases of the atmosphere except the inert gases, it has been used to obtain high vacua and in the preparation of argon, it is also used in metallurgy for improving castings by absorbing air from them. Metallic calcium can be used instead of lime as a drying agent in preparing absolute alcohol, the manufacture of calcium hydride also involves the use of the metal.

## Compounds of Calcium

**Calcium hydride**, $CaH_2$, is prepared by the direct absorption of hydrogen by metallic calcium at 350°. The hydride is a colourless or grey solid, of density 1·7, which retains the form of the metal from which it was prepared. It is decomposed rapidly by water, giving slaked lime and hydrogen

$$CaH_2 + 2H_2O = Ca(OH)_2 + 2H_2$$

Owing to the large yield of hydrogen, viz. 4 parts per 42 parts of calcium hydride, this compound has been used for preparing hydrogen for balloons (cf. p. 71). Calcium hydride combines with carbon dioxide to give calcium formate (p. 715)

$$CaH_2 + 2CO_2 = Ca(O\,CO\,H)_2$$

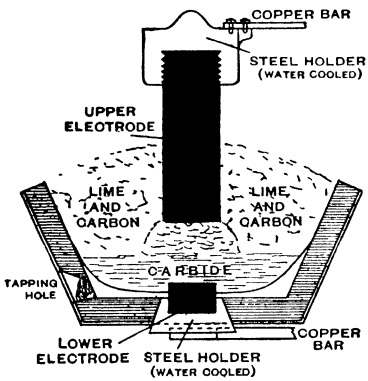



Fig. 23. Electric Furnace for Preparation of Calcium Carbide

**Calcium nitride**, $Ca_3N_2$, is formed by heating calcium at a dull red heat in a stream of nitrogen gas. It is decomposed by water, giving calcium hydroxide and ammonia

$$Ca_3N_2 + 6H_2O = 3Ca(OH)_2 + 2NH_3.$$

**Calcium carbide**, $CaC_2$, is manufactured on a large scale by heating a powdered mixture of coke and lime in an electric furnace (Fig. 23)

$$CaO + 3C = CaC_2 + CO.$$

The product is drawn off and cast at a temperature of about 1800°. It is decomposed by water, forming slaked lime and **acetylene** (p. 674):

$$CaC_2 + 2H_2O = Ca(OH)_2 + C_2H_2$$

The latter is the starting point for the commercial synthesis of **acetaldehyde** $C_2H_4O$, and **acetic acid**, $C_2H_4O_2$ (p. 709). Calcium carbide combines with nitrogen at a temperature of about 1000° (or at about 700° in the presence of fluoride or chloride), to form **calcium cyanamide**, $CaCN_2$:

$$CaC_2 + N_2 = CaCN_2 + C.$$

Calcium cyanamide liberates ammonia slowly in the soil,

$$CaCN_2 + 3H_2O = CaCO_3 + 2NH_3,$$

and therefore finds application as a fertiliser. The same decomposition has been developed on a large scale for the manufacture of ammonia (p. 181).

**Calcium oxide or quicklime**, CaO —(*a*) *Preparation* —Pure lime is prepared in the laboratory by igniting calcium carbonate or calcium nitrate. The decomposition of the carbonate is a reversible action

$$CaCO_3 \rightleftharpoons CaO + CO_2 - 42{,}000 \text{ cal}$$

Below 500° C the DISSOCIATION PRESSURE of the carbonate is insignificant, but it rises to about 1/10 atmosphere at 750° and to 1 atmosphere at about 900° In order to decompose it in a retort, or similar vessel, the carbonate must be heated nearly to 1000°, when the dissociation pressure of the system (p 540) is sufficient to drive back the atmosphere (compare the boiling of water) The decomposition can, however, be brought about

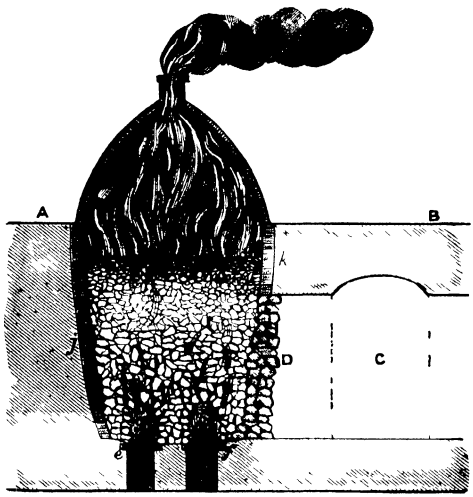



FIG 24 LIME-KILN

*AB* Roof *C* Arch through which lime is removed *D* Side-opening, closed with lumps of chalk and lime-dust *cd*, ashpits, *e*, *f*, fire bars, *g*, *h*, burning fuel, *j*, *k*, firebrick lining

at a much lower temperature by sweeping away the carbon dioxide in a current of air or gas (compare the evaporation of water), and this is the method used industrially for burning chalk to lime Formerly, lime was prepared by burning LIMESTONE over a coal fire as depicted in Fig 24, but shaft kilns or rotary kilns are now in general use Details and a diagram of a shaft kiln are given under carbon dioxide, pp 144-145 The rotary kiln is fired by producer gas or oil, and is advantageous in that it can be made to give a larger output than the shaft kiln, and is not clogged like the latter by small pieces of limestone

(*b*) *Physical properties of lime* —Lime is a white solid of density 3 30 It is generally obtained in large lumps, corresponding in shape with the rough limestone from which it was prepared It is very infusible and gives a brilliant white LIMELIGHT when heated in an oxyhydrogen flame (p 153)

(*c*) *Chemical properties of lime.*—Lime combines readily with chlorine to form bleaching powder, $CaOCl_2$, $H_2O$, with carbon dioxide to form chalk, $CaCO_3$, and with sulphur dioxide to form calcium sulphite, $CaSO_3$, but it is quite unaffected by these gases when they are carefully dried In the same way dry hydrogen chloride does not attack dry lime, although it is readily absorbed in presence of moisture, giving rise to calcium chloride and water ·

$$CaO + 2HCl = CaCl_2 + H_2O$$

When quicklime is sprinkled with water it becomes intensely hot, steam is given off, and a fine powder, consisting of calcium hydroxide, $Ca(OH)_2$, is formed, even if the lime was originally in lumps

$$CaO + H_2O = Ca(OH)_2 + 15{,}000 \text{ calories}$$

This process is known as SLAKING and the product as SLAKED LIME

**Uses of lime.**—Quicklime is used in the laboratory for drying alcohol, and was used formerly in the production of "limelight" (p 153) Slaked lime is used for the manufacture of bleaching powder and of caustic soda (p 96), in the recovery of ammonia in the ammonia-soda process, in the purification of coal gas and sugar, in glass-making, and in the production of mortar and cement

(i) *Mortar* is made by mixing slaked lime with sand (3 or 4 parts) and water so as to give a thick paste It sets by loss of water, after it has been put into position between the bricks of the building in which it is used After setting, it gradually hardens by absorbing carbon dioxide, whereby the calcium hydroxide is converted into calcium carbonate

(ii) *Portland cement* is made by heating chalk or limestone with clay, and grinding the resulting "clinker" into a fine powder When mixed with water, it sets in the course of a few hours to a solid mass, which grows steadily harder during a period extending over several years The SETTING depends on the hydrolysis of the calcium aluminates and silicates formed during burning The exact mechanism is not yet known, but it is possible that the products of hydrolysis separate in interlocking crystals, thus giving rise to the strength of the cement

(iii) *Concrete* is made by mixing Portland cement with sand, gravel, etc The tensile strength of concrete can be increased very greatly by allowing it to set round a skeleton of steel rods This combination is known as REINFORCED CONCRETE, and is one of the most economical materials for the construction of bridges, buildings, etc

**Calcium hydroxide**, $Ca(OH)_2$, is formed by the addition of water to quicklime It dissolves in 440 parts of water at 15° and in 1700 parts of water at 80° The solution is known as LIME-WATER, and is used as a test for carbon dioxide

**Calcium peroxide**, $CaO_2$, is prepared by adding a solution of hydrogen peroxide to lime-water. It is precipitated as a crystalline powder having the composition of an **octahydrate**, $CaO_2,8H_2O$ Strontium and barium form similar hydrated peroxides which are prepared in the same way

**Calcium carbonate**, $CaCO_3$, is dimorphous, in the forms of CALCITE and ARAGONITE It is almost insoluble in water, but it dissolves to the extent of 1 1 grams per litre in the presence of carbon dioxide, owing to the

formation of the much more soluble **calcium bicarbonate,** giving rise to "temporary hardness" (p 76)

$$CaCO_3 + CO_2 + H_2O = Ca(O\,CO\,OH)_2 \text{ (Calcium bicarbonate)}$$

The formation of STALACTITES on the roof and STALAGMITES on the floor of caves is due to the precipitation of calcium carbonate, brought about by loss of carbon dioxide from hard water containing calcium bicarbonate

**Calcium fluoride**, $CaF_2$, unlike the other halogen salts of calcium, is insoluble in water It occurs as FLUORSPAR in cubic crystals which often show a violet "fluorescent" colour

**Calcium chloride**, $CaCl_2$, can be prepared by dissolving lime or chalk in dilute hydrochloric acid, it is also produced in immense quantities as a by-product in the Solvay process (p 101) It is very soluble in water, and separates from aqueous solutions as the **hexahydrate,** $CaCl_2,6H_2O$ This compound melts at 30° and deliquesces in moist air, but in the very dry air of a Canadian winter it is efflorescent When heated strongly, it loses water and (unlike magnesium chloride) gives the anhydrous salt without hydrolysis The anhydrous salt is used as a dehydrating agent in the laboratory, but cannot be used for drying ammonia or alcohol owing to the formation of the compounds, $CaCl_2,8NH_3$ and $CaCl_2,4C_2H_6O$ It is also soluble in alcohol

**Calcium nitrate,** $Ca(NO_3)_2$, was formerly manufactured on a large scale by the action of dilute nitric acid (formed by the action of an electric discharge in air) on limestone It was also manufactured (as an intermediate stage in the preparation of ammonium nitrate from ammonium sulphate, p 186) by double decomposition of calcium chloride and sodium nitrate

$$CaCl_2 + 2NaNO_3 = Ca(NO_3)_2 + 2NaCl$$

The sodium chloride was crystallised out from the hot solution and the calcium nitrate from the cold solution, after diluting to prevent further separation of salt Like the other nitrates of the alkaline earths it is decomposed by heat to give the oxide

$$2Ca(NO_3)_2 = 2CaO + 4NO_2 + O_2$$

With excess of lime it forms a basic nitrate, $Ca(OH)_2,Ca(NO_3)_2$, which is used in preference to the normal nitrate as a fertiliser as it is less deliquescent (see p 539)

**Calcium sulphide**, CaS, which was formerly produced in very large quantities as a by-product in the Leblanc process, may be prepared by heating calcium sulphate with powdered coke

$$CaSO_4 + 4C = CaS + 4CO$$

It is only sparingly soluble in water, in which it is partially hydrolysed to the hydrosulphide,

$$2CaS + 2H_2O \rightleftharpoons Ca(OH)_2 + Ca(SH)_2,$$

but it is too soluble to be precipitated by ammonium sulphide in Group 5 (p 383) In the impure state it has the remarkable property of becoming phosphorescent after a short exposure to bright sunlight It is used in the

tanning industry to remove hair from hides and is a common constituent of hair-removers

**Calcium sulphate**, $CaSO_4$.—Calcium sulphate occurs as ANHYDRITE, $CaSO_4$, and GYPSUM, $CaSO_4,2H_2O$. It is sparingly soluble in water and has a maximum solubility of 0·21% at 38°. When gypsum is heated, it loses water and forms the **half-hydrate**, $CaSO_4,\frac{1}{2}H_2O$, or $2CaSO_4,H_2O$. This half-hydrate is the chief constituent of PLASTER OF PARIS, so called because it was first manufactured at the quarries of Montmartre near Paris.

When made into a paste with a little water, plaster of Paris sets in a few minutes to a firm mass, which gradually hardens with expansion; it is therefore used largely for making casts. The final product has the same composition, $CaSO_4,2H_2O$, as the original gypsum, but the setting is a more complex change than the mere reversal of the dehydration of the salt. Thus, when gypsum, which is a **monosymmetric dihydrate** of the formula, $CaSO_4,2H_2O$, is heated, it first changes into an **orthorhombic dihydrate**, $CaSO_4,2H_2O$, which loses water and gives a rhombohedral half-hydrate:

$$\underset{\text{Gypsum (monosymmetric)}}{CaSO_4,2H_2O} \overset{\text{HEATING}}{\underset{\text{SETTING}}{\rightleftharpoons}} \underset{\text{Orthorhombic dihydrate}}{CaSO_4,2H_2O} \overset{\text{HEATING}}{\underset{\text{SETTING}}{\rightleftharpoons}} \underset{\text{Half-hydrate (rhombohedral)}}{CaSO_4,\tfrac{1}{2}H_2O}$$

When the plaster is mixed with water, the half-hydrate, which is soluble to the extent of about 1·2 grams per 100 c.c., passes into solution and the orthorhombic dihydrate separates as a mass of small needles until the whole of the half-hydrate has disappeared. The orthorhombic form of the dihydrate being more soluble than the monosymmetric form is then converted more slowly into ordinary gypsum. This second change is accompanied by an expansion, which is of value in ensuring that the plaster fills the mould completely. The solid product is held together by small interlacing crystals which have separated from a solution saturated with a metastable form, and therefore supersaturated as regards the stable form, of the sulphate.

**Estimation of Calcium.**—Calcium may be estimated by precipitating the oxalate, which is almost insoluble in water; it is then dissolved in dilute sulphuric acid, and the free oxalic acid estimated by titration with standard permanganate (p. 428). Alternatively, the calcium oxalate can be collected, in a weighed Gooch crucible, ignited and weighed as the carbonate or oxide

$$CaC_2O_4 \rightarrow CaCO_3 + CO.$$

## 38. STRONTIUM. Sr = 87·63

The most important sources of strontium are CELESTINE, $SrSO_4$, and STRONTIANITE, $SrCO_3$. The element is intermediate between calcium and barium in nearly all its properties, including those of its compounds, but is characterised by the crimson colour of its flame.

**Strontium oxide**, SrO, prepared by heating the carbonate or nitrate, is a white powder which combines vigorously with water to form the hydroxide.

**Strontium hydroxide**, $Sr(OH)_2$, is more soluble in water than lime, but

less soluble than baryta It is used in extracting cane-sugar from molasses which will no longer deposit crystals of sugar

**Strontium nitrate**, $Sr(NO_3)_2$, is used in fireworks on account of the red colour which it produces

**Strontium sulphate**, $SrSO_4$, is less soluble than calcium sulphate, but is sufficiently soluble to precipitate barium sulphate from solutions of barium chloride or nitrate In estimating strontium, the sulphate is precipitated in presence of alcohol, which lowers its solubility

## 56 BARIUM Ba = 137 36

The most important sources of barium are BARYTES, $BaSO_4$, and WITHERITE, $BaCO_3$ The element can be prepared by the electrolysis of the fused chloride or by distilling the oxide with aluminium It is a silver-white metal of density 3 78, melts at 850° and can be distilled at slightly higher temperatures It burns to the monoxide, BaO, and decomposes water, forming the hydroxide When heated in hydrogen the **hydride**, $BaH_2$, is formed

**Barium oxide**, BaO, is only formed from the carbonate by heating to extremely high temperatures, but is readily produced by heating it with charcoal

$$BaCO_3 + C = BaO + 2CO$$

It is a white infusible powder, which melts, however, at a lower temperature than CaO

**Barium peroxide**, $BaO_2$, is produced when the monoxide is heated to 500° in air It was at one time of importance as an intermediate product in the preparation of oxygen from air by Brin's process (p 231) The **octahydrate**, $BaO_2, 8H_2O$, crystallises out when hydrogen peroxide is added to a cold saturated solution of barium hydroxide (compare $CaO_2, 8H_2O$)

**Barium hydroxide**, $Ba(OH)_2$, is produced by dissolving the oxide in hot water,

$$BaO + H_2O = Ba(OH)_2 + 23{,}000 \text{ cal},$$

compare

$$SrO + H_2O = Sr(OH)_2 + 19{,}000 \text{ cal},$$

$$CaO + H_2O = Ca(OH)_2 + 15{,}000 \text{ cal}$$

It is manufactured by heating barium sulphate with carbon to form the sulphide, converting this into the carbonate by the action of a current of moist carbon dioxide, and then into the hydroxide by the action of superheated steam

$$BaSO_4 + 4C = BaS + 4CO,$$

$$BaS + CO_2 + H_2O = BaCO_3 + H_2S,$$

$$BaCO_3 + H_2O = Ba(OH)_2 + CO_2$$

Like lime, it dissolves in water, forming a strongly alkaline solution, which is known as BARYTA WATER, thus, 100 grams of a saturated solution contain at 20°

0 123 grams CaO, or 0 16 grams $Ca(OH)_2$,
0 69 ,, SrO, or 1 8 ,, $Sr(OH)_2, 8H_2O$,
3·36 ,, BaO, or 6·9 ,, $Ba(OH)_2, 8H_2O$

Since barium hydroxide is a stronger base than lime or strontia, and only inferior to the caustic alkalis, baryta water is used in analysis when a strong alkali free from carbonate is required

**Barium carbonate,** $BaCO_3$, occurs as WITHERITE It resembles chalk, but is more stable towards heat When heated with carbon, it yields baryta and carbon monoxide

$$BaCO_3 + C = BaO + 2CO$$

**Barium chloride**, $BaCl_2$, is prepared from the carbonate or sulphide by the action of hydrochloric acid It crystallises from solution as the **dihydrate,** $BaCl_2, 2H_2O$, but it is not deliquescent like calcium chloride It is used as a reagent in the laboratory for testing for sulphates

**Barium sulphate**, $BaSO_4$, occurs as BARYTES or HEAVY SPAR, in massive veins and is mined in very large quantities, the annual output being more than 300,000 tons It is practically insoluble in water, only 2 3 mg dissolving in 1 litre at 18° Finely ground barytes is used instead of white lead as a basis for paints , it has the advantage of not being blackened by hydrogen sulphide, but has less " covering power " than white lead It is also used for weighting rubber and paper, and for many other purposes

**Barium sulphide**, BaS, is prepared by reducing barium sulphate with coke or coal Like crude calcium sulphide, the anhydrous compound is phosphorescent It dissolves readily in water, forming the hydroxide and hydrosulphide,

$$2BaS + 2H_2O = Ba(OH)_2 + Ba(SH)_2,$$

but under special conditions it can be crystallised out as an unstable **hexahydrate,** $BaS,6H_2O$ It is used in the preparation of barium salts from barytes and in making LITHOPONE (p 334), a mixture of zinc sulphide and barium sulphate, prepared for use as a paint by the interaction of barium sulphide and zinc sulphate,

$$BaS + ZnSO_4 = ZnS + BaSO_4$$

**Barium nitrate**, $Ba(NO_3)_2$, is prepared by dissolving witherite in hot nitric acid, and evaporating the solution to the crystallising point It can also be prepared by the action of dilute nitric acid on barium sulphide, or by mixing hot solutions of barium chloride and sodium nitrate, when barium nitrate separates in crystals on cooling It is sparingly soluble in water , a saturated solution contains 8 per cent of barium nitrate at 20° as compared with 26 per cent of barium chloride It is used in pyrotechny to produce a green fire, and in the preparation of certain explosives

**Estimation of barium.**—Barium salts are estimated by precipitating the sulphate from a boiling solution with dilute sulphuric acid, and then washing the precipitate with plenty of hot water If the precipitation is carried out in the cold, a semi-colloidal precipitate is formed which cannot be filtered easily

# CHAPTER XIII

## BORON AND ALUMINIUM

**Classification.**—Boron, with atomic number $Z = 5$, is placed at the head of the third column of Mendeléeff's table, immediately above aluminium, but it bears only a very remote resemblance to aluminium, and a very close resemblance to silicon. This diagonal relationship recalls the analogy between lithium and magnesium, and between beryllium and aluminium. It appears that in the pairs of ions,

$$Li^{+} \text{ and } Mg^{++}, \qquad Be^{++} \text{ and } Al^{+++}, \qquad B^{+++} \text{ and } Si^{++++},$$

the additional charge on the heavier nucleus is balanced by the additional size of the ion, so that its affinity for electrons is nearly the same. On the other hand, the affinity for electrons increases steadily in the series Li, Be, B, and Mg, Al, Si, so that the elements in each series become progressively less metallic and more like the typical non-metals. Thus

(i) *Lithium* and *magnesium* form chlorides, LiCl and $MgCl_2$, which are salt-like in character and may be regarded as ionic aggregates of the same type as NaCl or KCl.

(ii) *Beryllium* and *aluminium* form chlorides which behave as salts in aqueous solutions, but are readily vaporised. Since ionised salts like NaCl are not easily vaporised, on account of the electrostatic forces between the ions, we may conclude that beryllium and aluminium chlorides are covalent compounds, which are ionised, and not merely dissociated, by the action of water in aqueous solutions (compare mercuric chloride, p. 340).

(iii) *Boron and silicon* are metals, with a steely lustre and marked electrical conductivity, but in combination with other elements they behave as non-metals, since (like carbon) they do not form simple ions, either positive or negative, and are therefore covalent in all their common compounds.

**Properties of boron, silicon and aluminium.**—The properties of boron may be compared and contrasted with those of silicon and aluminium with the help of Table 9.

TABLE 9.—PROPERTIES OF SILICON, BORON AND ALUMINIUM

| | SILICON | BORON | ALUMINIUM |
|---|---|---|---|
| **Physical properties** | Steel-grey metals | | Silver-grey metal |
| Density | 2 5 | 2 6 | 2 7 |
| Melting-point | 1420° | 2200° ? | 658° |
| **Valency** | 4 | 3 or 4 | 3 |
| **Chemical properties.** | | | |
| Action of oxygen | Burns in air to $SiO_2$ | Burns in air to $B_2O_3$ and BN | Burns in air to $Al_2O_3$ |
| Action of alkalis | Soluble with liberation of hydrogen | | |
| Action of acids | Soluble only in HF and $HNO_3$ | Soluble in oxidising acids | Soluble in HCl, insoluble in $HNO_3$ |
| Behaviour with metals | Forms silicides, $MnSi$, $MnSi_2$, $Ni_2Si$, etc | Forms borides, MnB, $Ni_2B$, $NiB_2$, etc | Forms light alloys |
| **Compounds.** | All covalent | | Salts may be ionised |
| Hydrides | $SiH_4$, $Si_2H_6$, etc | $B_2H_6$, etc | None |
| Fluorides | Gaseous, hydrolysed by water $3SiF_4 + 4H_2O = 2H_2SiF_6 + Si(OH)_4$ $4BF_3 + 3H_2O = 3HBF_4 + B(OH)_3$ | | Insoluble solid like $CaF_2$ |
| Chlorides. | Liquids hydrolysed by water $SiCl_4 + 4H_2O = Si(OH)_4 + 4HCl$ $BCl_3 + 3H_2O = B(OH)_3 + 3HCl$ | | Volatile solid, ionised and partially hydrolysed by water |
| | Boils at 58° | Boils at 18° | Sublimes at 183° |
| Hydroxides | Acidic | Acidic | Amphoteric |

## 5 BORON B = 10 82

**Occurrence.**—**Sodium borate** in the form of BORAX, $Na_2B_4O_7,10H_2O$, occurs in alkaline lakes in California and elsewhere Free **boric acid**, $H_3BO_3$, is found in the hot springs or " fumaroles " of Tuscany, in which volcanic vapours are condensed, since ammonia is also found, as **ammonium borate** $(NH_4)_2B_8O_{13},4H_2O$, it has been suggested that the acid is formed by hydrolysis of the nitride

$$BN + 3H_2O = B(OH)_3 + NH_3$$

**Preparation and properties.**—Elementary boron is prepared by similar methods to those used in making silicon, namely

(i) By the action of potassium or magnesium on potassium borofluoride

$$3K + KBF_4 = 4KF + B$$

(ii) By the action of potassium, sodium, magnesium or aluminium on the oxide

$$B_2O_3 + 2Al = Al_2O_3 + 2B$$

The amorphous product which is obtained by the above methods is purified by extracting with hydrochloric acid and then heating to 1200° in a vacuum After melting in an electric arc in an atmosphere of

ıydrogen, the element ıs obtaıned as a hard steel-grey metal of high neltıng-poınt, lıke sılıcon, from whıch ıt dıffers ın burnıng to a nıtrıde ıs well as to an oxıde, and ın ıts solubılıty ın dılute nıtrıc and strong ,ulphurıc acıds It dıssolves ın alkalıs to form a borate

$$2B + 2KOH + 2H_2O = 2KBO_2 + 3H_2$$

The element forms metallıc borıdes, whıch resemble the metallıc sılıcıdes ınd have sımılar formulae, ın spıte of a dıfference ın the ordınary valency )f the two elements

**Boron hydrıdes.**—Several hydrıdes ot boron have been prepared by the ıctıon of dılute hydrochlorıc acıd on magnesıum borıde, and can be ,eparated by lıquefactıon and subsequent dıstıllatıon They show a very ·lose resemblance to those of carbon ın theır physıcal propertıes, *e g*

| | |
|---|---|
| $B_2H_6$ boıls at $-92°$ | $B_4H_{10}$ boıls at $+18°$ |
| $C_2H_6$ boıls at $-93°$ | $C_4H_{10}$ boıls at $+16°$ |

The boron ın these compounds appears to be quadrıvalent




Each atom of boron, however, has one electron less than an atom of carbon, and the defıcıency of two electrons ın $B_2H_6$ as compared wıth $C_2H_6$ presents a problem whıch ıs stıll not completely solved The sımple hydrıde, $BH_3$, does not appear to exıst

These hydrıdes are much more actıve than the correspondıng hydrocarbons, *e g* they are readıly hydrolysed by water gıvıng hydrogen and borıc acıd

$$B_2H_6 + 6H_2O = 2H_3BO_3 + 6H_2$$

**Boron trıfluorıde**, $BF_3$, can be prepared ın a sımılar way to sılıcon tetrafluorıde, $SiF_4$, by heatıng a mıxture of borıc oxıde and fluorspar wıth concentrated sulphurıc acıd

$$B_2O_3 + 3CaF_2 + 3H_2SO_4 = 2BF_3 + 3CaSO_4 + 3H_2O$$

It ıs a colourless gas (m p $-127°$, b p $-101°$), whıch fumes ın moıst aır, and chars organıc compounds by removıng water from them. It does not attack glass dırectly, but parts wıth ıts fluorıne to sodıum and potassıum, whıch burn brılhantly ın the gas Lıke sılıcon tetrafluorıde, ıt combınes wıth gaseous ammonıa, formıng compounds such as $BF_3,NH_3$

When decomposed by water ıt gıves borıc acıd and **borofluorıc acıd**, $HBF_4$, compare sılıcıfluorıc acıd, $H_2SiF_6$

$$4BF_3 + 3H_2O = 3HBF_4 + B(OH)_3,$$

compare
$$3SiF_4 + 4H_2O = 2H_2SiF_6 + Si(OH)_4$$

Thıs acıd gıves a serıes of borofluorıdes, cbrrespondıng wıth the sılıcı-

fluorides, *e g* **sodium borofluoride,** $NaBF_4$, is formed by bringing together sodium hydrogen fluoride and boric acid

$$2NaHF_2 + B(OH)_3 = NaBF_4 + NaOH + 2H_2O$$

The remarkable stability of the borofluoride is indicated by the fact that in this action two acid solutions interact to form a liquid which is strongly alkaline

**Boron trichloride**, $BCl_3$, prepared by the action of chlorine on boron, melts at $-104°$ and boils at $18°$ Like phosphorus trichloride, it is decomposed by water, as shown in the equation

$$BCl_3 + 3H_2O = H_3BO_3 + 3HCl,$$

compare

$$PCl_3 + 3H_2O = H_3PO_3 + 3HCl$$

**Boric oxide**, $B_2O_3$, is prepared by heating boric acid at a red heat

$$2H_3BO_3 = B_2O_3 + 3H_2O$$

It is a glassy solid, which recombines with water to form boric acid and dissolves in alkalis to form borates , but it also acts as a weak base, since it interacts in solution with phosphoric acid to give **boron phosphate,** $BPO_4$, which (like aluminium phosphate) is insoluble in water and dilute acids but soluble in alkalis

**Boric acid**, $H_3BO_3$, is prepared by adding concentrated hydrochloric acid to a hot saturated solution of borax , on cooling, boric acid separates in crystals

$$Na_2B_4O_7 + 2HCl + 5H_2O = 2NaCl + 4H_3BO_3$$

Boric acid is a valuable antiseptic, and was formerly used for preserving food It is sparingly soluble in cold water but dissolves freely in hot water It is a weak acid and its salts are therefore hydrolysed by water In presence of an excess of glycerol (with which it interacts to form a strong monobasic acid) it can be titrated with sodium hydroxide, phenolphthalein being used as an indicator

$$NaOH + H_3BO_3 = NaBO_2 + 2H_2O$$

Like phosphoric acid it yields a **pyroboric acid,** $H_2B_4O_7$, and **metaboric acid,** $HBO_2$, with corresponding series of salts

**Sodium pyroborate**, $Na_2B_4O_7,10H_2O$, in the form of BORAX, is the principal source of the element , but it can also be prepared from native calcium salts by boiling with sodium carbonate solution for a few hours, and then passing in carbon dioxide The **decahydrate,** $Na_2B_4O_7,10H_2O$, crystallises from aqueous solutions When heated it loses water, and forms a voluminous white mass, which on further heating melts to a colourless glass Although it contains a large excess of boric acid, it is alkaline in solution, owing to hydrolysis

$$Na_2B_4O_7 + 3H_2O \rightleftharpoons 2H_3BO_3 + 2NaBO_2,$$
$$NaBO_2 + 2H_2O \rightleftharpoons NaOH + H_3BO_3$$

It may be titrated against hydrochloric acid, if methyl orange is used as the indicator

The presence of an excess of boric acid accounts for the fact that molten borax dissolves metallic oxides and is therefore used as a flux in soldering The colours produced in " borax beads " (*e g* CuO blue, $Cu_2O$ red, $MnO_2$ violet) are used in qualitative analysis for the detection of certain metals (p 397) Borax is used in the manufacture of optical and hard glass and in preparing glazes , it is also used in laundering, on account of its cleansing properties and because it imparts a gloss to linen on ironing

## 13 ALUMINIUM Al = 26 97

**Occurrence of aluminium** —After silicon and oxygen, aluminium is the most abundant element in the solid crust of the earth, which contains 15% of alumina, $Al_2O_3$ This is present mainly in the form of **alumino-silicates,** such as FELSPAR, $NaAlSi_3O_8$, $KAlSi_3O_8$ or $CaAl_2Si_2O_8$ in igneous rocks, and as CLAY, $H_4Al_2Si_2O_9$, in sedimentary rocks The metal, which is not found in the free state, is prepared from the **hydrated oxide,** BAUXITE, $Al_2O_3,2H_2O$, and the **double fluoride,** CRYOLITE, $Na_3AlF_6$ The **anhydrous oxide,** $Al_2O_3$, also occurs as CORUNDUM or EMERY, and as a gem-stone in the form of SAPPHIRE (blue) and RUBY (red)

**Manufacture of aluminium** —No cheap method has yet been discovered for preparing aluminium from the very abundant aluminosilicates It was formerly prepared by converting the oxide into chloride by the combined action of charcoal and chlorine, and then reducing the double chloride, $NaAlCl_4$, with sodium

$$3Cl_2 + Al_2O_3 + 3C = 2AlCl_3 + 3CO, \qquad NaAlCl_4 + 3Na = 4NaCl + Al$$

At the present time aluminium is manufactured by the electrolysis of a fused mixture of cryolite, $Na_3AlF_6$, and pure alumina, $Al_2O_3$ The latter is prepared from the mineral bauxite, $Al_2O_3,2H_2O$, which contains impurities, such as oxide of iron and silica , these must be removed before the electrolytic process, otherwise the resulting aluminium contains iron and silicon, and is readily attacked by water

The bauxite is freed from silica, $SiO_2$, and oxides of iron by heating to bright redness with sodium carbonate, when sodium aluminate, $NaAlO_2$, is produced The product is extracted with water, when a solution of sodium aluminate and sodium silicate is obtained, whilst the oxide of iron is left undissolved Aluminium hydroxide, $Al(OH)_3$, but not silica, is precipitated from the solution by passing carbon dioxide into it at 60° and is ignited to the oxide

$$2NaAlO_2 + 3H_2O + CO_2 = Na_2CO_3 + 2Al(OH)_3$$

The sodium carbonate is recovered from the solution and used over again Alternatively the bauxite may be digested with aqueous caustic soda under pressure, and the aluminium oxide precipitated from the solution of sodium aluminate by mere contact with the ordinary insoluble form of alumina The precipitate is then ignited to give the anhydrous oxide

The electrolysis is carried out in an iron box lined with carbon (Fig 25), which serves as the cathode, and is provided with a series of carbon anodes A mixture of alumina (20 parts), and cryolite (80 parts) is used, with a little fluorspar, $CaF_2$ (7 parts) to lower the melting-point of the mixture

Aluminium is liberated by the electric current and sinks to the bottom of the bath, whilst the expensive carbon anodes are unavoidably burnt to oxides The electrical resistance generates sufficient heat to keep the cryolite liquid, but it increases as the alumina is used up, until at the end of about 2 hours more alumina is added to replace that which has been decomposed by the current

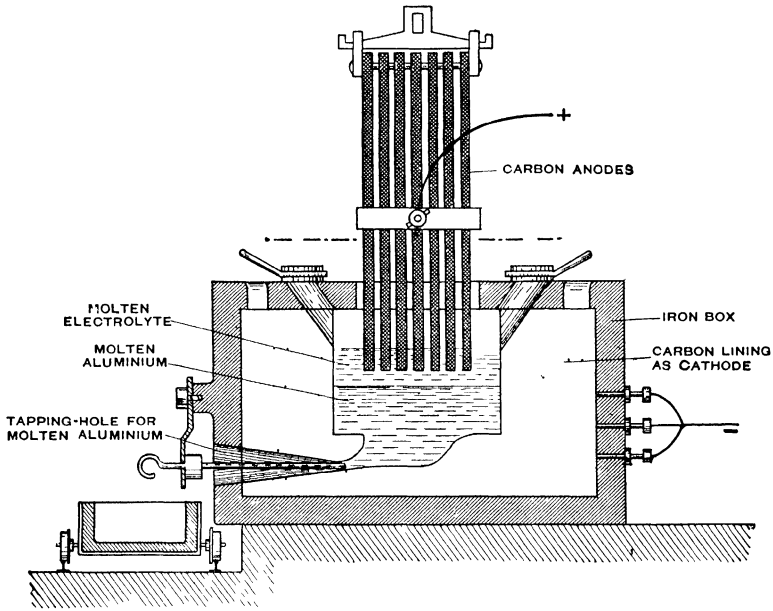



FIG 25 MANUFACTURE OF ALUMINIUM

The simplest interpretation of this action is to assume that the cryolite acts merely as a solvent for the bauxite, which is decomposed by the current according to the equation,

$$2Al_2O_3 = 4Al + 3O_2$$

It is, however, possible that the sodium salt is first decomposed by the current according to the equation,

$$Na_3AlF_6 = 3Na + AlF_6,$$

aluminium being set free by the secondary action of the sodium upon the cryolite, whilst the $AlF_6$ radical attacks the bauxite and converts it into fluoride as shown in the equations,

$$3Na + Na_3AlF_6 = Al + 6NaF,$$
$$4AlF_6 + 2Al_2O_3 = 8AlF_3 + 3O_2$$

**Properties and uses of aluminium.**—(1) Aluminium is a light silvery-white metal of density 2 7, which melts at 658°, and can be drawn into wire or rolled into foil The latter is now used extensively in place of

tin foil for wrapping cigarettes, etc Large quantities of aluminium are used in the manufacture of cooking utensils, etc On account of its lightness, aluminium is used in the construction of parts of motor-cars, a light alloy, Duralumin (4% Cu, 0 5% Mn, 0 5% Mg) is used in the construction of aeroplanes The electric conductivity of aluminium is 60% of that of an equal volume of copper, or 200% for a conductor of equal weight, thus, although copper is almost always used for electric cables which have to be coated with an insulator, aluminium (often with a steel core, as in the British grid system) is frequently used for naked conductors

(ii) Aluminium has a very great affinity for oxygen, as may be seen by a comparison of the heats of formation of the following oxides

| | | |
|---|---|---|
| $MgO$ | 143,000 | calories |
| $\frac{1}{3}Al_2O_3$ | 127,000 | ,, |
| $Na_2O$ | 100,000 | ,, |
| $H_2O$ | 68,360 | ,, |
| $CO$ | 29,000 | ,, |

In spite of its large heat of oxidation, aluminium is not easily ignited and does not readily tarnish in air, since on exposure to air a coherent film of oxide is formed which protects the metal from further action If, however, the film is broken, *e g* by amalgamating with mercury, a feathery growth of oxide develops at once on the surface, and the metal becomes quite warm from the heat of oxidation

Owing to its great affinity for oxygen, aluminium is used to prepare metals (such as chromium) which cannot be easily prepared from the oxide by reduction with carbon, and for the preparation of molten metals *in situ* Thus, THERMITE is a mixture of aluminium filings and ferric oxide, which can be ignited by a strip of magnesium Molten iron can then be drawn off from the bottom of the mixture and used to weld a broken rail, etc, while the aluminium oxide forms an upper layer of slag

$$Fe_2O_3 + 2Al \rightarrow Al_2O_3 + 2Fe$$

Thermite is used for incendiary bombs, and ammonal, a mixture of ammonium nitrate and aluminium powder, has been used for explosive bombs

EXPT 11 **Thermite process**

Aluminium filings (one part) and powdered magnetic oxide of iron (three parts) are mixed together and placed in a Battersea crucible embedded in a box of sand A small hole is made in the centre of the mixture and filled with a mixture of magnesium powder and barium peroxide (1 3) A strip of magnesium is placed in this and ignited by means of a Bunsen burner The heat of ignition starts the thermite reaction and molten iron falls to the bottom of the crucible The experiment should be carried out in the fume chamber

(iii) Aluminium dissolves readily in hydrochloric acid, but is almost unaffected by dilute or concentrated nitric acid, it dissolves slowly in concentrated sulphuric acid, sulphur dioxide being evolved These results are explained by assuming that nitric acid coats the aluminium with a

protective layer of oxide For a similar reason water and air are without action on aluminium at ordinary temperature Aluminium dissolves rapidly in caustic alkalis, forming aluminates and liberating hydrogen, *e g*

$$2NaOH + 2Al + 2H_2O = 2NaAlO_2 + 3H_2$$

(iv) Aluminium combines directly with *chlorine* and *sulphur*, and with *nitrogen*, to form a **nitride**, AlN, which is decomposed by water with liberation of ammonia As in the case of calcium, a **carbide**, $Al_4C_3$, is formed when attempts are made to prepare the metal by reduction of the oxide with carbon The carbide is of interest because it gives methane and not acetylene when it interacts with water

$$Al_4C_3 + 6H_2O = 2Al_2O_3 + 3CH_4$$

(v) The compounds of aluminium, such as alum, are used extensively as pure products in dyeing and in the preparation of paints Emery, clay, bricks, porcelain, cement, and the hard igneous rocks used as road-metal and for building, consist very largely of alumina combined with silica and with oxides of other metals

## Compounds of Aluminium

**Aluminium oxide**, $Al_2O_3$, occurs naturally as CORUNDUM, $Al_2O_3$, DIASPORE, $Al_2O_3,H_2O$, and BAUXITE, $Al_2O_3,2H_2O$ The blue colour of the sapphire and the red colour of the ruby are due to traces of oxides of cobalt and chromium Synthetic rubies can be made by dropping powdered alumina containing about 2 5% of chromium sesquioxide through the centre of an oxyhydrogen flame and catching the fused mass on a rod of alumina Freshly precipitated aluminium oxide is readily soluble in dilute acids, but it is changed into an insoluble form by heating to about 900°

**Aluminium hydroxide**, $Al(OH)_3$, is one of the weakest of the metallic bases Although it is not precipitated from its salts by the addition of water, it is thrown down by ammonia even in the presence of ammonium chloride The feeble basicity of the hydroxide is further shown by the fact that it does not form a carbonate, so that carbon dioxide is set free when a carbonate is added to a solution of an aluminium salt such as alum

$$Al_2(SO_4)_3 + 3Na_2CO_3 + 3H_2O = 2Al(OH)_3 + 3Na_2SO_4 + 3CO_2$$

The hydroxide also behaves as a weak acid, since it dissolves in alkalis to form aluminates , but it is precipitated from these by the action of carbon dioxide or even by mere contact with its own stable form (p 129)

**Aluminium chloride**, $AlCl_3$, is formed when the metal or hydroxide is dissolved in hydrochloric acid, and may be crystallised out from solution as a **hexahydrate**, $AlCl_3,6H_2O$ The anhydrous chloride cannot be obtained from these crystals by heat alone, since hydrolysis takes place and alumina, $Al_2O_3$, is left It is therefore prepared by heating the metal in a stream of dry chlorine or hydrogen chloride, or by heating the oxide with carbon in a stream of chlorine

$$Al_2O_3 + 3C + 3Cl_2 = 2AlCl_3 + 3CO.$$

EXPT 12 **Preparation of aluminium chloride**

Chlorine, prepared by dropping concentrated hydrochloric acid on to crystals of permanganate, and dried by bubbling through concentrated sulphuric acid, is passed over heated aluminium turnings (about 15 grams) in a hard glass tube (Fig 26) This leads directly into a wide-mouthed bottle provided with a cork and a small exit tube for surplus chlorine Anhydrous aluminium chloride sublimes and collects in the bottle, which must be tightly corked at the end of the experiment to exclude moisture

Aluminium chloride is a white hygroscopic substance which fumes in the air owing to hydrolysis It melts at 190° under a pressure of two atmospheres, but vaporises at 183° under one atmosphere pressure, so that it

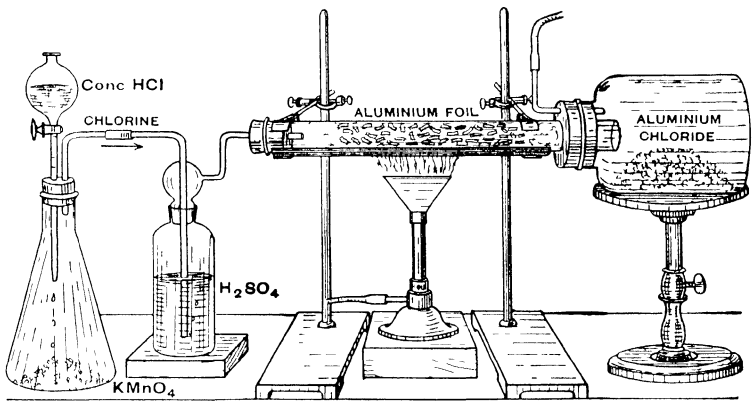



FIG 26 PREPARATION OF ALUMINIUM CHLORIDE

usually sublimes without melting Measurements of vapour density show that below 400° the chloride has the formula $Al_2Cl_6$, but that dissociation to $AlCl_3$ is complete at about 800° (cf $Fe_2Cl_6$, p 360)

Anhydrous aluminium chloride is very soluble in water and is hydrolysed to a small extent in solution It is a valuable catalyst in reactions involving the elimination of hydrogen chloride (p 775)

**Aluminium sulphide**, $Al_2S_3$, may be prepared by heating a mixture of sulphur and aluminium It is completely hydrolysed by water, so that, when an alkali sulphide is added to a solution of an aluminium salt, aluminium hydroxide and not aluminium sulphide is precipitated

$$2AlCl_3 + 3(NH_4)_2S + 6H_2O = 6NH_4Cl + 2Al(OH)_3 + 3H_2S,$$

**Aluminium sulphate**, $Al_2(SO_4)_3$, can be prepared by the action of hot concentrated sulphuric acid on the metal or on china clay .

$$2Al + 6H_2SO_4 = Al_2(SO_4)_3 + 3SO_2 + 6H_2O,$$
$$Al_2O_3,2SiO_2,2H_2O + 3H_2SO_4 = Al_2(SO_4)_3 + 2SiO_2 + 5H_2O.$$

It is very soluble in water and crystallises with $18H_2O$ The hydrate loses water when heated gently and forms the anhydrous salt , but when

heated to redness the sulphate decomposes into alumina, sulphur dioxide and oxygen

$$2Al_2(SO_4)_3 \rightarrow 2Al_2O_3 + 6SO_2 + 3O_2$$

It forms an important series of isomorphous ALUMS or double sulphates, $M^+M^{+++}(SO_4)_2, 12H_2O$, where $M^+$ is a univalent metal (or an ammonium radical) and $M^{+++}$ is a tervalent metal such as Al, Cr, Fe Thus **potash alum,** $K_2SO_4,Al_2(SO_4)_3,24H_2O$ or $KAl(SO_4)_2,12H_2O$, can be made by mixing hot solutions of potassium and aluminium sulphates, containing equimolecular quantities of the two sulphates, and setting aside to crystallise It can also be prepared by roasting the mineral ALUNITE,

$$K_2SO_4,Al_2(SO_4)_3,4Al(OH)_3,$$

and extracting with water, when potash alum goes into solution, whilst alumina is left behind

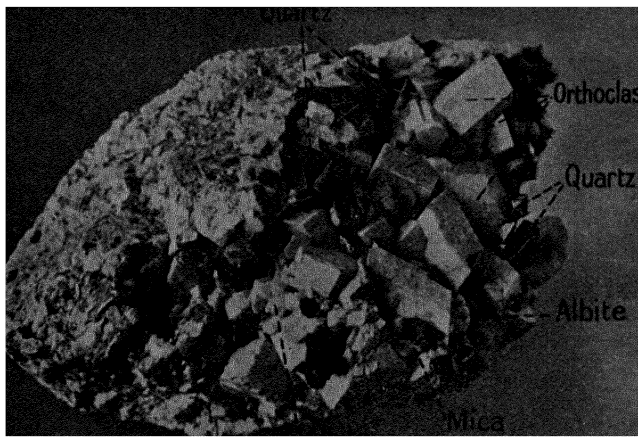



FIG 27 GRANITE (British Museum, Natural History)

Showing on the left hand the normal crystallisation and cleavage of the mass, and on the right hand larger crystals of smoky quartz (black) and orthoclase (grey), with smaller crystals of albite (white) and mica (black) which have grown into a cavity (About $\frac{5}{6}$ full size)

EXPT 13 **Preparation of potash alum**

Potash alum may be prepared from aluminium by heating 2 grams of aluminium foil with 50 c c of normal potassium hydroxide solution in a conical flask When no further action takes place, 50 c c of distilled water are added, and the mixture filtered to remove excess aluminium and insoluble impurities The solution is heated with 100 c c of $2N$ sulphuric acid until the precipitate of aluminium hydroxide, which is first formed, redissolves, it is then evaporated and left to crystallise

$$2Al + 2KOH + 2H_2O \rightarrow 2KAlO_2 + 3H_2,$$
$$2H_2O + 2KAlO_2 + H_2SO_4 \rightarrow K_2SO_4 + 2Al(OH)_3,$$
$$2Al(OH)_3 + 3H_2SO_4 \rightarrow Al_2(SO_4)_3 + 6H_2O$$

**Mordants.**—Potash alum is used extensively in the dye industry When materials are dyed, it is essential that the dye should adhere so firmly that it cannot be removed by washing Many dyes are incapable of doing this unless the material has been impregnated previously with a basic or acidic substance, called a MORDANT (Latin, *mordeo*, I bite) Thus alizarin will not bite on to cotton fabrics unless a mordant such as aluminium hydroxide is used This process, known as "mordanting," is often carried out by dipping the material in a solution of alum (or aluminium acetate) and then treating it with steam, or with sodium carbonate, to convert the alum on the threads into aluminium hydroxide The latter attaches itself to the fabric, and on immersion in the dye-bath reacts with the dye to form a coloured LAKE, so that it is held firmly Stannic acid and tannic acid are commonly used as acidic mordants for basic dye-stuffs Silk and wool do not require mordants

**Felspar and clay.**—The most important of the igneous rocks are the FELSPARS, *e g* ALBITE, $NaAlSi_3O_8$, ORTHOCLASE, $KAlSi_3O_8$, ANORTHITE, $CaAl_2Si_2O_8$ Thus GRANITE (Fig 27) is a coarsely-crystalline mixture of transparent quartz, black mica and white felspar, in which the crystals of felspar are often an inch or two in length When "weathered," the felspar is converted into KAOLINITE, the chief constituent of CHINA-CLAY ·

$$2KAlSi_3O_8 + CO_2 + 2H_2O = H_4Al_2Si_2O_9 + 4SiO_2 + K_2CO_3$$

The china-clay is separated by washing from a sediment, consisting chiefly of quartz and mica, and is used in the manufacture of porcelain Less pure forms of clay are used in making earthenware and bricks

# CHAPTER XIV

## CARBON AND SILICON

| | | | | | |
|---|---|---|---|---|---|
| | | 6 CARBON | C = 12 00. | | |
| | | 14 SILICON | Si = 28 06 | | |
| 22 | TITANIUM | Ti = 47 90 | 32 GERMANIUM | Ge = 72 60 | |
| 40 | ZIRCONIUM | Zr = 91 22 | 50 TIN | Sn = 118 70 | |
| 72 | HAFNIUM | Hf = 178 6 | 82 LEAD | Pb = 207 22 | |
| 90 | THORIUM | Th = 232 12 | | | |

**Classification.**—(*a*) *Carbon*, the central element of the first short period, lies midway between the inert gases, helium, $Z = 2$, and neon, $Z = 10$ It must therefore lose or gain *four* electrons in order to acquire the electronic configuration of an inert gas, but the ions, $C^{+4}$ and $C^{-4}$, are too unstable to exist under normal conditions, so that carbon is quadricovalent in nearly all of its compounds Thus methane, $CH_4$, and carbon tetrachloride, $CCl_4$, may be represented by the electronic formulae



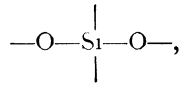
A striking feature of the chemistry of carbon is its ability to link up into long chains and rings, especially in combination with hydrogen, oxygen and nitrogen, in animal and vegetable products This is the principal justification for recognising a separate science of ORGANIC CHEMISTRY, in contrast to INORGANIC CHEMISTRY or MINERAL CHEMISTRY, which is concerned mainly with aggregates of ions, either simple or complex Calcium carbide, however, contains *diatomic* carbide ions

$$Ca^{++}\,C^{-}\equiv C^{-},\quad \text{compare}\quad Fe^{++}\,S^{-}—S^{-}\ \text{in iron pyrites},$$

and carbon in the form of graphite evidently contains mobile electrons, since it possesses a peculiar form of metallic conductivity, which increases instead of decreasing with rise of temperature and is therefore distinguished as GRAPHITIC CONDUCTIVITY

(*b*) *Silicon*, the central element of the second short period, is definitely metallic in the free state, but resembles carbon in its readiness to form covalent compounds rather than simple ions The chief points of contrast between carbon and silicon arise from the inability of silicon to form

stable covalent links between its own atoms, or to form " double bonds " with oxygen Thus, whilst carbon dioxide, O = C = O, is a gas which condenses to a volatile solid, silicon dioxide is a non-volatile solid composed of giant molecules containing the grouping,



in which each silicon atom is bound by single links to four oxygen atoms In its oxidised form, therefore, silicon has the same facility for forming chains and rings that is possessed by carbon in the hydrocarbons

Another point of contrast is found in the ability of silicon to develop a maximum covalence * of *six* in its coordination compounds Thus whilst carbon tetrafluoride is a very inert gas, silicon tetrafluoride is reactive and in particular unites with two fluoride ions (by sharing two pairs of lone electrons belonging to the latter) to form the silicifluoride ion, $SiF_4 + 2F^- = [SiF_6]^{--}$ In the same way, methane is a very stable gas, since it carries a complete octet of valency-electrons shared between carbon and hydrogen, so that the central atom is exerting its maximum covalency of four , but silicane, $SiH_4$, is still unsaturated in that the silicon can assume a higher covalence, and so can combine with reagents to give unstable compounds which split up into new products Thus silicane, unlike methane, reacts with potassium hydroxide according to the equation $SiH_4 + 2KOH + H_2O = K_2SiO_3 + 4H_2$

**Properties of carbon and silicon.**—The properties of carbon and silicon are summarised in Table 10 (p 138)

## 6 CARBON C = 12 00

**Occurrence of carbon** —Carbon is found as **carbon dioxide** in the air (0 03%), as **sodium bicarbonate** in sea-water, and as **calcium** and **magnesium carbonates** in sedimentary rocks such as chalk and dolomite (p 117) It is also an essential constituent of all vegetable and animal matter, in which it often occurs, in combination with hydrogen and oxygen in the same proportions as in water, as CARBOHYDRATES, $C_mH_{2n}O_n$ In petroleum it is present as HYDROCARBONS, in combination with hydrogen only Elementary carbon is found as diamond and as graphite

**Allotropy of carbon.**—(*a*) *Diamond* —Diamonds are found in the " blue earth " of the Kimberley mine (which appears to be the neck of a volcano), and elsewhere They form transparent octahedra of density 3 5, which are harder than any other crystals Diamonds can be burnt to carbon dioxide in an atmosphere of oxygen at 800° , they also burn in gaseous fluorine at 700°, but are not attacked by acids, by alkalis, by fused potassium chlorate, or by chlorine Analysis by X-rays (Fig 28) has shown that each atom is at the mass-centre of *four* others, arranged at the corners of a regular tetrahedron, and separated from the central atom by

* The maximum covalence of an element is the largest **number** of covalent linkages which it can make with other elements

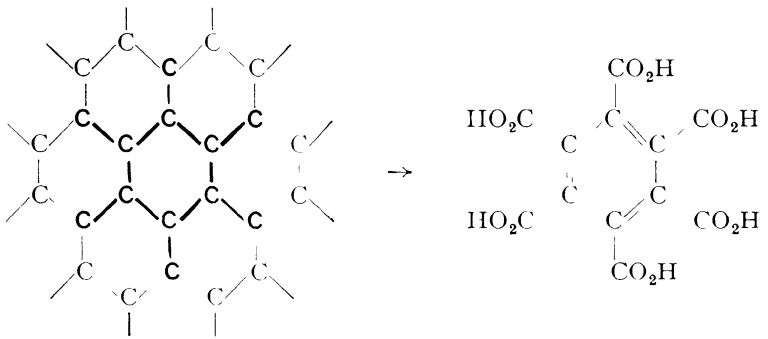
a constant distance of 1 52 A U. The crystal is therefore believed to consist of a GIANT MOLECULE, in which the atoms are linked together by a network of bonds extending throughout the crystal In this network the carbon is obviously quadrivalent, and has the same configuration as in the saturated compounds of the "fatty" or ALIPHATIC SERIES (p 771), of which methane, $CH_4$, may be taken as the type The hardness of the crystals is explained by the fact that fracture involves a rupture of chemical bonds, and their chemical inertness is also explained by the great stability of the carbon-to-carbon bonds

TABLE 10 —PROPERTIES OF CARBON AND SILICON

| | CARBON | SILICON |
|---|---|---|
| **Physical properties.** | | |
| Melting-point | 3500° | 1550° |
| Density | 1 76 amorphous<br>2 25 graphite<br>3 5 diamond | 2 35 amorphous<br>2 5 crystalline |
| **Chemical properties.** | Graphite is oxidised by $HNO_3 + KClO_3$<br>Burns to $CO_2$ | Attacked by fluorine and by hydrofluoric acid<br>Burns to $SiO_2$ |
| **Compounds** | | |
| Hydrides | $CH_4$, $C_2H_6$, etc , are inert gases, not attacked by KOH, $KMnO_4$, etc | $SiH_4$ (gas), $Si_2H_6$ (liquid) are spontaneously inflammable, attacked by KOH, $KMnO_4$, etc |
| Fluorides | $CF_4$, inert gas, not decomposed by water | $SiF_4$, gas, hydrolysed by water to $H_2SiF_6$ and $Si(OH)_4$ |
| Chlorides | $CCl_4$, inert liquid | $SiCl_4$, liquid, hydrolysed by water to $Si(OH)_4$ |
| Oxides | $CO_2$, soluble gas, feebly acidic, forms carbonates and bicarbonates | $SiO_2$, crystalline solid, melting above 1700°, insoluble in water, but forms a complex series of silicates |
| | CO, gas | SiO, solid product of partial reduction of $SiO_2$ |
| Oxychlorides | $COCl_2$, fuming gas known as phosgene | Complex solid oxychlorides are known |
| Sulphides | $CS_2$, inflammable liquid | $SiS_2$, inert solid |
| Metallic compounds | Forms carbides, such as $CaC_2$, $Fe_3C$, etc | Forms silicides, such as $CaSi_2$ $Mg_2Si$, etc |

Small diamonds have been detected in meteoric iron and were prepared artificially by Moissan by quenching solutions of carbon in molten iron or silver As the diamond is about 50% denser than graphite, it was thought that the high pressure produced by the quenching was responsible for the separation of diamonds in place of graphite, but it has not been found possible to convert graphite into diamond by pressure alone, even at the highest attainable temperatures The thermo-chemical data indicate that the diamond should be slightly more stable than graphite, but the difference in the heats of combustion is very small, and the general behaviour of the diamond resembles that of a metastable substance, which can only be persuaded to crystallise out by a trick, *e g* by separation from a particular solvent

(*b*) *Graphite* —Graphite is found in Ceylon and elsewhere in flaky hexagonal crystals of density 2 25 Unlike diamond, the crystals are opaque and conduct electricity, but with a negative temperature coefficient of electrical resistance , and, instead of being hard, the flakes slide over one another so easily that it is an excellent lubricant Analysis by X-rays has shown that the crystals consist of " giant molecules " *in two dimensions*, the flakes forming a hexagonal network of indefinite extent in which each atom is at a distance of 1 42 A U from *three* others (Fig 29) In this respect, graphite resembles the hydrocarbons of the AROMATIC SERIES (p 771), of which benzene, $C_6H_6$, is the simplest example This relationship is confirmed by the fact that graphite, unlike diamond, is oxidised below 100° by a mixture of nitric acid and potassium chlorate, to a yellow solid, **graphitic acid**, which breaks down into **mellitic acid**, $C_6(CO_2H)_6$ in which the six hydrogens of benzene have been replaced by six carboxyl-groups (p 710)



Graphite Mellitic acid

Graphite is more stable than diamond at high temperatures and is manufactured on a large scale by heating anthracite in an electric furnace A residue of pure carbon is left, from which the iron, as well as the hydrogen and oxygen, has been vaporised, so that the mineral ash is reduced to less than 0 1% Graphite is used in the manufacture of " lead " pencils, as " black lead " for polishing iron stoves, etc , and as a suspension in oil for lubricating heavy machinery Since it conducts electricity and is stable up to 3300° (when it vaporises without melting) it is used for making electrodes for electric furnaces , its resistance to attack by chlorine has also led to its use for anodes in electrolysis , and its resistance to oxidation, although less than that of diamond, is sufficient for it to be used in making crucibles for use at high temperatures

(*c*) *Amorphous carbon* —When wood or coal is heated, hydrogen and oxygen are expelled, in combination with part of the carbon, in the form of gas and tar The residue of charcoal or of coke consists mainly of carbon, but it is doubtful if a pure product is formed until the amorphous carbon is converted into graphite

On account of its low bulk density, charcoal is extremely porous, and its large surface area and high surface activity make it a very good

absorbent Thus charcoal from coco-nut shells, when cooled in liquid air, absorbs all gases but hydrogen, neon and helium, and produces an almost perfect vacuum Animal charcoal (prepared by igniting bones and containing 10% charcoal with 90% calcium phosphate) and specially active wood charcoal (prepared by heating wood in steam with or without the addition of zinc chloride) are used to decolorise sugar syrups Sugar charcoal, prepared by igniting sugar, has the merit of being free from ash, and the last traces of hydrogen can be removed from it by ignition in chlorine

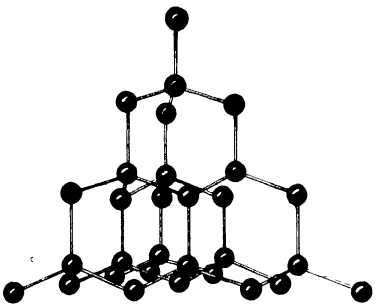


FIG. 28 STRUCTURE OF DIAMOND

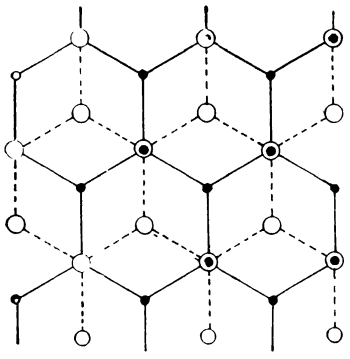


FIG 29 STRUCTURE OF GRAPHITE

Charcoal ignites in oxygen a little above 400°, whereas graphite does not burn until about 700°, and diamond at about 800° , it also ignites at once in fluorine at atmospheric temperatures, to give **carbon tetrafluoride,** $CF_4$, whilst graphite burns only at 500°, and diamond at 700° At high temperatures, charcoal combines with sulphur to form **carbon disulphide,** $CS_2$ (p 147), and with a few metals to form carbides such as **calcium carbide,** $CaC_2$ (p 118) and **aluminium carbide,** $Al_4C_3$ Chlorine, bromine, iodine and their hydrogen acids are without action on charcoal, but hot concentrated sulphuric acid, which is without action on diamond or graphite, oxidises charcoal to carbon dioxide

$$C + 2H_2SO_4 = CO_2 + 2H_2O + 2SO_2$$

At the same time a small amount of mellitic acid is produced

EXPT 14 **Adsorption by charcoal**

(*a*) Place weak solutions of litmus, tea and port wine in three test tubes, and boil each with a few pieces of animal charcoal, when they will be decolorised

(*b*) Place 50 c c of dry ammonia gas in a closed tube over mercury and add a few pieces of freshly-ignited coco-nut charcoal The mercury column rapidly rises in the tube owing to the absorption of ammonia by the charcoal

**Carbon monoxide,** CO —(*a*) *Preparation* —Carbon monoxide is usually prepared in the laboratory by removing the " elements " of water from either (i) formic acid, HCOOH, or (ii) oxalic acid, $(COOH)_2$, by the action of hot concentrated sulphuric acid

(i) $HCOOH - H_2O = CO$, (ii) $(COOH)_2 - H_2O = CO + CO_2$

The first method is advantageous because the gas is sufficiently pure for most purposes, and its rate of liberation is easily controlled by adjusting the rate at which formic acid is added to the sulphuric acid In the second case, however, an equal volume of carbon dioxide is liberated at the same time and has to be removed by bubbling the mixture through a concentrated solution of caustic potash (sodium hydroxide is cheaper, but it is unsatisfactory when a large amount of carbon dioxide has to be removed, since sodium carbonate is sparingly soluble in caustic soda and may crystallise out and block the bubbler) If very pure carbon monoxide is required, the gas from the first method should be washed with a solution of caustic soda or caustic potash to remove traces of carbon dioxide and sulphur dioxide, and dried with phosphorous pentoxide or calcium chloride before being collected over mercury

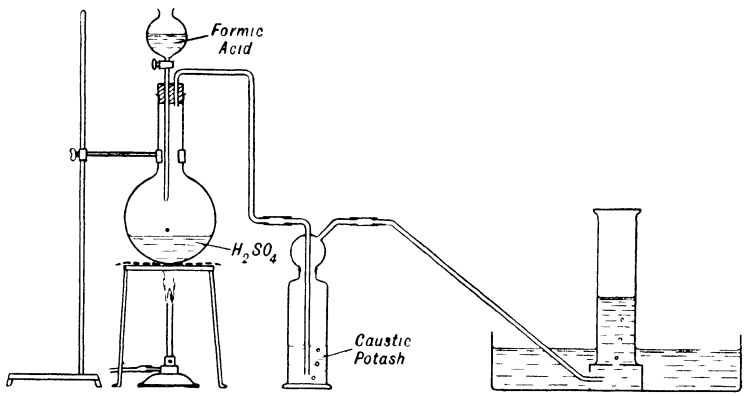



FIG 30 PREPARATION OF CARBON MONOXIDE

EXPT 15 **Preparation of carbon monoxide.**

*N B.—Take care not to inhale carbon monoxide*

Fit up the apparatus shown in Fig 30, being careful to draw out the end of the dropping funnel tube into a jet so as to obtain a sufficient " head " of formic acid to drive the gas through the liquid in the wash bottle and trough Place 100 c c of concentrated sulphuric acid in the flask and warm it gently Add formic acid slowly from the tap funnel and collect four jars of the gas (discard the first jar after first applying a light to it, as it will consist largely of air) Add to separate gas jars (i) a few c c of lime water and shake, then apply a light, and reshake when the flame has died out , (ii) about 30 c c of an ammoniacal solution of cuprous chloride,

replace the lid, shake vigorously for a minute, then remove the lid and apply a light, (iii) a few c.c of an alkaline solution of potassium permanganate and shake

Draw conclusions from your observations.

Carbon monoxide can also be obtained in the laboratory by heating a formate, oxalate, cyanide or ferrocyanide with concentrated sulphuric acid, but these reactions are perhaps more usually carried out for the identification of the acid radicals in qualitative analysis (p. 392) rather than as a means of preparing the gas The formate and oxalate react to give their respective acids, which then undergo dehydration, as above, but the reactions with the cyanide and ferrocyanide are more complex, and are therefore discussed later (see pp 157, 362)

Carbon dioxide can be reduced to the monoxide by passing it over red-hot coke or charcoal,

$$CO_2 + C \rightleftharpoons 2CO - 38{,}960 \text{ cals.},$$

but the reduction is reversible, and because it is rather slow below 800° C, the method is not really suitable for the laboratory However, immense quantities of carbon monoxide, mixed with nitrogen, are manufactured as PRODUCER GAS by forcing air through red-hot coke (p 151), when the intermediate formation of carbon dioxide is followed by the above reduction, *i e* (i) $C + O_2 = CO_2$, (ii) $CO_2 + C = 2CO$.

Another very important industrial source of carbon monoxide is WATER GAS, which is manufactured by blowing steam through red-hot coke (p 151)

$$C + H_2O = CO + H_2$$

And finally, carbon monoxide is obtained as a by-product when the more refractory oxides are reduced with carbon, *e g.*

$$ZnO + C = Zn + CO.$$

(*b*) *Properties* —Carbon monoxide is a colourless gas, which is almost identical with nitrogen in many of its physical properties Thus its vapour-density (14), boiling-point (− 190°) and solubility in water (3%) correspond closely with those of nitrogen (14, − 196°, 2%) It is poisonous at a concentration of less than 1%, and is particularly dangerous because it has no odour Its poisonous character is due to the fact that it combines with haemoglobin, the oxygen-carrier of the blood, and so prevents it from fulfilling its normal function

Carbon monoxide burns in air with a blue flame to form carbon dioxide; but the oxidation is retarded to such an extent by drying that when a jet of the burning gas is plunged into a jar of dry oxygen the flame is extinguished The mechanism of the catalytic effect of water is too complex to be discussed here, but it is presumed that the initial action is:

$$CO + H_2O = CO_2 + H_2,$$

and that this is followed by a series of reactions in which the hydrogen is reoxidised and then reduced again by more carbon monoxide.

Carbon monoxide is a reducing agent of the same general character as hydrogen; thus iron and the metals below it in the electrochemical

series (p. 53) can be obtained by reducing their oxides with carbon monoxide or hydrogen, *e.g.*

$$CuO + CO = Cu + CO_2; \quad CuO + H_2 = Cu + H_2O;$$

whilst the oxides of elements which are above iron in this series cannot be reduced to the metallic state by either of these gases. (See pp 53, 54)

In addition to combining with oxygen, carbon monoxide will unite with chlorine, in sunlight or in presence of an active form of charcoal, to form **carbonyl chloride,** $COCl_2$ (p 149) It will also unite with nickel and a few other metals, forming volatile CARBONYLS, such as **nickel carbonyl** (p. 344), which are decomposed at higher temperatures ·

$$Ni + 4CO \rightleftharpoons Ni(CO)_4$$

It dissolves in acid or ammoniacal solutions of cuprous chloride, which may absorb 20 volumes of the gas, forming coordination-compounds, such as $Cu_2Cl_2$, CO, $2H_2O$

(*c*) *Uses* —Carbon monoxide plays an important part in the preparation of metals such as iron and nickel (p 344) and is used as a fuel in the form of PRODUCER GAS or WATER GAS **Methyl alcohol,** $CH_4O$ (p 677), is prepared synthetically from carbon monoxide and hydrogen, and **sodium formate,** $NaHCO_2$ (p 715), can be made by heating sodium hydroxide with carbon monoxide under pressure

$$NaOH + CO = NaO\ CO\ H \text{ (Sodium formate)}$$

In spite of this last reaction, however, carbon monoxide is classed as a neutral oxide, because it does not form salts with either acids or bases under normal conditions

(*d*) *Formula* —Carbon monoxide yields only carbon dioxide when burnt in oxygen, and is therefore a lower oxide of carbon When exploded with oxygen in a eudiometer, two volumes unite with one volume of oxygen to form two volumes of carbon dioxide These contain their own volume of oxygen, of which one-half is derived from gaseous oxygen, so that the other half must be present in the lower oxide, hence

*2 vols carbon monoxide = 2 vols carbon dioxide − 1 vol oxygen*
*2 mols ,, ,, = 2 mols ,, ,, − 1 mol. ,,*

The molecules of oxygen and carbon dioxide are known to be $O_2$ and $CO_2$, hence

$$2\ mols\ carbon\ monoxide = 2CO_2 - O_2 = 2CO.$$

The formula thus deduced is in agreement with the observed density of the gas, which is 14 times as heavy as hydrogen (CO = 28)

(*e*) *Detection and estimation* —Carbon monoxide may be identified by the blue colour of its flame and by the formation of carbon dioxide as the only product of combustion Small quantities of carbon monoxide in air may be detected by shaking with diluted blood, and then examining the blood either spectroscopically, or by adding a solution of tannin to it, when normal blood gives a brown precipitate, whilst blood containing carbon monoxide gives a red precipitate

Carbon monoxide may be estimated by absorbing it in ammoniacal cuprous chloride, after removing acid impurities with potash

**Carbon dioxide,** $CO_2$ —(*a*) *Preparation* —In the laboratory, carbon dioxide is usually prepared, *e g* in Kipp's apparatus (Fig 12, p 70), by the action of dilute hydrochloric acid on marble

$$CaCO_3 + 2HCl = CaCl_2 + H_2O + CO_2$$

Carbon dioxide is produced on a large scale as a by-product of fermentation (p 679) and is collected for use in making " aerated waters ", drikold, etc It can also be prepared industrially by burning coke, and purifying the product from nitrogen, dust, etc , by dissolving in water under pressure , on releasing the pressure carbon dioxide is liberated in a concentrated form, and after drying with sulphuric acid is compressed into cylinders for transport and sale

The very large quantities of carbon dioxide which are required for making sodium carbonate by the Solvay process (p 100), are made by burning a mixture of limestone and coke in a kiln provided with an artificial draught

$$C + O_2 = CO_2 \qquad CaCO_3 = CaO + CO_2$$

The kiln (Fig 31) is an iron shell lined with fire-bricks and supported on iron columns It is charged with alternate layers of coke (about 10%) and limestone (about 90%), and brought to redness by opening the cover, *A*, of the central chimney during the early stages of combustion , the temperature of the charge is judged by viewing it through mica windows as at *aa* The cover is then closed and the gases are drawn out through the pipe, *B*, by means of a suction-pump Fresh lime and coke are introduced through a conical hopper by lifting up the cylindrical collar, *C*, and the lime and ashes are raked out from the base of the cone, *D* The gas on its way to the pump is purified by passing through a trap, *E*, to remove condensed water and dust

(*b*) *Properties* —Carbon dioxide is a colourless gas, which resembles nitrous oxide in its physical properties just as closely as carbon monoxide resembles nitrogen At temperatures below 31° it can be compressed to a liquid, which has a pressure of 34 atmospheres at 0° When the liquid is allowed to escape into the air, it solidifies to " carbon dioxide snow," which is used on a very large scale as DRIKOLD for cooling ice-creams, packing fish, etc , since it evaporates without leaving any residue The snow sublimes without melting at −79° under a pressure of 1 atmosphere, but it melts at −57° under a pressure of 5 atmospheres Under atmospheric pressure, water dissolves its own volume of the gas and acquires a fresh mildly-acid taste

Carbon dioxide is a very stable compound, but when heated strongly it dissociates into carbon monoxide and oxygen The observed proportions of these gases when equilibrium is reached at different temperatures are approximately as follows

TABLE 11 —DISSOCIATION OF CARBON DIOXIDE

| | $2CO_2$ | $\rightleftharpoons$ | $2CO + O_2$ |
|---|---|---|---|
| At 1200° | 99 98% | | 0 02% |
| At 2000° | 98 | | 2 |
| At 2600° | 50 | | 50 |

It can be reduced to carbon monoxide by the action of red-hot carbon or metallic iron, and to carbon by burning sodium, potassium or magnesium

$$2Mg + CO_2 = 2MgO + C$$

Its principal properties, however, are those of an acid anhydride as set out below under the title " Carbonic acid "

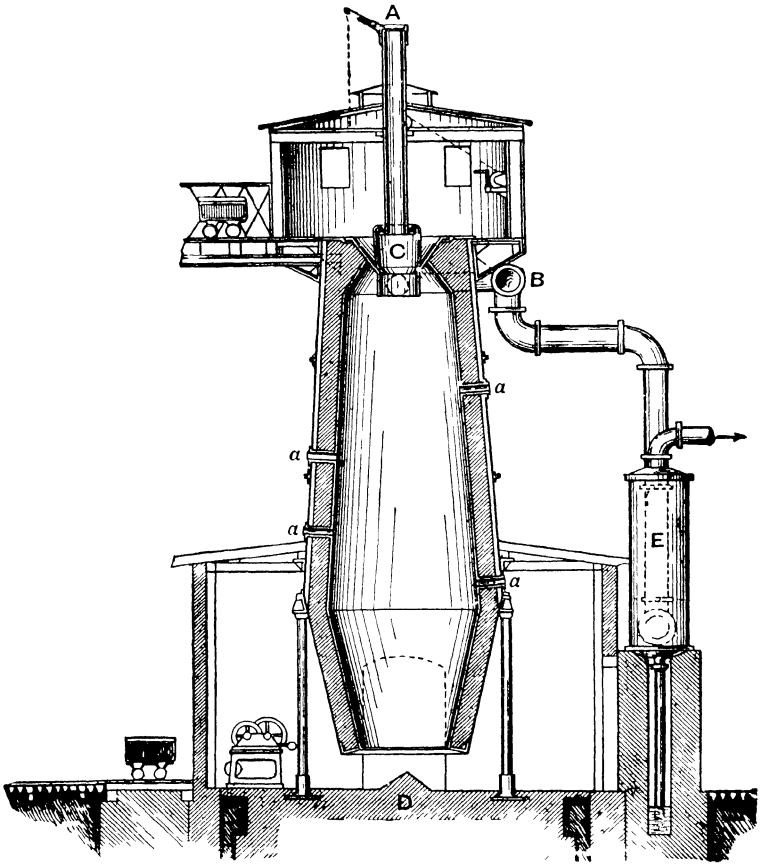



FIG 31 LIME-KILN FOR MANUFACTURE OF CARBON DIOXIDE

(*c*) *Composition* —The gravimetric composition of carbon dioxide was established by burning a known weight of diamond or of purified charcoal, collecting the gas in potash and weighing it Its volumetric composition was established by experiments which showed that it contained its own volume of oxygen Since it was denser than carbon monoxide, it was assumed that it had the formula $CO_2$, whilst the combustible oxide (which contained only half as much oxygen in combination with carbon) was CO

These formulae were afterwards established by means of Avogadro hypothesis as described on p 21

EXPT 16 **Volumetric composition of carbon dioxide**

The volumetric composition of carbon dioxide may be shown by mean of the apparatus in Fig 32 A small piece of charcoal is placed on a iron spoon in a globe filled with oxygen at atmospheric pressure Th charcoal is ignited by passing a current through a heating coil Whe the apparatus has cooled down it will be foun that the mercury is at the same level in the tw limbs, *i e* no change in volume has taken plac in converting oxygen into carbon dioxide Car must be taken not to heat the charcoal to strongly, otherwise the reaction may be so violen that mercury is forced out of the left-han limb

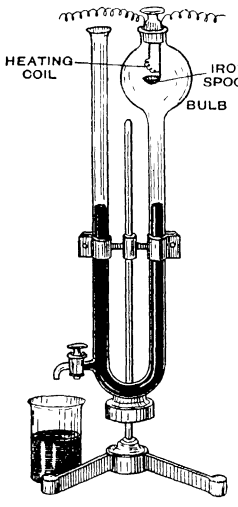



FIG 32 VOLUMETRIC COMPOSITION OF CARBON DIOXIDE

(*d*) *Detection and estimation* —Carbon dioxid is usually detected by its power of precipitatin chalk from lime-water It can be estimate gravimetrically by absorption in a strong solu tion of potash (p 448) or volumetrically b titration (see Pettenkofer's method for $CO_2$ i air, p 241)

**Carbonic acid and its derivatives.**—(*a*) *Carboni acid* —A solution of carbon dioxide in wate has a slight acid taste, which is attributed t the presence in it of small quantities of **carbon acid,** $H_2CO_3$

$$CO_2 + H_2O \rightleftharpoons H_2CO_3$$

The solution is not acid to methyl orange, but it produces a dull red tir with litmus, which reverts to a blue colour when the solution is boilec The acid gives two series of salts, namely, CARBONATES, such as $K_2CC$ and $CaCO_3$, in which both atoms of hydrogen are replaced by meta and BICARBONATES, in which only half the hydrogen is displaced, as i $KHCO_3$ and $Ca(CO_3H)_2$

(*b*) *Carbonates* are produced by direct combination of carbon dioxid with basic oxides in the presence of a trace of moisture,

$$CaO + CO_2 = CaCO_3,$$

by displacement of water from hydroxides,

$$Ca(OH)_2 + CO_2 = CaCO_3 + H_2O,$$

$$2KOH + CO_2 = K_2CO_3 + H_2O,$$

or by double decomposition,

$$CaCl_2 + Na_2CO_3 = CaCO_3 + 2NaCl$$

The alkali carbonates are freely soluble in water and are not decomposed by heat (Li excepted) All other carbonates are either sparingly soluble or quite insoluble in water, and are decomposed by heat into the oxide and carbon dioxide Solutions in water of alkali carbonates are alkaline, owing to hydrolysis

$$Na_2CO_3 + H_2O \rightleftharpoons NaOH + NaHCO_3$$

They may be titrated directly with acids, using methyl orange as an indicator

$$Na_2CO_3 + H_2SO_4 = Na_2SO_4 + H_2O + CO_2$$

If phenolphthalein is used, the end-point is indicated at the half-way stage,

$$2Na_2CO_3 + H_2SO_4 \rightarrow 2NaHCO_3 + Na_2SO_4,$$

since sodium bicarbonate is neutral to this indicator

(*c*) *Bicarbonates* —Sodium and potassium bicarbonates may be prepared by the direct action of carbon dioxide on the solid hydroxides Other bicarbonates are too unstable to exist in the solid state, but may be prepared in solution by the action of carbonic acid ($CO_2 + H_2O$) on hydroxides, carbonates, silicates and certain metals, *e g*

$$KOH + CO_2 = KHCO_3,$$
$$CaCO_3 + H_2CO_3 = Ca(CO_3H)_2,$$
$$Fe + 2H_2CO_3 = Fe(CO_3H)_2 + H_2$$

It is noteworthy that, whilst the bicarbonates of the alkalis (lithium excepted) are less soluble than the carbonates, the alkaline earths which form insoluble carbonates give rise to soluble bicarbonates Carbonates may be distinguished from bicarbonates by the fact that they give with mercuric chloride an immediate precipitate of a basic carbonate, whilst bicarbonates give a precipitate only on heating

(*d*) *Percarbonates* —When a saturated solution of potassium carbonate is electrolysed at $-30°$ with platinum electrodes, the anode being enclosed in a porous pot, **potassium percarbonate,** $K_2C_2O_6$, is precipitated at the anode as a bluish-white, deliquescent amorphous powder It is a strong oxidising and bleaching agent and liberates iodine from potassium iodide

$$K_2C_2O_6 + 2KI = 2K_2CO_3 + I_2$$

When heated, it decomposes into potassium carbonate, carbon dioxide and oxygen

$$2K_2C_2O_6 = 2K_2CO_3 + 2CO_2 + O_2$$

**Carbon disulphide**, $CS_2$, is an endothermic compound

$$C\,(\text{charcoal}) + S_2\,(\text{rhombic}) = CS_2\,(\text{vapour}) - 26{,}010$$

It is prepared by the direct combination of carbon with sulphur either in a retort or in an electric furnace (Fig 33)

In the electric process heat is supplied by currents passing between four electrodes, *AA*, each containing 25 blocks of carbon, $4 \times 4 \times 48$ inches, and separated by about 12 inches from one another in the centre of the furnace

The space between these is bridged by broken carbons fed in at *BB* The shaft of the furnace is filled with charcoal, *C* The space, *D*, below the electrodes is filled with sulphur, and sulphur fed in at *E* and *F* is also used to jacket the walls of the furnace, so that almost the whole of the heat escaping from the surface is caught and carried back either by the charcoal or by the sulphur passing down to the electrodes The furnace is about 8 feet in diameter at the base and about 20 feet in height over all (hearth = 6 feet, shaft = 8 feet, head = 4 feet) It has a capacity of about 10 tons of carbon disulphide per day of 24 hours

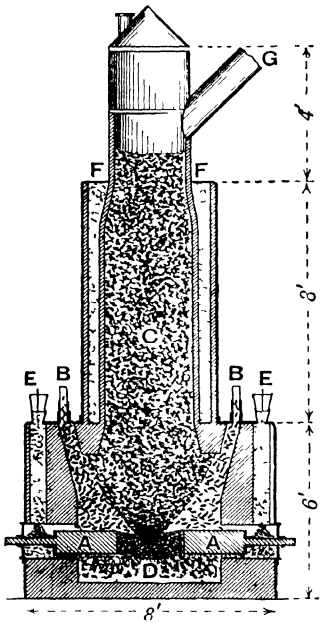



FIG 33 ELECTRIC FURNACE FOR CARBON DISULPHIDE

Carbon disulphide is a volatile liquid, of density 1 3 at 0°, boiling at 46° and freezing at −110° It is a poisonous substance, which is used as an insecticide and for killing vermin It is a good solvent for many substances, including sulphur, phosphorus, rubber, and many organic compounds such as fats, but on account of its extreme inflammability it has been largely displaced by carbon tetrachloride, $CCl_4$, and by acetylene dichloride, $C_2H_2Cl_2$ The heavy vapour forms a highly explosive mixture with air When pure it has a fragrant odour, but it is usually contaminated with malodorous sulphur compounds, these may be removed by contact with mercury, or by the prolonged action of concentrated sulphuric acid, followed by distillation

Carbon disulphide reacts slowly with a concentrated solution of caustic soda forming a solution of sodium carbonate and **sodium thiocarbonate,** $Na_2CS_3$

$$3CS_2 + 6NaOH = Na_2CO_3 + 2Na_2CS_3 + 3H_2O$$

Sodium thiocarbonate is the salt of a weak acid, **thiocarbonic acid,** $H_2CS_3$ (the sulphur analogue of carbonic acid) and is more readily prepared by the action of carbon disulphide on a solution of sodium sulphide

$$CS_2 + Na_2S = Na_2CS_3$$

**Carbon tetrachloride**, $CCl_4$, cannot be prepared from its elements by direct combination, since chlorine does not act on carbon It is therefore made by the action of chlorine or of sulphur chloride on carbon disulphide, in the former case, antimony pentachloride is used as a "carrier" of chlorine

$$CS_2 + 2Cl_2 = CCl_4 + 2S,$$

$$CS_2 + 2S_2Cl_2 = CCl_4 + 6S.$$

It is a volatile, fragrant liquid, insoluble in water, and boiling at 77° It contains more than 90% of chlorine, and is of special value as a non-inflammable solvent, it is also used extensively as a fire extinguisher, under the name of PYRENE It has been used as a hair-wash, but is very dangerous, as it is more toxic than chloroform and has been known to produce fatal effects

**Carbonyl chloride** or PHOSGENE, $COCl_2$, is the acid chloride of carbonic acid, $CO(OH)_2$, from which it can be derived by replacing two hydroxyls by chlorine It is formed when a mixture of carbon monoxide and chlorine is exposed to bright sunlight or passed over heated charcoal as a catalyst In the laboratory, it can be prepared by heating carbon tetrachloride with twice its weight of fuming sulphuric acid

$$2SO_3 + CCl_4 = COCl_2 + S_2O_5Cl_2$$

Phosgene is a colourless gas, which condenses readily to a liquid boiling at 8° It has a pungent and suffocating smell and is highly poisonous Since chloroform (p 702) is oxidised to phosgene in the presence of air and sunlight,

$$2CHCl_3 + O_2 = 2COCl_2 + 2HCl,$$

it is highly important that chloroform for use as an anaesthetic should be stored in full bottles, closely stoppered and in the dark

Phosgene is decomposed into carbon monoxide and chlorine by heating, the decomposition is complete at about 800°

$$COCl_2 \rightleftharpoons CO + Cl_2$$

It does not fume in moist air, but is readily hydrolysed by water, forming carbon dioxide and hydrochloric acid

$$H_2O + COCl_2 = CO_2 + 2HCl$$

It reacts with ammonia to form **urea**, $CON_2H_4$ (p 747)

$$COCl_2 + 4NH_3 = CON_2H_4 + 2NH_4Cl$$

## COMBUSTION

**Coal gas**, prepared by distilling coal in fireclay retorts, consists principally of hydrogen (about 48%) and methane (about 32%) with smaller quantities of ethylene, carbon monoxide, carbon dioxide and nitrogen Its luminosity is due chiefly to ethylene, and to the uncondensed vapours of benzene, naphthalene, etc A residue of COKE is left in the retorts, whilst the liquid products include

(i) An aqueous AMMONIACAL LIQUOR, from which ammonia is distilled out into sulphuric acid and converted into ammonium sulphate

(ii) COAL TAR, from which **benzene**, $C_6H_6$ (p 774), **naphthalene**, $C_{10}H_8$, and a number of other volatile organic compounds are obtained by distillation, while pitch is left behind as a non-volatile residue

The fireclay retorts in which the coal is distilled are arranged either vertically or horizontally (Fig 34) and are heated by producer gas (p 151) from a coke furnace below the retorts. The "primary air" serves to

burn the carbon to carbon monoxide, whilst the "secondary air" burns the carbon monoxide to carbon dioxide round the retorts

The hot gases are taken off by a "rising main" (Fig 34), and pass through a trap in the "tar-main" into the "gas-main" The impurities at this stage are roughly $NH_3$ 1%, HCN 0 1%, $H_2S$ 1 3%, $CS_2$ 0 04% and a little tar Air-cooled condensers (Fig 35) throw down a further quantity of tar, water, and ammonia The gas then passes through a rotary air-pump, known as the exhauster, which serves to maintain a slightly reduced pressure on the retorts Washers and scrubbers are used to extract the ammonia from the gas by means of water Hydrogen

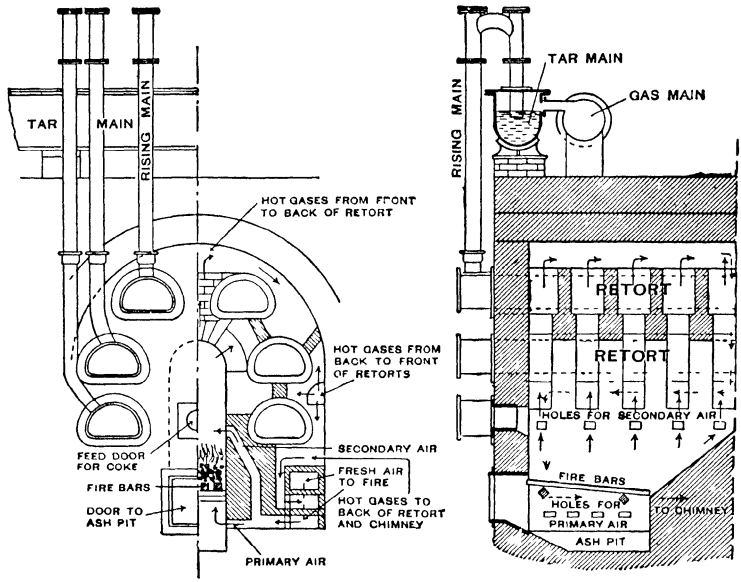



FIG 34 COAL GAS RETORTS

sulphide and prussic acid are removed by passing the gas over trays of moist hydrated ferric oxide

$$Fe_2O_3 + 3H_2S = Fe_2S_3 + 3H_2O,$$
$$Fe_2O_3 + 6HCN = 2Fe(CN)_3 + 3H_2O$$

The oxide of iron is revived from time to time by exposure to air,

$$2Fe_2S_3 + 3O_2 = 2Fe_2O_3 + 6S,$$

and can be used until it contains about 50% of sulphur After extraction of cyanogen compounds (such as Prussian blue, $Fe_7C_{18}N_{18}$), the "spent oxide" is sold to the sulphuric acid manufacturers to be burnt to sulphur dioxide

The carbon disulphide in coal gas is sometimes converted into hydrogen sulphide, carbon and methane by passing the gas over finely-divided nickel at 400°.

$$CS_2 + 2H_2 = 2H_2S + C \text{ (main reaction)},$$
$$CS_2 + 4H_2 = 2H_2S + CH_4$$

The hydrogen sulphide is then removed as above The purified gas should not contain more than 1 volume of hydrogen sulphide in 10,000,000, and should not blacken lead acetate paper

**Producer gas** —A mixture of carbon monoxide (29%) and nitrogen (62%), prepared by blowing air through red-hot coke in a "gas-producer" (Fig 36), is known as PRODUCER GAS This has a lower calorific value than coal gas but is much cheaper On account of its ease of manipulation and cleanliness it is often used in preference to a solid fuel, *e g* for heating retorts in the manufacture of coal gas If the producer gas is used on the spot, without being cooled, very little of the original heat value of the coke is lost, but in practice about 30% is usually lost, *e g* when the gas is washed to remove grit before being used in a gas-engine Producer gas also contains a little hydrogen and methane owing to the presence of water vapour in the air blast, especially when this is injected into the producer by means of a steam jet

**Water gas** —When steam instead of air is blown through incandescent coke a mixture known as WATER GAS is obtained This consists of hydrogen (49%), carbon monoxide (42%), carbon dioxide (4%) and nitrogen (5%) The reactions which take place are

(i) $C + H_2O$ (steam) $\rightarrow$ $CO + H_2 - 29{,}000$ calories;

(ii) $CO + H_2O \rightleftharpoons CO_2 + H_2 + 10{,}200$ calories

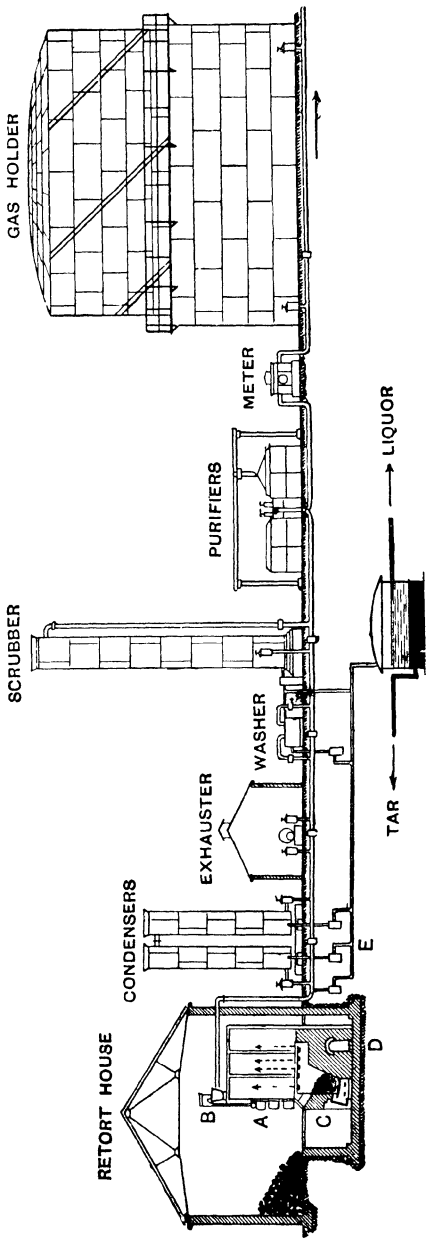



FIG 35 PLANT FOR MAKING COAL GAS (after Cristopherson)

Since the decomposition of steam absorbs a large amount of heat, the coke has to be heated up intermittently by a blast of air

$$(111)\quad C + O_2 = CO_2 + 96{,}960 \text{ calories}$$

In order to secure continuous operation, SEMI-WATER GAS is often made by blowing steam and air through red-hot coke in such proportions that the temperature of the coke is maintained The product consists mainly of

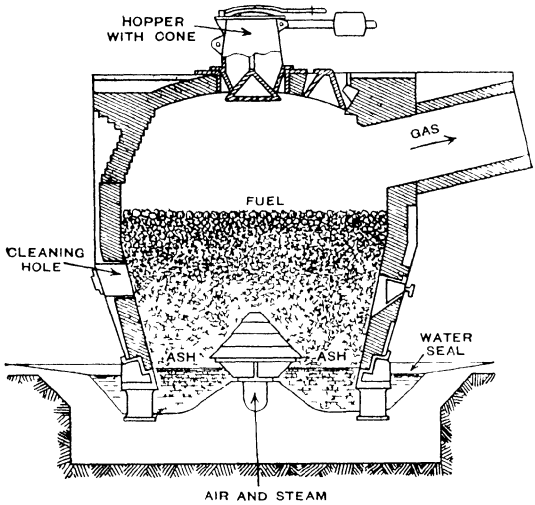



FIG 36 GAS PRODUCER

carbon monoxide (27%) and hydrogen (14%) diluted with about 50% of nitrogen

The proportion of carbon monoxide to carbon dioxide in water gas varies according to the temperature of the coke, since reaction (i) is favoured by a rise in temperature, while reaction (ii) is hindered This is clearly illustrated in Table 12

TABLE 12 —COMPOSITION OF WATER GAS

| Temperature | Steam decomposed | Composition of gas by volume | | |
|---|---|---|---|---|
| | | $H_2$ | CO | $CO_2$ |
| 675° C | 8 8% | 65 2 | 4 9 | 29 8 |
| 840 | 41 0 | 61 9 | 15 1 | 22 9 |
| 1010 | 94 0 | 48 8 | 49 7 | 1 5 |
| 1125 | 99 4 | 50 9 | 48 5 | 0 6 |

Water gas is the cheapest source for the preparation of hydrogen on a large scale (p 72) It also provides a suitable mixture of hydrogen and

carbon monoxide for use in the synthesis of **methanol** or **methyl alcohol** (p 677) Thus when water gas, at 350° to 400° and under a pressure of 150 to 250 atmospheres, is passed over a catalyst, such as a mixture of zinc oxide and chromic oxide, the following reaction takes place

$$CO + 2H_2 = CH_3\,OH$$

Finally, since it is not diluted with atmospheric nitrogen, " water gas " has a much higher calorific value than " producer gas " or " semi-water-gas " and is often added to coal gas

**Flame.**—(*a*) *Flames produced by burning gases* —When two gases burn together, the hot gas which is produced by their combustion is described as a FLAME Thus, a flame may be produced either by burning coal gas in air or by burning air in coal gas, as may be shown by using the apparatus represented in Fig 37 Again, whilst carbon, which cannot be vaporised except at very high temperatures, burns in oxygen without a flame, sulphur and phosphorus, which are easily vaporised, burn, the one with a pale blue flame and the other with a brilliant, luminous flame

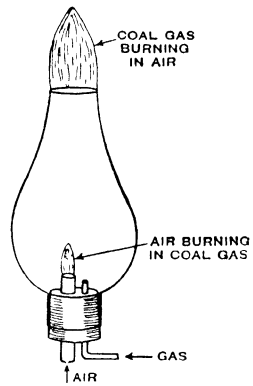



FIG 37 BURNING OF COAL GAS AND AIR

The gas is lighted at the tip of the L-shaped glass tube and the lamp glass is then placed in position The gas is then turned on full, when the gas-flame moves to the top of the lamp glass, whilst an air-flame appears at the top of the air tube

(*b*) *Temperature of flames* —The maximum temperatures of various flames are estimated to be as follows

| | |
|---|---|
| Bunsen burner - - - - - | 1870° |
| Air blowpipe - - - - - | 2200° |
| Oxy-hydrogen blowpipe - - - | 2400° |
| Oxy-acetylene blowpipe - - - | 2600° |

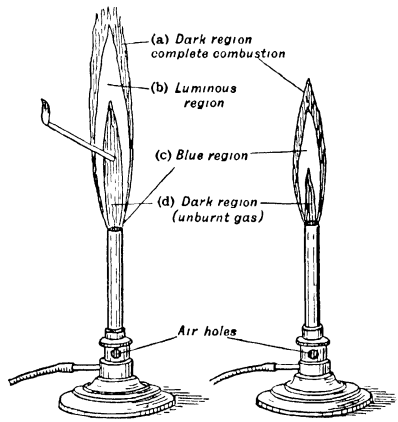
(*c*) ***Luminosity due to hot solids*** —The intensely hot oxy-hydrogen flame is almost invisible when burning under atmospheric pressure owing to the poor radiating power of the gases, but a brilliant incandescence is produced when the flame is directed against a block of lime, as in the LIMELIGHT LANTERN So, also, the almost invisible flame produced by burning a mixture of coal gas and air is made to produce a brilliant light by inserting in the flame an INCANDESCENT MANTLE (composed mainly of thorium dioxide, $ThO_2$, mixed with about 1 5% of cerium sesquioxide, $Ce_2O_3$), which emits a very high proportion of visible light rays at the temperature of the flame

Many luminous flames owe their luminosity to solid particles formed during combustion Thus, the flame of the BATSWING BURNER, in which coal gas is burned directly in air, owes its luminosity, at least in part, to

the presence of solid particles of unburnt carbon, or soot, in the smoky flame

The flame of nickel carbonyl, $Ni(CO)_4$, from which metallic nickel is deposited readily on a cold piece of porcelain, is highly luminous On the other hand, the flame of stibine, $SbH_3$, is practically non-luminous, although it deposits metallic antimony upon a cold surface

(*d*) *Luminosity of hot gases* —In some cases a luminous flame is produced when solid particles would not be expected to appear in the flame, thus, phosphoretted hydrogen, $PH_3$, carbon disulphide, $CS_2$, and arsenic burn in oxygen with luminous flames, although the products of combustion are all gaseous at the temperature of combustion Again, some non-luminous mixtures burn brilliantly when the constituents are heated before combustion, *e g* marsh gas and air, if passed through red-hot tubes, burn together with a very luminous flame




Air-hole closed Air-hole open

FIG 38 BUNSEN BURNER

Luminosity can also be produced by compression Thus, the flames of alcohol vapour and of hydrogen burning in air become luminous under pressure

**Structure of flame.**—When coal gas is to be used as a source of heat, or to produce light indirectly with the help of an incandescent mantle, special methods are used to burn the soot completely, and thus to give a clean and almost invisible flame This is done by mixing the gas with a considerable quantity of air as in the Bunsen burner (Fig 38)

Coal gas is admitted through a narrow pin-hole in a nipple The stream of gas flows past an adjustable air-hole and draws in a quantity of air which can be varied by regulating the opening The mixture of gas and air passes up the tube and is ignited at the top The air introduced at the air-hole may be called the " primary air," whilst the atmosphere supplies " secondary air " to the flame

(1) When the primary air is cut off, by closing the air-hole, the gas burns at the top of the tube with a luminous but not very hot flame This flame includes a thin outer non-luminous cone *a*, of a blue colour, in which combustion takes place with the help of the secondary air, whilst the interior of the cone is occupied in part by a luminous cone, *b*, in which the hydrocarbons in the gas are decomposed and raised to a high temperature by the hot shell of flame outside The fact that this cone is hollow can be proved by inserting a narrow tube, and igniting at the upper end of this tube the unburnt gas drawn off from the interior of the flame (region *d*) Lastly there is a bright blue edge *c*, at the base of the flame where intense combustion occurs owing to the up-draughts of air

(ii) When primary air is introduced into the gas, the outer zone of complete combustion increases in thickness, the luminous region disappears, and an inner cone, *c*, of a lighter blue colour is seen In this inner cone the gas is partially burnt with the help of the primary air, the combustion being completed with secondary air in the outer zone

(iii) When a lower cone is formed, the mixture of gas with primary air is within the " limits of inflammability," that is, the mixture can sustain a flame without the aid of secondary air The flame is therefore continually travelling downwards, but the velocity of propagation downwards is less than the upward velocity of the mixture If, however, the quantity of

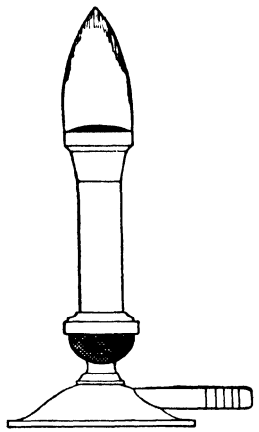


FIG 39 BUNSEN BURNER WITH GAUZE

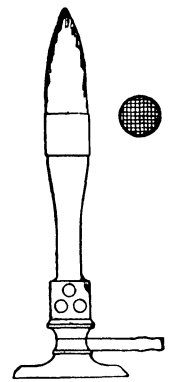


FIG 40 MÉKER BURNER

primary air be increased still further, the velocity of propagation will increase until it exceeds the rate of flow of the gas in the tube , when this occurs the inner cone will travel down the tube and burn at the bottom The flame in this position is described as having " struck back " Striking back may be prevented by covering the top of the burner with wire gauze as in Fig 39 , this conducts away the heat of the flame so that the gases below the gauze never reach the " ignition point " A nickel grid is used for the same purpose in the Méker burner (Fig 40) The air inlet may also be covered with gauze to prevent ignition at this point Davy's safety lamp for miners was an application of the same principle, since direct ignition of the contaminated air by the flame of the lamp was prevented by a shield of copper gauze

## CARBON AND NITROGEN

**The cyanogen radical.**—The compounds of carbon and nitrogen are of special interest on account of the fact that the COMPOUND RADICAL, CN, behaves very much like the SIMPLE RADICALS of the halogens This is sometimes expressed by writing the radical **cyanogen** as Cy, just as if it

were an element It differs from the halogens in that the **cyanide ion** is more ready than a halide ion to share its electrons with other atoms Hydrogen cyanide is therefore a weak acid , its salts are hydrolysed to a large extent in solution, and are decomposed even by carbon dioxide For the same reason, the cyanides are much more ready than the halogens to form coordination compounds , and some of the double cyanides, *e g* the ferrocyanides, are so stable that the metallic ion can no longer be detected by the ordinary reagents On the other hand, cyanogen differs from the halogens (just as the ammonium radical differs from the alkali metals) in that the radical can be decomposed, *e g* by concentrated sulphuric acid with formation of ammonium sulphate and carbon monoxide (p 142)

**Cyanogen**, $C_2N_2$, may be prepared by heating mercuric or silver cyanide to a red heat

$$Hg(CN)_2 = Hg + (CN)_2 , \qquad 2AgCN = 2Ag + (CN)_2$$

It is a colourless, poisonous gas, with a characteristic smell, and condenses to a colourless liquid which boils at $-21°$ Cyanogen unites with hydrogen to form prussic acid, HCN, and burns in air with a purple flame forming carbon dioxide and nitrogen

$$(CN)_2 + 2O_2 = 2CO_2 + N_2$$

Like chlorine, it is moderately soluble in water, and reacts with it to give a small amount of prussic acid, HCN, and cyanic acid, HCNO,

$$(CN)_2 + H_2O \rightleftharpoons HCN + HCNO,$$

compare $$Cl_2 + H_2O \rightleftharpoons HCl + HClO ,$$

but when this solution is exposed to sunlight the cyanogen is hydrolysed to ammonium oxalate $(CO\,ONH_4)_2$

**Hydrogen cyanide** or HYDROCYANIC ACID or PRUSSIC ACID, HCN, may be prepared by distilling a cyanide with dilute sulphuric acid

$$KCN + H_2SO_4 = KHSO_4 + HCN$$

The anhydrous acid may be prepared by heating a powdered mixture of potassium cyanide and potassium hydrogen sulphide

$$KCN + KSH = K_2S + HCN$$

It is a colourless liquid, which boils at 26° and has a characteristic odour Since prussic acid is extremely poisonous, very great care must be taken in handling it , the best antidote is freshly precipitated ferrous hydroxide (*e g* a mixture of ferrous sulphate and sodium carbonate) accompanied by the stimulating action of ammonia The vapour burns with a beautiful peach-blossom coloured flame

$$4HCN + 5O_2 = 4CO_2 + 2H_2O + 2N_2$$

Prussic acid is freely soluble in water and reacts with it slowly to give **ammonium formate** (p 716)

$$HCN + 2H_2O \rightleftharpoons H{\cdot}CO\,ONH_4$$

It forms a series of CYANIDES, but these are hydrolysed by water, so that a solution of potassium cyanide has an alkaline reaction and smells of hydrogen cyanide (p 156)

$$KCN + H_2O \rightleftharpoons HCN + KOH$$

When the acid, or a cyanide, is acted on by concentrated sulphuric acid, it is decomposed completely and carbon monoxide is set free

$$2KCN + 2H_2SO_4 + 2H_2O = K_2SO_4 + (NH_4)_2SO_4 + 2CO$$

In this action formic acid, which gives carbon monoxide when acted on by sulphuric acid (p 716), is perhaps an intermediate product

**Cyanides.**—(*a*) *Preparation* —**Potassium cyanide** can be prepared by fusing potassium ferrocyanide (p 361) either alone or with potassium carbonate

$$K_4Fe(CN)_6 = 4KCN + FeC_2 + N_2,$$
$$K_4Fe(CN)_6 + K_2CO_3 = 5KCN + KCNO + CO_2 + Fe$$

The cyanate produced in the last reaction may be reduced to cyanide by adding a little charcoal to the fused mass A mixture of sodium and potassium cyanides is sometimes prepared by fusing the ferrocyanide with metallic sodium, when no cyanogen is lost

$$K_4Fe(CN)_6 + 2Na = 4KCN + 2NaCN + Fe$$

The sodium cyanide used in commerce is prepared by CASTNER'S PROCESS **Sodamide**, $NaNH_2$, is first prepared by passing ammonia over sodium heated in iron retorts to about 400°

$$2Na + 2NH_3 = 2NaNH_2 + H_2,$$

the fused sodamide is then poured on to red-hot charcoal to form the cyanide

$$NaNH_2 + C = NaCN + H_2$$

Potassium cyanide is prepared by passing a stream of ammonia over fused potassium carbonate and carbon

$$K_2CO_3 + 2NH_3 + C = 2KCN + 3H_2O$$

(*b*) *Properties* —Sodium and potassium cyanides are freely soluble in water Most of the other cyanides are insoluble, but often dissolve in excess of alkali cyanide owing to the formation of complex cyanides Thus, silver cyanide dissolves in excess of potassium cyanide, forming **potassium argentocyanide**, $KAg(CN)_2$, which is used in electroplating (p 323)

$$KCN + AgCN = KAg(CN)_2$$
(ppt) (soluble)

Large quantities of sodium cyanide are used in the extraction of gold (p 327)

**Cyanic acid and the cyanates.**—**Sodium** and **potassium cyanates** may be prepared by adding red lead gradually to the fused cyanide and stirring

$$4KCN + Pb_3O_4 = 4KCNO + 3Pb$$

The product is powdered in a mortar and warmed with dilute alcohol,

when the cyanate dissolves and may be crystallised from solution Cyanates are slowly hydrolysed by water , thus potassium cyanate is gradually converted into potassium and ammonium carbonates

$$2KCNO + 4H_2O = K_2CO_3 + (NH_4)_2CO_3$$

Dilute acids liberate **cyanic acid,** HCNO, which is rapidly hydrolysed to carbon dioxide and ammonia

$$HCNO + H_2O = NH_3 + CO_2$$

When a solution containing potassium cyanate and ammonium sulphate is evaporated, the **ammonium cyanate,** $NH_4CNO$, which is first formed is converted into **urea**

$$NH_4CNO \rightleftharpoons CON_2H_4$$

This isomeric change is reversible, but the urea crystallises out first when the solution is evaporated to dryness and the reaction then proceeds to completion

**Thiocyanic acid and the thiocyanates** —**Potassium thiocyanate** or **potassium sulphocyanide,** KCNS, may be prepared by heating potassium cyanide with sulphur, and crystallising the crude product from alcohol

$$KCN + S = KCNS$$

It crystallises in anhydrous prisms and is very deliquescent and readily soluble in water It gives a white precipitate of **silver thiocyanate,** AgCNS, with aqueous solutions of silver salts, and may be used to estimate silver by titration With ferric chloride, it gives a blood-red colouration owing to the formation of the complex anion, $Fe(CNS)_6^{---}$,

$$Fe^{+++} + 6CNS^- \rightleftharpoons Fe(CNS)_6^{---},$$

and this serves as a qualitative test for ferric salts and for thiocyanates

## 14 SILICON Si = 28 06

**Occurrence.**—Silicon holds the same prominent position in mineral chemistry as is occupied by carbon in vegetable and animal chemistry Whereas, however, carbon forms very few oxides and a vast number of hydrides, the hydrides of silicon are only of theoretical interest, and it is the oxide, $SiO_2$, which dominates mineral chemistry Thus **silica,** $SiO_2$, occurs free as QUARTZ, etc , and in combination with a host of metallic oxides as silicates, *e g* as FELSPAR, $KAlSi_3O_8$, in igneous rocks, and as KAOLINITE, $H_4Al_2Si_2O_9$, in clay and other sediments Silicon is the second most abundant element in the earth's crust, occurring to the extent of 26% as compared with 50% of oxygen

**Preparation and properties of silicon.**—Amorphous silicon can be prepared by the action of potassium, sodium, or aluminium on the vapour of silicon tetrachloride

$$4Na + SiCl_4 = Si + 4NaCl$$

It can also be prepared by reducing silica with aluminium or magnesium

$$3Si_2O_2 + 4Al = 2Al_2O_3 + 3Si$$

Metallic silicon is prepared by crystallising amorphous silicon from a metal such as aluminium, or by reducing silica with carbon in the electric furnace

$$SiO_2 + 2C = Si + 2CO$$

Although silicon is usually classified with the non-metals, on account of the acidic properties of its oxide, etc , it is undoubtedly metallic in its physical characteristics Thus, when obtained in a crystalline form it has a steely *metallic lustre* , it also possesses marked *metallic conductivity*, its electrical resistance being a little greater than that of arsenic or antimony, but less than that of bismuth It also dissolves freely in metals , from some of these, *e g* aluminium and silver, it crystallises unchanged , with others it combines to form SILICIDES such as $Mn_2Si$ $MnSi$, $Fe_2Si$, $FeSi$, etc

The element burns in oxygen to form silicon dioxide and is also attacked by chlorine It does not dissolve in any of the common acids except hydrofluoric acid, and is therefore used extensively in acid-resisting cast-iron , but it is attacked by steam and more rapidly by caustic alkalis, liberating hydrogen

$$Si + 2KOH + H_2O = K_2SiO_3 + 2H_2$$

## COMPOUNDS OF SILICON

**Silicon hydrides** —**Silicomethane** or **silicane**, $SiH_4$ (b -pt $-116°$), and small quantities of other silicon hydrides, such as **silicoethane**, $Si_2H_6$ (b -pt $+52°$), may be isolated by liquefying and distilling the gaseous product which is evolved when **magnesium silicide**, $Mg_2Si$, is attacked by hydrochloric acid

$$Mg_2Si + 4HCl = 2MgCl_2 + SiH_4$$

Pure silicomethane is a colourless gas with an unpleasant smell It burns readily in air and in chlorine (cf methane)

$$SiH_4 + 2O_2 = SiO_2 + 2H_2O ,$$

$$SiH_4 + 4Cl_2 = SiCl_4 + 4HCl$$

It decomposes into its elements above 400°, and reacts vigorously with alkalis giving hydrogen and a silicate

$$2NaOH + SiH_4 + H_2O = Na_2SiO_3 + 4H_2,$$

compare $2NaOH + B_2H_6 + 2H_2O = 2NaBO_2 + 6H_2$

**Silicon tetrafluoride**, $SiF_4$, is formed by the action of hydrofluoric acid on silica or a silicate,

$$4HF + SiO_2 \rightleftharpoons SiF_4 + 2H_2O ,$$

but it is more conveniently prepared by heating a mixture of powdered fluorspar and sand with strong sulphuric acid

$$2CaF_2 + 2H_2SO_4 + SiO_2 = SiF_4 + 2CaSO_4 + 2H_2O$$

The sulphuric acid removes water which otherwise reacts with the silicon tetrafluoride to form **silicic acid**, $Si(OH)_4$ and **silicifluoric acid**, $H_2SiF_6$

$$3SiF_4 + 4H_2O = 2H_2SiF_6 + Si(OH)_4$$

Silicon tetrafluoride is a pungent gas which does not burn, it reacts with a solution of hydrofluoric acid to form the fairly stable silicifluoric acid, and with ammonia to form a white crystalline compound, $SiF_4,2NH_3$

EXPT 17 **Preparation of silicon tetrafluoride**

Concentrated sulphuric acid, 200 c c , is poured down a thistle funnel on to a mixture of white sand (30 grams), and calcium fluoride (30 grams) in a 500 c c round-bottomed flask (Fig 41) The flask is heated on a sand bath, when gaseous silicon fluoride is evolved and bubbled through a thin layer of mercury in the bottom of a gas jar containing water The silicon

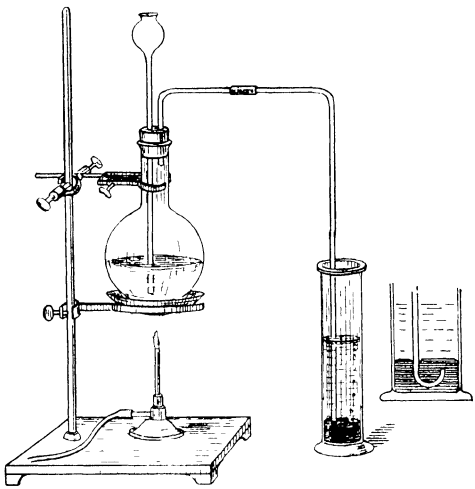


FIG 41 PREPARATION OF SILICON TETRAFLUORIDE

fluoride reacts with the water to give a solution of silicifluoric acid and a gelatinous mass of silicic acid, which must be stirred occasionally to liberate imprisoned gas bubbles The layer of mercury protects the end of the delivery tube from the water and so prevents it from becoming clogged with the gelatinous silicic acid Pure silica may be prepared from the gelatinous mass by washing it several times with water and then drying The solution, left after filtering off the silica, contains silicifluoric acid, which gives with barium chloride a white precipitate of barium silicifluoride, $BaSiF_6$, insoluble in dilute acids (cf barium sulphate)

**Silicon tetrachloride**, $SiCl_4$, is prepared by heating silicon in a stream of chlorine It is a colourless liquid which boils at 58° It is decomposed by water, giving silicic and hydrochloric acids

$$SiCl_4 + 4H_2O = Si(OH)_4 + 4HCl$$

**Silica or silicon dioxide**, $SiO_2$ —Silica exists in an amorphous form in flints, and in the crystalline state as quartz, tridymite and cristobalite It

is insoluble in water and does not act on indicators, but dissolves in alkalis, forming a series of silicates

$$2NaOH + SiO_2 = Na_2SiO_3 + H_2O$$

It is not attacked by acids, with the exception of hydrofluoric acid which converts it into gaseous silicon fluoride, $SiF_4$ (p 159) When heated in the electric furnace with sufficient carbon to remove only one-half of the oxygen, silica is converted into **silicon monoxide**, SiO

$$SiO_2 + C = SiO + CO$$

Under similar conditions, an excess of carbon gives the carbide, SiC, which is used as an abrasive under the name of CARBORUNDUM

Quartz is used for spectacle lenses since, owing to its great hardness, it is not easily scratched, and for lenses and prisms in optical apparatus because of its transparency to infra-red and ultra-violet light SILICA GLASS is obtained by fusing sand or quartz, and has the following properties

(i) It does not begin to soften until it is heated to 1500°, whereas ordinary chemical glass softens above 500°

(ii) Its coefficient of expansion is very small, less than 1/1,000,000 per degree It is therefore very resistant to sudden changes of temperature, *e g* it can be heated to redness and quenched in water without fracture For this reason silica glass is specially suited for experiments in which a transparent glass is required which will stand very high temperatures and rapid changes of temperature

(iii) It is quite free from alkali and very resistant to attack by acids It can therefore be used for delicate chemical operations in which complete freedom from alkalis is required, as well as for condensing nitric acid and concentrating sulphuric acid

(iv) It is very transparent, not only to visible light, but also to ultra-violet and infra-red radiations

**Silicic acid**, $SiO_2,xH_2O$, is the acid of which silica is the anhydride It has not been isolated in a crystalline form, but is obtained as a jelly, containing very variable proportions of water, by the action of acids on a soluble silicate, *e g*

$$Na_2SiO_3 + H_2SO_4 = H_2SiO_3 \text{ aq } + Na_2SO_4$$

It can be retained in solution in a colloidal form (p 644) and separated from soluble salts by diffusion through parchment, which retains the colloidal acid but allows the " crystalloid " salts to escape The colloidal solution, which is tasteless and has a slight acid reaction, coagulates readily, especially in the presence of multivalent cations, *e g* $Al^{+++}$

**Metallic silicates.**—Metallic silicates, with the exception of those of the alkali metals, are insoluble in water and difficult to prepare artificially, mainly because they melt to viscous liquids, which crystallise with extreme slowness even under the most favourable laboratory conditions

**Sodium silicate** or WATER GLASS, $Na_2SiO_3$, is prepared by fusing white sand with nearly double its weight of sodium carbonate in a reverberatory furnace

$$Na_2CO_3 + SiO_2 = Na_2SiO_3 + CO_2$$

The solution in water is strongly alkaline owing to hydrolysis and may be titrated against an acid using methyl orange as the indicator Sodium silicate is used as an adhesive, as a cement for joining broken surfaces of porcelain, as an adulterant of soap and in solution as a preservative for eggs

**Glass.**—Glass is a complex mixture of silicates, to which phosphates and borates are sometimes added The bases include the oxides of calcium, lead, barium, zinc, magnesium, aluminium, sodium, potassium iron and chromium, etc Thus common glass for bottles, windows, etc consists mainly of silica, soda and lime, whilst glass for chemical purposes may contain also alumina, zinc oxide and boric oxide Coloured glass is made by adding oxides which form coloured silicates, such as those of cobalt and chromium, which are blue and green respectively These constituents, *e g* sand, sodium carbonate or sulphate and calcium carbonate, are melted in pots or in tanks heated by producer gas

The essential property of a glass is that it solidifies gradually, *without crystallising*, to a transparent amorphous mass, which is completely "isotropic," *i e* which exhibits similar properties in all directions The viscosity of the glass shows no abrupt increase during cooling , the glass therefore passes through a plastic stage in which it can be shaped either by pressing or blowing, or it may be allowed to solidify and then reheated without showing any tendency to crystallisation.

# CHAPTER XV

## TIN AND LEAD

**Classification.**—The electronic structures of the elements tin and lead are represented by the following schemes

$$\begin{array}{lcccccccc} & & K & L & M & N & O & P \\ \text{Sn} & Z=50=2+8+18+18+ & 4, & & & & & \\ \text{Pb} & Z=82=2+8+18+32+18+4 & & & & & & \end{array}$$

The atoms contain four electrons less than the inert gases xenon, $Z=54$, and radon, $Z=86$ They might therefore be expected to show a negative valence of *four*, but the formation of quadruply-charged ions is so difficult that this function is probably non-existent, and the negative valency of these elements is shown only by electron-sharing As in the case of carbon and silicon, therefore, tin and lead are *quadricovalent* in many of their compounds Thus the tetrachlorides, $SnCl_4$ and $PbCl_4$, are obviously covalent since they are oily liquids like $CCl_4$ and $SiCl_4$ They are, however, soluble in water (with hydrolysis) and yield conducting solutions, probably as a result of hydration, *e g*

$$SnCl_4 + H_2O \rightleftharpoons [SnCl_3,H_2O]^+Cl^-, \text{ etc}$$

The metallic character of the elements, on the other hand, is clear evidence of a much greater tendency than in the case of carbon or silicon to *lose* electrons The loss of the outer incomplete shell of valency electrons would give an ion having the same number of electrons as palladium or platinum, instead of producing the electronic configuration of an inert gas There is therefore no strong tendency to form quadrivalent cations, and these are probably non-existent, like the quadrivalent anions discussed above On the other hand, tin and lead (like the transition elements of the first long period) very readily lose two electrons to form bivalent cations, $Sn^{++}$ and $Pb^{++}$, and thus yield well-defined series of STANNOUS AND PLUMBOUS SALTS The bivalent salts can be converted into quadrivalent STANNIC and PLUMBIC COMPOUNDS, which are no longer salt-like, and probably yield ions only by hydration as described above

**The properties of tin and lead.**—Tin and lead resemble one another in many respects, but they differ in that stannic compounds are usually more stable than stannous compounds, whilst the reverse is generally the case for the corresponding compounds of lead Thus stannous

salts readily oxidise on exposure to air and reduce mercuric salts to mercury, *e g*

$$SnCl_2 + HgCl_2 = SnCl_4 + Hg$$

On the other hand, plumbous salts are not reducing agents and can sometimes be prepared by heating the corresponding plumbic compound, *e g*

$$PbCl_4 \xrightarrow{\text{heat}} PbCl_2 + Cl_2$$

Tin and lead may also be compared with the elements antimony and bismuth which follow them in the periodic classification of the elements Thus plumbous oxide is more basic than stannous oxide, just as the sesquioxide of bismuth is more basic than that of antimony Table 13 summarises the chief properties of these four elements and shows that tin is more similar to lead than to the other elements

TABLE 13 —PROPERTIES OF TIN, ANTIMONY, LEAD AND BISMUTH

| | TIN | ANTIMONY | LEAD | BISMUTH |
|---|---|---|---|---|
| **Physical properties** | | | | |
| Density | 7 31 | 6 68 | 11 34 | 9 80 |
| Melting-point | 232° | 630° | 327° | 271° |
| Conductance, etc | Malleable and fair conductor of electricity | Brittle, but fair conductor | Like tin | Brittle and poor conductor |
| Electrovalence | +2 | +3 | +2 | +3 |
| Covalence | 4 | 5 (?) | 4 | 5 (?) |
| **Chemical properties** | Untarnished in air, but when heated burns to $SnO_2$<br>Readily soluble in conc HCl, and in dilute $HNO_3$ to give salts<br>Conc $HNO_3$ gives $SnO_2$ | Untarnished in air, but when heated burns to $Sb_2O_3$<br>Unaffected by dilute acids, but conc $HNO_3$ gives $Sb_2O_5$ (compare tin) | Tarnishes in air, burns mainly to PbO<br>Slowly soluble in conc HCl, easily soluble in dilute $HNO_3$ to give salts | Like Sb, forming $Bi_2O_3$<br>Unaffected by dilute acids, but conc $HNO_3$ gives $Bi(NO_3)_3$ and not the oxide |
| **Hydrides** | Gaseous, formed only in traces | Gaseous, $SbH_3$ is reasonably stable | Gaseous, formed only in traces | Gaseous, formed only in traces |
| **Chief oxides** | SnO, amphoteric<br>$SnO_2$, amphoteric, not an oxidising agent | $Sb_2O_3$, amphoteric<br>$Sb_2O_5$, acidic, oxidising agent | PbO, mainly basic, alkaline to litmus<br>$PbO_2$, amphoteric, oxidising agent | $Bi_2O_3$, mainly basic<br>$Bi_2O_5$, acidic, oxidising agent |
| **Sulphides** | SnS and $SnS_2$, precipitated in acid solution, soluble in $Am_2S_2$ | $Sb_2S_3$ and $Sb_2S_5$, precipitated in acid solution, soluble in $Am_2S_2$ | PbS, precipitated in acid solution, insoluble in $Am_2S_2$ | $Bi_2S_3$, very similar to PbS |
| **Chlorides** | $SnCl_2$, a white salt, hydrolysed by water<br>$SnCl_2 + H_2O \rightleftharpoons Sn(OH)Cl + HCl$ (precipitate)<br>$SnCl_4$, colourless fuming liquid, hydrolysed by much water, forms double salts, *e g* $(NH_4)_2SnCl_6$ | $SbCl_3$, a white salt, hydrolysed by water<br>$SbCl_3 + H_2O \rightleftharpoons SbOCl + 2HCl$ (precipitate)<br>$SbCl_5$, yellow fuming liquid, hydrolysed by water, forms double chlorides, *e g* $(NH_4)SbCl_6$ | $PbCl_2$, a white salt, not hydrolysed by water, in which it is sparingly soluble<br>$PbCl_4$, yellow fuming liquid, hydrolysed by water, forms double chlorides, *e g* $(NH_4)_2PbCl_6$ | $BiCl_3$, a white salt hydrolysed by water<br>$BiCl_3 + H_2O \rightleftharpoons BiOCl + 2HCl$ (precipitate)<br>Higher chlorides have not been isolated, but many double chlorides of $BiCl_3$ are known, *e g* $(NH_4)_3BiCl_6$ |

## 50 TIN Sn = 118 70

**Occurrence of tin.**—Tin is found occasionally in the native state, but the principal ore is the dioxide, CASSITERITE, or TINSTONE, $SnO_2$

**Preparation of tin.**—Tin may be prepared from ores which contain as little as 1% of the oxide The ore is first crushed and then washed with water to separate the heavy tin oxide from the lighter siliceous material The concentrated ore is roasted to remove arsenic and sulphur, and again washed to remove soluble oxidation products such as copper sulphate It is then mixed with anthracite and smelted in a reverberatory furnace (Fig 42, p 169)

$$SnO_2 + C = Sn + CO_2$$

In some processes the molten metal is tapped from the furnace on to a sloping hearth, when the tin flows away, leaving behind the less fusible impurities Alternatively, the crude product may be run into pots and stirred, when the impurities are preferentially oxidised and rise to the surface as a scum The purified product contains less than 1% of impurities, the chief of which is lead

**Properties of tin.**—(*a*) *Physical properties* —Tin is a white lustrous metal which melts at 232° It can exist in two allotropic modifications called **white tin** and **grey tin**, the transition temperature being 18° Below 18° the ordinary white tin of density 7 28 is liable to pass into grey tin of density 5 7, the change being accompanied by expansion and disintegration of the metal At ordinary temperatures the change is very slow, and may not set in for many centuries , but it is stimulated by inoculation with grey tin and is accelerated very considerably by cooling, *e g* to − 50 ° Several cases are on record in which ingots of tin, tin buttons, organ pipes, medals, pewter pots, etc , have been attacked by "tin plague" during severe winters The reverse change, which is accompanied by a marked contraction of the metal, takes place rapidly when hot water is poured over grey tin

(*b*) *Chemical properties* —Tin does not tarnish at ordinary temperatures, but when heated in air it is readily converted into white **stannic oxide**, $SnO_2$ It does not combine directly with nitrogen and carbon, and, like lead and bismuth, gives only minute traces of a **tin hydride**, presumably $SnH_4$, when reduced with hydrogen

Tin combines directly with chlorine to give **stannic chloride**, $SnCl_4$ It dissolves slowly in dilute, but rapidly in hot concentrated hydrochloric acid, giving hydrogen and a solution of **stannous chloride**, $SnCl_2$ The reaction between tin and nitric acid varies according to the conditions Cold dilute nitric acid gives mainly **stannous nitrate** and ammonium nitrate, but **stannic nitrate** and nitrous oxide, $N_2O$, are also formed

$$4Sn + 10HNO_3 = 4Sn(NO_3)_2 + NH_4NO_3 + 3H_2O.$$

Concentrated nitric acid oxidises tin to insoluble **β-stannic acid**, $H_2Sn_5O_{11},4H_2O$, which is decomposed by heat into stannic oxide and water Tin dissolves slowly in dilute sulphuric acid with evolution of

hydrogen, and in hot concentrated sulphuric acid with evolution of sulphur dioxide, to form **stannous sulphate** and some stannic sulphate (p 168).

$$Sn + H_2SO_4 = SnSO_4 + H_2,$$
$$Sn + 2H_2SO_4 = SnSO_4 + SO_2 + 2H_2O$$

Hot concentrated soda attacks tin (but not lead) very slowly, forming a stannite and hydrogen

$$Sn + NaOH + H_2O = NaHSnO_2 + H_2$$

(*c*) *Uses of tin* —Thin sheets of tin, known as TINFOIL or SILVER PAPER are used extensively for wrapping The "tins" used for packing biscuits, etc, consist of TINNED PLATE, made by dipping thin sheet steel, after cleaning or pickling it with acid, into molten tin covered with molten fat to prevent atmospheric oxidation The surface thus produced is brighter and cleaner than that of galvanised iron Unlike zinc, the tin has no protective action unless the surface of the iron is covered completely, since iron is more electropositive than tin Thus, when the iron is exposed, a galvanic cell is set up and the metal is dissolved more quickly than if no tin were present

$$Fe + 2H_2CO_3 = Fe(CO_3H)_2 + H_2$$

Zinc, on the other hand, is more electropositive than iron and is therefore preferentially dissolved

Tin is also used in the production of important alloys, such as BRONZE (Cu with 8 to 24% Sn), SOLDER (50% Sn, 50% Pb) and PEWTER (80% Sn, 20% Pb) TIN AMALGAM was formerly used for coating glass mirrors, but is now being replaced by silver The amalgam was prepared by the addition of mercury to a sheet of tinfoil, which was pressed against the surface of the glass so as to squeeze out the excess of mercury

## STANNOUS COMPOUNDS

**Stannous oxide**, SnO, may be prepared by heating stannous oxalate in the absence of air

$$SnC_2O_4 = SnO + CO_2 + CO$$

It is a dark grey substance, which dissolves in dilute acids to give stannous salts, and in alkalis to form STANNITES, which are said to be analogous to formates

$$SnO + NaOH = H\,SnO\,ONa \text{ (Sodium stannite)},$$

compare

$$CO + NaOH = H{\cdot}CO\,ONa \text{ (Sodium formate)}$$

The **hydroxide**, $Sn(OH)_2$, is precipitated by the addition of alkalis to stannous solutions, but dissolves in excess of alkali to give a stannite

**Stannous sulphide**, SnS, can be prepared by direct combination of tin and sulphur It is obtained as a brown precipitate by the action of sulphuretted hydrogen on a solution of stannous chloride

$$SnCl_2 + H_2S = SnS + 2HCl$$

Yellow ammonium sulphide converts it into stannic sulphide and thence into a soluble **ammonium thiostannate** (cf PbS)

$$SnS + (NH_4)_2S_2 = (NH_4)_2SnS_3$$

**Stannous chloride**, $SnCl_2$, is prepared by dissolving tin in hot concentrated hydrochloric acid It separates from solution as the **dihydrate**, $SnCl_2,2H_2O$, which is known as TIN-SALT. It dissolves in less than its own weight of water, but, unless some additional hydrochloric acid is added, a basic chloride is deposited on dilution

$$SnCl_2 + H_2O \rightleftharpoons Sn(OH)Cl + HCl$$

The solutions in hydrochloric acid contain the complex acid, $H_2SnCl_4$, of which salts have been isolated. The anhydrous salt, which may be prepared by heating tin in a current of hydrogen chloride, melts at 247° and boils at 603°, giving a vapour which contains $SnCl_2$ and $Sn_2Cl_4$

Stannous chloride, unlike plumbous chloride, is a powerful reducing agent, it will reduce mercuric chloride to mercurous chloride or mercury,

$$SnCl_2 + 2HgCl_2 = SnCl_4 + Hg_2Cl_2, \text{ or } Sn^{++} + 2Hg^{++} = Sn^{++++} + Hg_2^{++},$$

$$SnCl_2 + HgCl_2 = SnCl_4 + Hg, \text{ or } Sn^{++} + Hg^{++} = Sn^{++++} + Hg,$$

and ferric chloride to ferrous chloride,

$$SnCl_2 + 2FeCl_3 = SnCl_4 + 2FeCl_2, \text{ or } Sn^{++} + 2Fe^{+++} = Sn^{++++} + 2Fe^{++}$$

## STANNIC COMPOUNDS

**Stannic oxide**, $SnO_2$, occurs as CASSITERITE or TINSTONE in Cornwall and elsewhere It may be prepared by burning the metal in air or by oxidising it with concentrated nitric acid and igniting the precipitate of $\beta$-stannic acid It is insoluble in water and in concentrated acids, with the exception of sulphuric acid, which converts it into an unstable **stannic sulphate**

$$SnO_2 + 2H_2SO_4 = Sn(SO_4)_2 + 2H_2O.$$

Unlike $PbO_2$ it is not an oxidising agent When fused with caustic alkalis, stannic oxide is converted into soluble stannates, *e g* **sodium stannate**, $Na_2SnO_3$ On addition of dilute acids to solutions of stannates, an **$\alpha$-stannic acid**, $H_2SnO_3$, is precipitated, it differs from the $\beta$-acid in being slightly soluble in water, to which it imparts an acid reaction, and in dilute acids **$\beta$-Stannic acid**, $H_2Sn_5O_{11},4H_2O$, which is prepared by the action of moderately concentrated nitric acid on tin, gives **stannates** of the type, $Na_2Sn_5O_{11},4H_2O$, which are only sparingly soluble in water

**Stannic sulphide**, $SnS_2$, is obtained as a dirty yellow precipitate when hydrogen sulphide is passed into a solution of a stannic compound

$$SnCl_4 + 2H_2S = SnS_2 + 4HCl$$

It dissolves in ammonium and alkali sulphides, forming soluble **thiostannates**, *e g* $(NH_4)_2SnS_3$

**Stannic chloride**, $SnCl_4$, may be prepared by passing chlorine over tin heated in a retort, the apparatus is similar to that used in the preparation of phosphorus trichloride (Fig 61, p 216)

The product is a liquid (b -pt 114°), which is soluble in organic solvents such as alcohol and ether, and is therefore a covalent compound like $CCl_4$ Unlike the latter, it also dissolves in water, forming hydrates such as $SnCl_4,5H_2O$, which can be crystallised out, it is hydrolysed, however,

in dilute solutions and deposits **stannic hydroxide**, $Sn(OH)_4$ Stannic chloride combines with hydrogen chloride to form the complex **acid**, $H_2SnCl_6$, and with ammonium chloride and alkali chlorides to form complex salts such as **ammonium stannichloride** $(NH_4)_2SnCl_6$, which is used in dyeing under the name of PINK SALT

**Stannic sulphate**, $Sn(SO_4)_2$, and **stannic nitrate**, $Sn(NO_3)_4$, have been prepared in presence of the strong acids, but are rapidly decomposed by water

$$Sn(SO_4)_2 + 4H_2O = Sn(OH)_4 + 2H_2SO_4$$

**Estimation of tin.**—The estimation of tin depends on converting it into the dioxide, $SnO_2$ This can often be obtained by the direct action of nitric acid upon alloys of tin , thus copper coinage, which contains 4% of tin, leaves an insoluble residue of $\beta$-stannic acid, whilst the copper and zinc are dissolved Tin can be precipitated from solution as hydroxide by means of ammonia, or as sulphide by means of hydrogen sulphide , the products are then converted into the dioxide by ignition

## 82 LEAD Pb = 207 22

**History.**—Lead was probably known to the Egyptians some 3000 years ago and is frequently mentioned in the Old Testament The Romans realised that tin and lead were different bodies, since Pliny refers to plumbum nigrum (lead) and plumbum album (tin), and lead pipes dating from the Roman period have been discovered which were evidently used as conduits for water

**Occurrence** —Native lead has been found occasionally The principal ore is **lead sulphide** or GALENA, PbS, which is widely distributed throughout the world **Lead carbonate**, $PbCO_3$, also occurs as CERUSSITE, and **lead sulphate**, $PbSO_4$, as ANGLESITE

**Preparation.**—Galena is first partially oxidised by heating it in air on the hearth of a reverberatory furnace (Fig 42)

$$2PbS + 3O_2 = 2PbO + 2SO_2,$$
$$PbS + 2O_2 = PbSO_4$$

The mass is well raked to prevent clotting When half the ore is judged to be oxidised, the temperature is raised and the supply of air is cut off, when lead is produced by the following reactions

$$2PbO + PbS = 3Pb + SO_2,$$
$$PbSO_4 + PbS = 2Pb + 2SO_2$$

Lime is added to stiffen the slag and the molten lead is run off into pots In modern practice galena is usually oxidised in a reverberatory furnace to the oxide and sulphate , the product is then reduced in a blast furnace with coke, together with iron or iron ore to remove sulphur

$$2PbO + C = 2Pb + CO_2$$

The REVERBERATORY FURNACE (Fig 42) is used extensively in metallurgical and chemical operations, when it is desired to heat a material

without mixing it with the fuel, the chief feature of the furnace is the throwing down upon the hearth of the furnace the heat radiated from the roof, on which the flames from the fire (on left of Fig 42) impinge

Ores which contain silica, and which yield lead silicate on roasting, are reduced by carbon in the presence of lime

$$2PbSiO_3 + 2CaO + C = 2CaSiO_3 + CO_2 + 2Pb$$

The crude lead may contain silver, arsenic, antimony, bismuth, copper, iron and zinc, which render the metal hard All these impurities, except bismuth, copper and silver, are more easily oxidised than lead, and can be burnt out by heating the metal in a furnace, copper forms with lead a compound or alloy of high melting-point which separates in the scum, bismuth is eliminated with silver in the Pattinson process of desilverising lead (p 320)

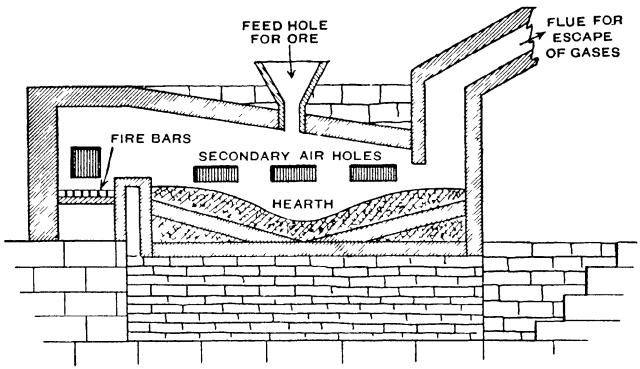



FIG 42 REVERBERATORY FURNACE

**Properties of lead.**—(*a*) *Physical properties* —Lead is a heavy metal of density 11 34 It is very soft and is so plastic that it can be squirted under pressure into the form of rods or pipes, it can also be rolled into sheets, which are used for roofing, and for lining vats, etc, in chemical plant, or into foil which is used for packing tea The freshly cut surface of lead possesses a bright lustre, although the metal is much darker than silver or tin, the clean metal can be cold-welded like gold, but the surface soon tarnishes and becomes dull on exposure to air Lead melts at 327°, and the eutectic alloy of lead and tin at 181°, mixtures of lead and tin are therefore used as solders Alloys of lead, tin, and bismuth, with or without cadmium, are used as fusible alloys Lead used for making lead shot is hardened by the addition of arsenic, whilst type metal consists of lead hardened by means of antimony Alloys, containing up to 1% of tellurium, are now used where harder and stronger lead is required, *e g* for resisting sulphuric acid in the lead chamber process and for pipes

(*b*) *Chemical properties* —Lead tarnishes in air, but the film of oxide which is formed protects it from further action The molten metal oxidises slowly in air to **litharge**, PbO, which on further roasting is converted into **red lead**, $Pb_3O_4$ Lead combines directly with chlorine to

form **lead chloride**, $PbCl_2$, and with sulphur to form **lead sulphide**, PbS It does not combine directly with carbon or nitrogen Like tin and bismuth it gives minute traces of a **hydride**, presumably $PbH_4$, when reduced

Lead is not attacked by pure water except in the presence of air, when it is slowly dissolved as **lead hydroxide**

$$2Pb + O_2 + 2H_2O = 2Pb(OH)_2$$

When carbon dioxide is also present, the hydroxide is converted into an unstable **lead bicarbonate**, $Pb(CO_3H)_2$ In the presence of mineral carbonates or sulphates, however, **lead carbonate** or **lead sulphate** is precipitated, the lead is therefore protected from further action, so that drinking water which is hard may safely be conducted through lead pipes

Like copper, lead is not readily attacked by non-oxidising acids in the absence of air, but, when air is present, it is rapidly corroded even by such weak acids as acetic and carbonic acid Dilute nitric acid readily dissolves lead with the liberation of nitric oxide, NO, and nitrous oxide, $N_2O$

$$3Pb + 8HNO_3 = 3Pb(NO_3)_2 + 2NO + 4H_2O,$$
$$4Pb + 10HNO_3 = 4Pb(NO_3)_2 + N_2O + 5H_2O,$$

but the concentrated acid is virtually without action on lead because lead nitrate is insoluble in it, and so forms a protective coating on the metal Conversely, lead is insoluble in dilute sulphuric acid but dissolves (like copper) in the hot concentrated acid, since the latter is an oxidising agent and can dissolve lead sulphate Like silver, lead is said to be attacked very slowly by concentrated hydrochloric acid with the liberation of hydrogen

Lead compounds, including many which are insoluble in water, are poisonous Poisoning may therefore result from the drinking of water containing lead or from the continual handling of compounds such as white lead The poison is cumulative, so that small doses, which have no immediate effect, may eventually prove fatal

## Compounds of Lead

**Plumbous and plumbic compounds.**—Lead forms two series of compounds, namely (i) PLUMBOUS COMPOUNDS, in which lead is electrovalent, since solutions in water yield the ion $Pb^{++}$, and (ii) PLUMBIC COMPOUNDS, in which the metal is generally quadricovalent like carbon Unlike plumbous salts, plumbic salts are usually difficult to prepare and readily decomposed by water

**Plumbous oxide** or LITHARGE, PbO (λίθος, a stone, ἄργυρος, silver), is obtained as a stony mass when lead is burnt to recover the silver from it In the laboratory it can be prepared most conveniently by heating lead nitrate

$$2Pb(NO_3)_2 = 2PbO + 4NO_2 + O_2$$

It is a heavy yellow compound of density 9 4 It dissolves slightly in water to give an alkaline solution of **plumbous hydroxide**, $Pb(OH)_2$ The latter is obtained as a white precipitate when an alkali is added to a plum-

bous salt Although this hydroxide is essentially basic in that it is alkaline to litmus and absorbs carbon dioxide from the air, yet it is feebly amphoteric because it dissolves in caustic alkalis to form plumbites, *e g* $NaHPbO_2$, or possibly $Na_2PbO_2$ These salts, however, are so unstable that they have not been isolated in the solid state

**Red lead**, $Pb_3O_4$, is obtained by roasting litharge in air for some hours at 400° It appears to be a compound of litharge, PbO, and lead dioxide, $PbO_2$, since it reacts with hot dilute nitric acid to give a solution of plumbous nitrate and a deposit of lead dioxide

$$Pb_3O_4 + 4HNO_3 = 2Pb(NO_3)_2 + PbO_2 + 2H_2O$$

When heated with concentrated hydrochloric acid, lead chloride is formed and chlorine evolved

$$Pb_3O_4 + 8HCl = 3PbCl_2 + Cl_2 + 4H_2O$$

Red lead is decomposed to litharge on heating strongly, and like all the other oxides of lead is easily reduced to the metal, *e g* when heated in a stream of hydrogen

**Plumbous nitrate,** $Pb(NO_3)_2$, the most important of the soluble salts of lead, is prepared by the action of dilute nitric acid on lead, or on the oxide or carbonate It crystallises without water of crystallisation and is consequently the most convenient nitrate to use for the preparation of nitrogen peroxide (p 194)

**Plumbous chloride,** $PbCl_2$, can be formed by the direct action of chlorine on lead, or by precipitation from a soluble salt of lead by the addition of hydrochloric acid, or of a soluble chloride It dissolves in hot water and crystallises out in needles on cooling , water dissolves 3% of the salt at 100° and 1% at 20° Lead chloride dissolves in concentrated hydrochloric acid owing to the formation of $H_2PbCl_4$, salts of which are known **Plumbous bromide**, $PbBr_2$, is very similar to the chloride, but **plumbous iodide,** $PbI_2$ is a yellow solid which is much less soluble in water ( 06% at 15° and 5% at 100°)

**Plumbous sulphide**, PbS, occurs naturally as GALENA It can be prepared by the direct combination of lead and sulphur, or by the action of hydrogen sulphide on a solution of a lead salt It is insoluble in cold dilute acids and in yellow ammonium sulphide (cf tin)

**Plumbous sulphate**, $PbSO_4$, cannot be prepared conveniently by the action of concentrated sulphuric acid on lead, but is precipitated by adding dilute sulphuric acid or a sulphate to a solution of a lead salt It is a heavy white substance, which is very sparingly soluble in water (1 part in 30,000), and is even less soluble in the presence of alcohol

**Plumbous acetate**, $Pb(O\,CO\,CH_3)_2,3H_2O$, prepared by the action of acetic acid on litharge, is an important soluble salt of lead It has a sweet taste and is therefore known as SUGAR OF LEAD In the middle ages it was used to sweeten sour wine (!), but, like all the soluble salts of lead, it is poisonous It is used in medicine as an eye-wash and in dyeing to precipitate chrome yellow (lead chromate) on cotton fibres

**Plumbous carbonate,** $PbCO_3$, occurs naturally as CERUSSITE, and may be prepared by passing carbon dioxide into a weak solution of lead acetate.

If a normal carbonate is added to a solution of a lead salt, a basic lead carbonate is precipitated The **basic carbonate**, $2PbCO_3,Pb(OH)_2$, prepared by the action of carbon dioxide on sheet lead, has been used from very early times as a pigment under the name of WHITE LEAD

In the Dutch process, rolls of sheet lead are placed in the upper portion of pots which are filled one-quarter full with vinegar (dilute acetic acid) These pots are arranged in tiers in special sheds and the intervening spaces are packed with dung Acetic acid is vaporised by the heat of the decaying dung and in the presence of air attacks the lead to form a basic lead acetate The fermentation of the dung liberates carbon dioxide which attacks the basic lead acetate forming the basic carbonate, white lead, and liberating acetic acid which then attacks more lead At the end of four or five weeks the white lead is separated from unchanged metal, ground, washed with water to remove soluble lead acetate, and finally dried The pigment prepared by this method has the advantage of very great covering power, and is the traditional basis for the majority of white and coloured paints, during the past fifty years it has been displaced in part by barytes, $BaSO_4$ (ground or precipitated, p 124), by zinc white or by lithopone (p 334), especially in France, where the use of lead paints has been prohibited on account of their poisonous properties Many attempts have been made to prepare white lead by more rapid methods, *e g* by precipitation These methods usually give rise to a coarse product, the covering power of which is inferior to white lead made by the old methods, some of the more recent processes have, however, achieved marked success in overcoming this fundamental difficulty

**The lead accumulator.**—The lead accumulator (Fig 43) consists of a series of *negative plates* containing finely-divided lead supported on a lead grid, a series of *positive plates* containing a paste of lead dioxide mounted in a lead grid, and an *electrolyte* consisting of pure sulphuric acid diluted with water to about 30% strength The discharge of the cell may be represented by the equation,

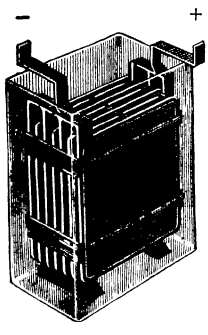



FIG 43 LEAD ACCUMULATOR

The cell shown has four negative and three positive plates

$$Pb + 2H_2SO_4 + PbO_2 = PbSO_4 + 2H_2O + PbSO_4,$$

and the charging of the cell by a reversal of this equation The action is, however, probably more complex, in particular, the normal product of discharge cannot be a fully-formed crystalline lead sulphate, since this is not reduced and oxidised to Pb and $PbO_2$ on recharging the cell, but appears as white patches on the plates in cells in which SULPHATING has taken place This formation of lead sulphate is most likely to occur when the cell is discharged, and the risk of sulphating is the principal factor which prevents the use of a higher concentration of sulphuric acid to increase the voltage and capacity of the cell

**Plumbic oxide** or **lead dioxide**, $PbO_2$, the oxide from which the PLUMBIC COMPOUNDS are derived, is prepared most readily by heating red lead with dilute nitric acid, when a colourless solution of lead nitrate and a brown

residue of lead dioxide are obtained The dioxide is washed with hot water and dried at 100°

$$Pb_3O_4 + 4HNO_3 = 2Pb(NO_3)_2 + PbO_2 + 2H_2O$$

It can also be prepared by heating litharge with potassium chlorate or with a suspension of bleaching powder in water

Lead dioxide is stable up to 300°, but decomposes into litharge and oxygen at higher temperatures Unlike stannic oxide it is a powerful oxidising agent, *e g* it oxidises hot concentrated hydrochloric acid to chlorine, combines spontaneously with sulphur dioxide to form lead sulphate, and oxidises many organic compounds, including oxalic acid Thus the available oxygen in lead dioxide (and in red lead) may be determined either by the liberation of chlorine (p 424), or by warming with excess of oxalic acid in the presence of dilute nitric acid, and estimating the residual oxalic acid by oxidation with potassium permanganate (p 426)

$$PbO_2 + 4HCl = PbCl_2 + Cl_2 + 2H_2O,$$
$$PbO_2 + 2HNO_3 + (COOH)_2 = Pb(NO_3)_2 + 2CO_2 + 2H_2O$$

Lead dioxide is amphoteric, since it yields unstable PLUMBIC SALTS with acids and PLUMBATES when acted on by alkalis Thus caustic soda gives **sodium plumbate,** $Na_2PbO_3$,

$$2NaOH + PbO_2 = Na_2PbO_3 + H_2O,$$

whilst cold concentrated hydrochloric acid gives **plumbic chloride,** $PbCl_4$

$$PbO_2 + 4HCl = PbCl_4 + 2H_2O$$

The double salt, **ammonium plumbichloride,** $(NH_4)_2PbCl_6$, compare ammonium stannichloride, $(NH_4)_2SnCl_6$, can be prepared by saturating a solution of plumbous chloride in hydrochloric acid with chlorine at 0°, and adding ammonium chloride When the double salt is added to cold concentrated sulphuric acid, **plumbic chloride,** $PbCl_4$, separates as a yellow oil of density 3 2, which solidifies when cooled to −15° Plumbic chloride is decomposed by heat into plumbous chloride and chlorine, and by water, giving first an unstable hydrate and then lead dioxide and hydrochloric acid

$$PbCl_4 = PbCl_2 + Cl_2 \qquad PbCl_4 + 2H_2O = PbO_2 + 4HCl$$

**Plumbic acetate** or **lead tetracetate,** $Pb(O\,CO\,CH_3)_4$, prepared by heating red lead with acetic acid, crystallises from the filtrate in colourless prisms and melts at 175° It is much more stable than the salts of stronger acids, which are hydrolysed more readily to the oxide and free acid, probably owing to the greater affinity of the strong acids for the ionising solvent

**Lead tetra-ethyl,** $Pb(C_2H_5)_4$, is added to petrol as an anti-knock constituent

**Estimation of lead.**—Lead is estimated most readily by precipitating the sulphate by means of dilute sulphuric acid in the presence of alcohol The precipitate is granular and easily filtered, so that it is sometimes preferred to barium sulphate for the estimation of sulphates (p 442)

# CHAPTER XVI

## NITROGEN

| Atomic number | Element | Symbol | Atomic weight |
|---|---|---|---|
| 7 | NITROGEN | N | 14 008 |
| 15 | PHOSPHORUS | P | 30 98 |
| 33 | ARSENIC | As | 74 91 |
| 51 | ANTIMONY | Sb | 121 76 |
| 83 | BISMUTH | Bi | 209 00 |

**Classification.**—The atomic numbers of the five elements cited above are *three* less than those of the inert gases, neon, argon, etc These elements therefore form a natural family, but nevertheless exhibit the widest possible diversity of properties Thus nitrogen is a gas like oxygen, phosphorus is an inflammable solid like sulphur, whilst in arsenic, antimony and bismuth metallic properties are progressively developed The link which binds the five elements into one family is, as usual, their valency This gives rise to similarity of formulae, and often to isomorphism, even in compounds derived from elements such as nitrogen and bismuth which bear no resemblance whatever to one another In particular, the elements of the family can all complete their octets by sharing three pairs of electrons with hydrogen , they therefore exhibit a covalence of *three* in the hydrides, $NH_3$, $PH_3$, $AsH_3$, $SbH_3$, $BiH_3$, although the last compound is formed only in minute traces On account of the wide diversity of properties in the elements of this family, it is convenient to consider first the non-metals, *nitrogen* and *phosphorus*, and to describe the metallic elements, *arsenic*, *antimony* and *bismuth*, in a separate chapter

**Properties of nitrogen and phosphorus.**—The principal properties of nitrogen and phosphorus are set out in Table 14, together with those of arsenic, which are shown again in comparison with those of antimony and bismuth in Table 18 (p 220)

**Valency of nitrogen and phosphorus.**—(*a*) Nitrogen and phosphorus have an incomplete outer shell of five valency electrons Their chemical properties are therefore dominated by a tendency to complete the octet This may be done either by sharing three pairs of electrons with other atoms as in the tercovalent compounds

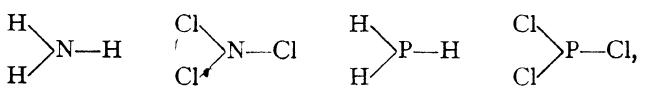


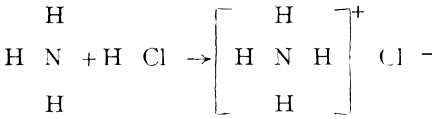
TABLE 14.—PROPERTIES OF NITROGEN, PHOSPHORUS AND ARSENIC

| | NITROGEN | PHOSPHORUS | ARSENIC |
|---|---|---|---|
| **Physical properties** | Gas | Transparent solid | Metallic solid |
| Melting-point | −210 5° | 44° (white phosphorus) | 814° (under pressure) |
| Boiling-point | −196° | 287° (white phosphorus) | 616° (sublimes) |
| Density | | 1 83 (white phosphorus) | 5 72 |
| Solubility | Slightly soluble in water | Readily soluble in $CS_2$ (white phosphorus only) | Soluble in metals |
| Molecule in vapour | $N_2$ | $P_4$ | $As_4$ |
| **Chemical properties** | Inert, but activated by electric discharge Oxidation is endothermic | Very active, but can be converted into less active allotropes Burns fiercely in air, oxidation is exothermic | Burns with a white smoke when heated, oxidation is exothermic |
| **Hydrides** | $NH_3$, basic gas | $PH_3$, feebly basic gas | $AsH_3$, neutral gas |
| | $N_2H_4$, basic liquid | $P_2H_4$, neutral liquid, burns spontaneously in air | |
| | $N_3H$, strong acid | | |
| **Oxides.** | $N_2O$ and NO, colourless, neutral, endothermic gases | $P_4O$ (?) | |
| | $N_4O_6$, blue ice, anhydride of $HNO_2$ | $P_4O_6$, colourless solid, anhydride of $H_3PO_3$ | $As_4O_6$, white solid, amphoteric |
| | $N_2O_4$, colourless ice, dissociating to brown gaseous $NO_2$, mixed anhydride of $HNO_2$ and $HNO_3$ | $(PO_2)$, colourless solid, mixed anhydride of $H_3PO_3$ and $H_3PO_4$ | $As_2O_4$, mixed acid anhydride of $H_3AsO_3$ and $H_3AsO_4$ |
| | $N_2O_5$, white solid, anhydride of $HNO_3$ | $P_4O_{10}$, colourless, hygroscopic solid, anhydride of $H_3PO_4$ | $As_4O_{10}$, white solid, anhydride of $H_3AsO_4$ |
| **Halides.** | $NCl_3$ and $NI_3$ are explosive, yield ammonia on hydrolysis, *e g* $NCl_3 + 3H_2O = NH_3 + 3HOCl$ | $PCl_3$ and $PCl_5$ are stable, yield acids on hydrolysis, *e g* $PCl_3 + 3H_2O = H_3PO_3 + 3HCl$ | $AsCl_3$, liquid hydrolysed reversibly by water, *e g* $2AsCl_3 + 3H_2O \rightleftharpoons As_2O_3 + 6HCl$ |
| **Metallic compounds** | Forms nitrides, *e g* $Li_3N$, $Ca_3N_2$ | Forms phosphides, *e g* $Ca_3P_2$, etc | Forms arsenides, *e g* NiAs, FeSAs |

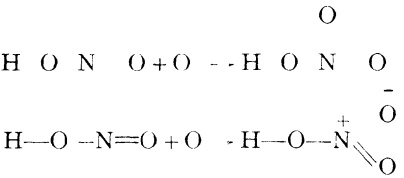
or less readily by accepting three electrons from a more electropositive element, as in the metallic nitrides and phosphides, which may be expected to have a salt-like or ionic structure, *e g* $Li_3^{+++}\ N^{---}$

(*b*) The converse process of shedding electrons in order to revert to an inert gas structure is not possible, since the atoms of both nitrogen and phosphorus would have to lose five electrons We therefore find that quinquevalent nitrogen and phosphorus cations do not exist

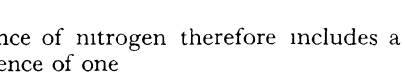
(*c*) In addition to its valency of three, nitrogen appears to have a valency of five in compounds such as nitric acid, $NO_2\ OH$, and the ammonium salts, *e g* $NH_4Cl$ The modern explanation of this is that the nitrogen atom, after it has built up a stable outer sheath of eight electrons by forming three covalent linkages, still has a lone pair of electrons which it can share with another atom Thus ammonia can accept a proton, $H^+$, from hydrochloric acid to form the ammonium ion, $NH_4^+$, together with the chloride ion of ammonium chloride



This interpretation is supported by experimental evidence, which indicates that a crystal of ammonium chloride is built up of ammonium ions, $NH_4^+$, and chloride ions, $Cl^-$ Similarly, nitrous acid, HO NO, can accept an oxygen atom to form nitric acid



or

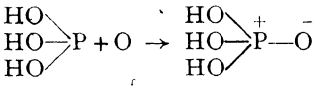


The quinquevalence of nitrogen therefore includes a covalence of four and an electrovalence of one

(*d*) Many of the quinquevalent compounds of phosphorus are similarly constituted to those of nitrogen Thus phosphine combines with hydrogen iodide to form the salt, phosphonium iodide,

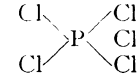
$$PH_3 + HI = [PH_4]^+\ I^- \quad \text{compare} \quad [NH_4]^+\ I^-$$

and phosphorous acid is readily oxidised to phosphoric acid .



Unlike nitrogen, the maximum covalence of phosphorus is not limited to *four* It is, therefore, possible that some of its quinquevalent compounds

are purely covalent, *e g* the halides may have the covalent structure I, rather than the salt-like structure II



I II $[PCl_4]^+Cl^-$

## 7 NITROGEN N = 14·008

**Occurrence of nitrogen.**—Nitrogen is present in the free state in air, of which it forms 78% by volume or 75½% by weight It also occurs in vegetable and animal tissues, mainly in the form of PROTEINS (p 765) Potassium nitrate is found as SALTPETRE as a product of oxidation of organic nitrogen in many soils, and very large deposits of sodium nitrate are found as CHILE SALTPETRE in desert soils in Chile

**The nitrogen cycle.**—Nitrogen is an essential constituent of vegetable and animal tissues A few leguminous plants can utilise atmospheric nitrogen, but most other plants depend on the presence in the soil of " fixed nitrogen " in the form of nitrates or ammonium salts When a plant dies, most of the organic nitrogen is liberated as ammonia by the bacteria which produce decay , in this form, it is returned to the soil, where " nitrifying bacteria " secure its oxidation to nitrates, so that the cycle is then complete

Animals, on the other hand, can only make use of nitrogen which has already been built up by plants into complex organic products, such as the proteins

Much of the nitrogen consumed by animals is returned to the soil when they eat crops on the fields, since only part of it is assimilated, the rest being excreted, *e g* in the form of urea (p 747), which is readily hydrolysed to ammonia and carbon dioxide

$$CON_2H_4 + H_2O = CO_2 + 2NH_3$$

The " denitrifying bacteria " of the soil make use of the oxygen of the nitrates, with the result that there is a constant loss of fixed nitrogen in the form of nitrogen gas , but this is more than counterbalanced by the washing down by rain of fixed nitrogen (mainly in the form of nitric acid), which is produced by the action of electric discharges in the air

In primeval times, the natural processes for the fixation of nitrogen, by leguminous plants and by lightning, led to a progressive accumulation of available nitrogen , but modern sewage works are responsible for the discharge of large quantities both of phosphates and of fixed nitrogen into the sea, where they are no longer available directly for terrestrial plants and animals This loss has been compensated (i) by rotation of crops, whereby corn, which depletes the soil of nitrogen, is followed by clover, which replenishes it with the aid of bacteria on the roots, (ii) by recovering ammonia as sulphate from the gas-liquors produced by the distillation of coal, whereby a part of the organic nitrogen of primeval forests is brought back again into circulation, (iii) by importing Chile

saltpetre, which may represent a concentration of nitrates washed out from fertile soils turned to desert, and thus rendered available for use in lands with an adequate rainfall, (iv) by fixation of atmospheric nitrogen, *e g* by the Haber process The modern processes for fixing atmospheric nitrogen are capable of indefinite expansion, and have put an end once for all to the risk of a shortage of nitrogeneous fertilisers , but no such comforting situation exists in reference to phosphates, since there is no similar inexhaustible reserve of this element available for exploitation

The various transformations of inorganic and organic nitrogen, which have been described above, are summarised diagrammatically in Fig 44

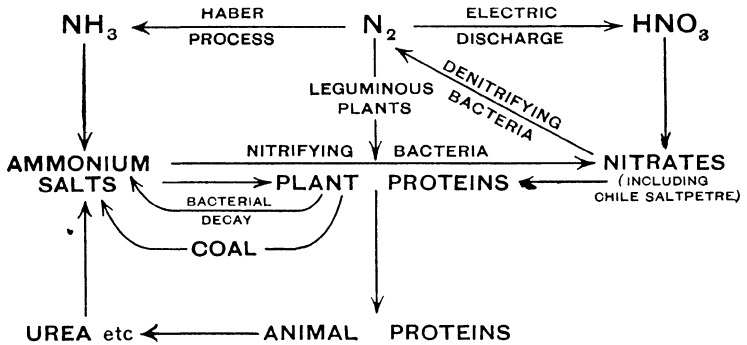



FIG 44 THE NITROGEN CYCLE

**Preparation of nitrogen.**—(*a*) *From air* —Crude nitrogen, containing about 1% of argon, may be prepared by passing dry air, freed from carbon dioxide by alkali, over heated copper turnings to remove the oxygen Nitrogen is prepared industrially by the distillation of liquid air (p 480) A mixture of nitrogen with hydrogen and oxides of carbon is produced on a very large scale for use in the Haber process by passing air and steam over red-hot coke (p 151)

(*b*) *From compounds of nitrogen* —Nitrogen, free from argon, can be prepared in the laboratory by mixing equimolar solutions of sodium nitrite and ammonium chloride, and heating to decompose the unstable ammonium nitrite which is formed by their interaction

$$(NH_4)NO_2 = N_2 + 2H_2O$$

Traces of chlorine may be removed by washing the gas with alkali, moisture and ammonia are removed with sulphuric acid, and the gas is then passed over heated copper to remove oxides of nitrogen

The best method of preparing nitrogen in the laboratory is to attack copper turnings with nitric acid (1 vol conc acid to 1 vol. water),

$$3Cu + 8HNO_3 = 3Cu(NO_3)_2 + 2NO + 4H_2O,$$

and pass the resulting nitric oxide over heated copper filings :

$$2Cu + 2NO = 2CuO + N_2.$$

**Physical properties of nitrogen.**—Nitrogen is a colourless, odourless gas, which condenses to a liquid that boils at $-196°$, and freezes to a colourless solid melting at $-210.5°$

The gas is sparingly soluble in water, which dissolves 2% of its volume of the gas at 8°, as compared with 4% of oxygen

**Chemical properties of nitrogen** —Gaseous nitrogen is a very inactive substance, which does not interact with any of the ordinary chemical agents at atmospheric temperatures, although it has been stated that traces of ammonium nitrite are produced by direct combination of nitrogen with water in sunlight

$$N_2 + 2H_2O = (NH_4)NO_2$$

This inactivity is attributed to the strength of the bonds by which the two atoms of nitrogen are united in the molecule, since atomic nitrogen and ammonia are much more active At higher temperatures, nitrogen combines with hydrogen to form ammonia (p 180), with oxygen to form oxides of nitrogen (p 191), with metals to form nitrides, *e g* $Mg_3N_2$, $Li_3N$, etc , and with calcium carbide to form cyanamide, CaNCN (p 181)

**Active nitrogen** —When nitrogen under low pressure is submitted to the action of a condensed electric discharge, about 2% of the gas is transformed into active nitrogen, which will combine directly with non-metals such as sulphur and iodine and with many metals The special activity of the product is due to the presence of atoms and activated molecules of nitrogen

## Compounds of Nitrogen

**Hydrides of nitrogen** —Nitrogen forms the following series of hydrides

Ammonia, $NH_3$
Hydrazine, $N_2H_4$
Azoimide or hydrazoic acid, $N_3H$
Ammonium azide, $NH_3 + N_3H = N_4H_4$
Hydrazine azide, $N_2H_4 + N_3H = N_5H_5$

**Preparation of ammonia.**—(*a*) *From ammonium salts* —Ammonia is usually prepared in the laboratory by heating an intimate mixture of ammonium chloride (one part) and slaked lime (three parts) (Fig 45)

$$Ca(OH)_2 + 2NH_4Cl = 2NH_3 + CaCl_2 + 2H_2O$$

It can also be prepared from other ammonium salts by the action of lime or an alkali It is dried by quicklime

(*b*) *From gas liquor* —When organic materials, such as peat, wood or coal, are distilled, a large proportion of the nitrogen escapes in the form of ammonia Many tons are thus obtained from the aqueous GAS-LIQUOR produced by the distillation of coal (p 149) The ammonia is distilled out, after adding a little lime to the solution to decompose any ammonium salts that may be present, and is then combined with sulphuric acid and put on the market, mainly for use as a fertiliser, in the form of **ammonium sulphate** :

$$2NH_3 + H_2SO_4 = (NH_4)_2SO_4$$

(*c*) *From nitrogen and hydrogen* —Ammonia is formed when nitrogen and hydrogen are heated together in the presence of a catalyst

$$N_2 + 3H_2 \rightleftharpoons 2NH_3 + 2 \times 12{,}000 \text{ calories}$$

Le Chatelier's principle (p 558) tells us that, since the action takes place with contraction of volume and is exothermic, the yield of ammonia will

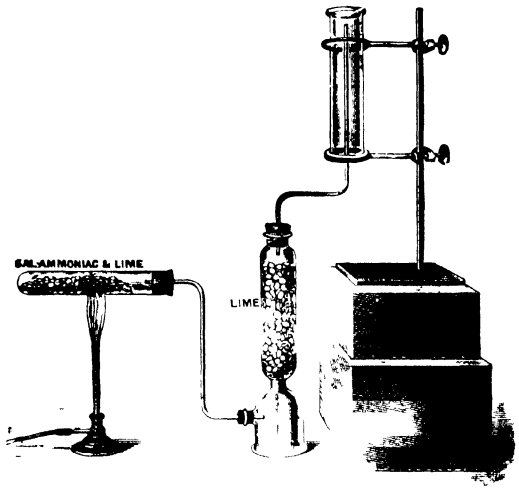



FIG 45 PREPARATION OF AMMONIA FROM SAL-AMMONIAC
The gas is dried with quicklime and collected in an inverted gas-jar

be increased by pressure and decreased by rise of temperature The final yields at equilibrium are set out in Table 15.

TABLE 15 —COMBINATION OF NITROGEN AND HYDROGEN

| Temperature | Equilibrium percentage of ammonia at | | | |
|---|---|---|---|---|
| | 1 atm | 50 atm | 100 atm | 200 atm |
| 450° | 0 24 | 9 5 | 16 2 | 25 3 |
| 500° | 0 13 | 5 7 | 10 4 | 17 6 |
| 550° | 0 08 | 3 7 | 6 9 | 12 0 |
| 600° | 0 05 | 2 3 | 4 5 | 8 2 |

Although a higher proportion of ammonia is obtained at 450°, the action is so slow that the working temperature has been fixed at 550°, as this gives a maximum output of ammonia from a given weight of catalyst In the HABER PROCESS (Fig 46) a yield of 12% is obtained by working under a pressure of 200 atmospheres

The ammonia is condensed to a liquid by cooling, or is absorbed under pressure by water The residual gases are dried, if necessary,

and recirculated with more nitrogen and hydrogen The ammonia is converted into ammonium sulphate by combination with carbon dioxide (see below) followed by double decomposition of the carbonate with anhydrite (calcium sulphate)

$$(NH_4)_2CO_3 + CaSO_4 = CaCO_3 + (NH_4)_2SO_4.$$

An appropriate mixture of gases can be prepared by the action of coke on air and steam (p 152) This yields a mixture of atmospheric nitrogen with hydrogen, carbon monoxide, and carbon dioxide

$$C + O_2 = CO_2, \quad C + CO_2 = 2CO, \quad C + H_2O = CO + H_2$$

The carbon monoxide is oxidised by steam (p 72) according to the equation,

$$CO + H_2O = H_2 + CO_2,$$

yielding an additional quantity of hydrogen The carbon dioxide is absorbed by water when the gaseous mixture is compressed prior to

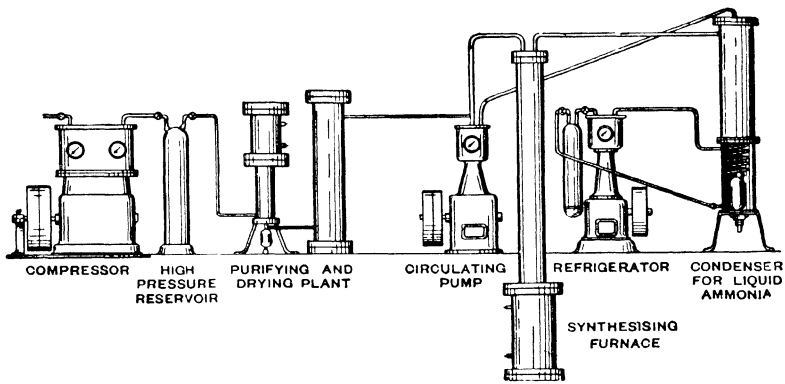



FIG 46 HABER'S PROCESS FOR SYNTHESIS OF AMMONIA
(*Chemical Age*, after Maxted )

catalysis, and is used subsequently to convert the ammonia into ammonium carbonate The unchanged carbon monoxide is absorbed by ammoniacal cuprous salts

The best catalyst appears to be metallic iron, but this must be specially prepared and purified to free it from traces of sulphur, and is usually activated by the addition of metals such as molybdenum

(*d*) *From cyanamide* —Ammonia can also be prepared commercially by the hydrolysis of calcium cyanamide (p 118)

$$CaCN_2 + 3H_2O = CaCO_3 + 2NH_3$$

The black powder is wetted to decompose any unchanged calcium carbide, and is hydrolysed in autoclaves holding 6 tons of water and 3 tons of cyanamide Steam is passed in under a pressure of 3 atmospheres, and any acetylene set free at this stage is allowed to escape , the ammonia is then driven out by increasing the pressure of steam gradually to 11 atmospheres and the temperature to 180°.

**Uses of ammonia.**—Very large quantities of ammonia are used in the manufacture of fertilisers, such as ammonium sulphate and phosphate, urea (p 747) and nitro-chalk (one part $CaCO_3$ to one part $NH_4NO_3$ by weight) Nitric acid, nitrates and nitrites (p 203) are also extensively manufactured by processes which depend upon the aerial oxidation of ammonia to oxides of nitrogen Liquid ammonia is used in refrigerators, as described below, it is also transported in cylinders and then "cracked" (*i e* decomposed into its elements) by an electrically heated catalyst in a "cracker" to give a cheap supply of hydrogen, which is suitable for welding, steel-cutting, etc, in spite of its dilution with 25% of nitrogen

**Physical properties of ammonia.**—Ammonia is a light, pungent gas It is the most soluble of all gases, 1300 volumes dissolving in one volume of water at 0° to give a 50% solution, the so-called 0 88 ammonia contains 35% $NH_3$ Ammonia condenses to a liquid boiling at $-33°$ under atmospheric pressure This liquid is used on a large scale in refrigerating plants The gas is liquefied by pressure (6 atm at 10°), the temperature being kept down by jacketing the compressors with cold water, the liquid is then allowed to vaporise under the low pressure caused by the suction of the compressors, and the cooling produced by the vaporisation is used for the preparation of ice, etc

**Chemical properties of ammonia.**—(*a*) *Addition* —The most important property of ammonia is the power which it possesses of uniting with acids to form ammonium salts, in which the AMMONIUM RADICAL, $NH_4$, plays the part of a univalent metal Thus it combines directly with hydrochloric and sulphuric acids to form ammonium chloride and ammonium sulphate

$$NH_3 + HCl = NH_4Cl,$$
$$2NH_3 + H_2SO_4 = (NH_4)_2SO_4$$

When ammonia is dissolved in water it appears to form a hydrate which is partially dissociated into ammonium and hydroxyl ions

$$NH_3 + H_2O \rightleftharpoons (NH_4)OH \rightleftharpoons NH_4^+ + OH^-$$

The solution contains free ammonia, which can be recognised by its strong ammoniacal smell or by extraction from the solution by chloroform The existence of free hydroxyl ions in aqueous ammonia is shown by (i) the alkalinity, (ii) the enhanced conductivity of the solution, (iii) its power of precipitating many metallic hydroxides, *e g*

$$CuSO_4 + 2(NH_4)OH = Cu(OH)_2 + (NH_4)_2SO_4$$

Two solid hydrates, with the composition of **ammonium hydroxide** $NH_3,H_2O$ or $(NH_4)OH$, and **ammonium oxide**, $2NH_3,H_2O$ or $(NH_4)_2O$ have been crystallised out at low temperatures from aqueous ammonia

Ammonia combines with carbon dioxide to form **ammonium carbamate** $NH_2\,CO\,ONH_4$, but in the presence of water **ammonium carbonate** $(NH_4)_2CO_3$, is formed It also unites with a large number of metallic salts to form addition compounds such as

$$CaCl_2,8NH_3, \quad NiCl_2,6NH_3, \quad CoCl_3,6NH_3, \text{ etc}$$

Some of these AMMINES are remarkably stable

(*b*) *Substitution*—(i) Liquid ammonia dissolves metallic sodium and potassium, probably forming loose *addition* compounds such as $NH_3Na$ and $NH_3K$ When, however, ammonia gas is passed over heated sodium or potassium, *substitution* takes place, hydrogen is liberated and the ammonia becomes fixed in the form of **sodamide,** $NaNH_2$, or **potassamide,** $KNH_2$ It should be noted that in this action hydrogen is displaced by a metal, and that ammonia gas, unlike aqueous ammonia, here displays acid rather than basic properties **Sodamide,** $NaNH_2$, is a white substance, which melts at 155° and sublimes at 400° with slight decomposition It is hydrolysed by water, forming ammonia and caustic soda

$$NaNH_2 + H_2O = NaOH + NH_3$$

Sodamide is used as a reagent in the laboratory and in manufacturing operations, often as a substitute for metallic sodium

(ii) By the action of an excess of chlorine, ammonia is converted into **nitrogen trichloride,** $NCl_3$

$$NH_3 + 3Cl_2 = NCl_3 + 3HCl$$

This is an oily liquid which detonates violently on the slightest provocation The violent explosion of this compound must be attributed to the affinity of chlorine atoms for chlorine atoms and of nitrogen atoms for nitrogen atoms, since the only products formed are the molecules of these elements

$$2NCl_3 = N_2 + 3Cl_2$$

When ammonia is in excess, chlorine merely removes the hydrogen and liberates one-third of its volume of nitrogen

$$8NH_3 + 3Cl_2 = N_2 + 6NH_4Cl$$

This action is sometimes used to demonstrate the volumetric composition of ammonia (p 184)

(iii) Iodine reacts with an aqueous solution of ammonia to form an explosive black compound, $NH_3.NI_3$, generally described as **nitrogen iodide,** but the real tri-iodide, $NI_3$, has also been prepared

(*c*) *Oxidation*—Ammonia will not ignite in air, but burns in oxygen with a yellow flame, forming water and nitrogen

$$4NH_3 + 3O_2 = 2N_2 + 6H_2O.$$

A similar oxidation takes place when ammonia is passed over heated copper oxide

$$2NH_3 + 3CuO = N_2 + 3H_2O + 3Cu$$

When, however, a mixture of ammonia and air is passed over red-hot platinum gauze, nitric oxide is produced as described on p 196

**Formula of Ammonia.**—When 2 volumes of ammonia are sparked for some hours in a eudiometer the volume is almost doubled (a little $NH_3$ remains) If a known excess of oxygen is then added and the mixture sparked, a contraction of $4\frac{1}{2}$ volumes occurs, two-thirds of this is due

to hydrogen, namely 3 volumes, so that the nitrogen occupies one volume, hence

1 vol nitrogen + 3 vols hydrogen = 2 vols ammonia

Applying Avogadro's hypothesis we may write

1 mol nitrogen + 3 mols hydrogen = 2 mols ammonia.

The molecules of nitrogen and hydrogen are diatomic,

$$N_2 + 3H_2 = 2 \text{ mols ammonia} = 2NH_3$$

This formula is in agreement with the relative density of ammonia, namely 8 5 (M Wt = 17)

The ratio of hydrogen to nitrogen in ammonia can also be determined by Hofmann's method A glass tube (Fig 47) is filled with chlorine gas, and strong ammonia from the cup at the top of the tube is allowed to enter in small portions by turning the tap The action is at first vigorous, each drop of ammonia producing a flash of light Excess of ammonia is added, and water is then allowed to enter freely from the cup The water enters until it occupies two-thirds of the tube, the residual gas being nitrogen Since chlorine combines with its own volume of hydrogen, 1 volume of nitrogen must be combined with 3 volumes of hydrogen in ammonia

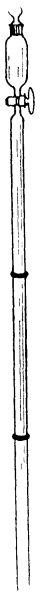


FIG 47 TUBE FOR DEMONSTRATING THE VOLUMETRIC COMPOSITION OF AMMONIA

$$\underset{3 \text{ vols}}{8NH_3} + \underset{1 \text{ vol}}{3Cl_2} = N_2 + 6NH_4Cl$$

**Detection and estimation of ammonia.**—Ammonia can be detected qualitatively by its smell, and by the formation of a white fume with gaseous hydrogen chloride Traces of ammonia in solution can be detected and estimated colorimetrically by means of NESSLER'S REAGENT, an alkaline solution of **potassium mercury iodide**, $K_2HgI_4$, which gives with ammonia a brown precipitate of the composition, $NHg_2I,H_2O$ Larger quantities of ammonia are estimated by titration against an acid (p 417) For this purpose the ammonia may be distilled over into a standard acid and the excess of acid estimated ; or the ammonium salt may be boiled with a standard alkali to remove the ammonia and the excess of alkali titrated

**Ammonium salts.**—When ammonia unites with acids, it forms salts, which are often isomorphous with those of the alkali metals, in spite of the fact that the metallic atom has been replaced by a group of 5 non-metallic atoms This can be explained by the fact that the ammonium ion has the same electronic shell as a sodium ion Its shell is, however,

expanded by the inclusion of four protons, so that its radius (1 43 A U) approximates more closely to that of the potassium ion (1 33 A U) than to that of the sodium ion (0 98 A U) For this reason ammonium salts are more like potassium salts than sodium salts Thus, potassium and ammonium salts are usually less hydrated than the corresponding sodium salts, *e g* potassium and ammonium sulphates crystallise from water in the anhydrous state, whilst sodium sulphate separates as the decahydrate, $Na_2SO_4,10H_2O$ The solubility of potassium and ammonium salts are also often very similar, thus the chlorates, perchlorates and platinichlorides are all sparingly soluble, whilst the corresponding sodium salts are much more soluble

**Ammonium chloride** or SAL-AMMONIAC, $NH_4Cl$, was first obtained as a sublimate from the distillation of camels' dung It can be prepared either by distilling a mixture of common salt and ammonium sulphate, when ammonium chloride volatilises,

$$(NH_4)_2SO_4 + 2NaCl = 2NH_4Cl + Na_2SO_4,$$

or by neutralising the ammoniacal liquor from gas works with hydrochloric acid It is also produced in very large quantities as an intermediate product in the Solvay process (p 100).

Ammonium chloride has a sharp saline taste, which is quite distinct from that of common salt It dissolves readily in water, producing a marked lowering of temperature When heated, it sublimes without melting and is dissociated into a mixture of ammonia and hydrogen chloride,

$$NH_4Cl \rightleftharpoons NH_3 + HCl,$$

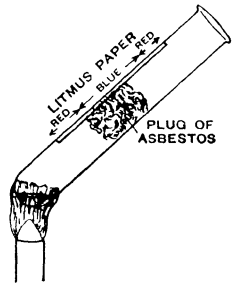



FIG 48 DISSOCIATION OF AMMONIUM CHLORIDE

Vapour-density measurements (p 525) show that about 65% of the ammonium chloride is dissociated at 330° C and 760 mm, and that the dissociation is virtually complete at 400° C

The dissociation of ammonium chloride may be demonstrated very easily by means of the apparatus shown in Fig 48 A fragment of the salt is heated in a test tube provided with a piece of damp red litmus-paper held in place by a plug of asbestos The ammonia produced by the dissociation of the salt diffuses up the tube more rapidly than the hydrogen chloride, the litmus inside the plug therefore turns blue On further heating, the litmus inside the plug becomes red again, owing to the progressive escape of ammonia, whilst a blue colour appears opposite the plug and extends gradually almost to the top of the tube

**Ammonium sulphide**, $(NH_4)_2S$, can be prepared by saturating one-half of a quantity of ammonia-liquor with sulphuretted hydrogen, thus forming **ammonium hydrosulphide**, $(NH_4)SH$, which is then converted into the sulphide by adding the other portion of ammonia

$$NH_3 + (NH_4)SH = (NH_4)_2S$$

Both the hydrosulphide and sulphide are gradually oxidised by air to **polysulphides**, *e g* $(NH_4)_2S_2$, which are further oxidised to thiosulphate and sulphate The yellow ammonium sulphide used in qualitative

analysis is a mixture of polysulphides prepared by allowing the sulphide to oxidise

**Ammonium sulphate**, $(NH_4)_2SO_4$, is prepared industrially on a large scale by passing ammonia from the " aqueous liquor " of gas works or coke-ovens into sulphuric acid Large quantities are also produced from synthetic ammonia by conversion into the carbonate, followed by double decomposition with calcium sulphate (p 181)

Ammonium sulphate is readily soluble in water, but separates without water of crystallisation The anhydrous salt is isomorphous with potassium sulphate. When crystallised from sulphuric acid or when partially decomposed by heat, it yields the **acid sulphate**, $(NH_4)HSO_4$

Ammonium sulphate is used very largely as a fertiliser in agriculture, and is the source from which ammonia and other ammonium salts are commonly prepared

**Ammonium nitrate**, $(NH_4)NO_3$ —Ammonium nitrate can be prepared by neutralising nitric acid with ammonia, and is manufactured by a modification of the Ostwald process (p 196)

$$2NH_3 + 2O_2 = (NH_4)NO_3 + H_2O$$

It can also be manufactured from ammonium sulphate by double decomposition with calcium or sodium nitrate In the former case, calcium sulphate is precipitated in the latter case, sodium sulphate crystallises out first from the hot solution and ammonium nitrate separates on cooling

$$(NH_4)_2SO_4 + 2NaNO_3 = Na_2SO_4 + 2(NH_4)NO_3$$

Ammonium nitrate is very soluble in water, which dissolves 11 times its weight of the salt at 100° and 1 2 times at 0° The molten salt decomposes at about 220° to nitrous oxide and water

$$NH_4NO_3 = N_2O + 2H_2O$$

It is not explosive under ordinary conditions, but when stored in bulk it is liable to detonation, with disastrous results High explosives can be prepared by mixing ammonium nitrate, (i) with charcoal or wood meal, (ii) with aluminium, as in AMMONAL, or (iii) with trinitrotoluene (p 779), as in AMATOL

(i) $C + NH_4NO_3 = N_2 + CO + 2H_2O$,

(ii) $2Al + 3NH_4NO_3 = 3N_2 + 6H_2O + Al_2O_3$,

(iii) $2C_6H_2(NO_2)_3CH_3 + 7NH_4NO_3 = 10N_2 + 14CO + 19H_2O$

**Ammonium nitrite**, $(NH_4)NO_2$, is very unstable and readily decomposes into nitrogen and water It is prepared in solution by mixing equimolecular quantities of sodium nitrite and ammonium chloride, but can be isolated in the solid state by evaporating in a vacuum at 60°

$$NH_4Cl + NaNO_2 = NH_4NO_2 + NaCl$$

**Ammonium carbonate** or SAL VOLATILE, $(NH_4)_2CO_3$, is prepared by subliming a mixture of chalk and ammonium sulphate,

$$(NH_4)_2SO_4 + CaCO_3 = (NH_4)_2CO_3 + CaSO_4,$$

but the product always contains some bicarbonate, $(NH_4)HCO_3$, and carbamate, $NH_2 CO ONH_4$

**Hydrazine and its salts.**—**Hydrazine**, $N_2H_4$, is a weak diacidic base derived from ammonia by splitting off one-third of its hydrogen This conversion can be effected by RASCHIG'S PROCESS, by adding sodium hypochlorite, NaOCl, to strong ammonia containing 0 2% of glue, and concentrating to a small volume , on adding sulphuric acid, **hydrazine sulphate**, $N_2H_4,H_2SO_4$, separates in colourless rhombic crystals In this process the hydrazine is derived from an unstable chloroamine, $NH_2Cl$

$$NH_3 + NaOCl = NH_2Cl + NaOH,$$
$$NH_3 + NH_2Cl + NaOH = NH_2 \quad NH_2 + NaCl + H_2O$$

The glue protects the hydrazine by eliminating traces of copper salts, which catalyse its oxidation by hypochlorite to gaseous nitrogen

**Hydrazine hydrate**, $N_2H_4,H_2O$, is prepared by distilling a salt of hydrazine with a caustic alkali in a silver or platinum vessel

$$N_2H_4,H_2SO_4 + 2KOH = N_2H_4,H_2O + K_2SO_4 + H_2O$$

It is a colourless, fuming liquid which smells like ammonia, corrodes glass like the caustic alkalis, and destroys cork and indiarubber It boils at 119°, and has a density of 1 03 at 21°

**Hydrazine**, $N_2H_4$, is prepared by heating the hydrate with barium oxide

$$N_2H_4,H_2O + BaO = Ba(OH)_2 + N_2H_4$$

It is a colourless liquid, of which the physical constants differ very little from those of water, *e g* melting-point 1 4°, boiling-point 113 5°, and density 1 0114 at 15° It combines readily with water to form the hydrate, and with acids to form salts, *e g* $N_2H_4,2HCl$ It is a very powerful reducing agent, reducing alkaline cupric solutions to cuprous oxide, ferric salts to ferrous salts and iodine to hydriodic acid In all of these reactions the hydrazine is oxidised to nitrogen, *e g*

$$N_2H_4 + 2I_2 = N_2 + 4HI$$

**Hydrazoic acid** or **azoimide**, $N_3H$, may be prepared by distilling **sodium azide** (see below) with dilute sulphuric acid

$$NaN_3 + H_2SO_4 = N_3H + NaHSO_4$$

It is a colourless, mobile liquid with an unpleasant odour , it boils at 37° and often explodes at this temperature Its solution is strongly acid and it dissolves most of the metals with evolution of hydrogen

$$2HN_3 + Zn = Zn(N_3)_2 + H_2$$

**Sodium azide**, $NaN_3$, may be obtained by passing nitrous oxide over sodamide heated to 190°

$$2NaNH_2 + N_2O = NaN_3 + NaOH + NH_3$$

**Hydroxylamine**, $NH_2 OH$, is a colourless, crystalline substance which melts at 33° and readily decomposes into nitrogen, ammonia, and water.

$$3NH_2 OH = NH_3 + N_2 + 3H_2O.$$

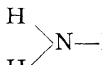
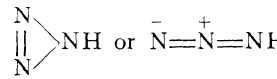
It is a monacidic base, combining with acids to form salts such as **hydroxylamine hydrochloride,** $NH_2OH,HCl$, which are powerful reducing agents This salt can be prepared by reducing nitric acid with tin and hydrochloric acid, and evaporating to crystallisation after removing the stannous chloride by means of sulphuretted hydrogen

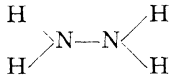
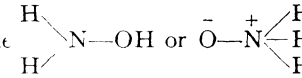
$$3Sn + HNO_3 + 6HCl = 3SnCl_2 + NH_2OH + 2H_2O$$

The free base is prepared by mixing the hydrochloride with sodium methoxide, $CH_3ONa$, in methyl alcohol (p 678), filtering from sodium chloride and evaporating to crystallisation

$$CH_3ONa + NH_2OH,HCl = CH_3OH + NaCl + NH_2OH$$

The structure of ammonia and its derivatives may be represented as follows

Ammonia  Hydrazoic acid 

Hydrazine  Hydroxylamine 

**Nitrogen and oxygen.**—The chief oxides and oxy-acids of nitrogen are

Nitrous oxide, $N_2O$ Hyponitrous acid, $H_2N_2O_2$
Nitric oxide, $NO$
Nitrous anhydride, $N_2O_3$ → Nitrous acid, $HNO_2$
Nitrogen peroxide, $NO_2$ or $N_2O_4$
Nitric anhydride, $N_2O_5$ → Nitric acid, $HNO_3$
Nitrogen trioxide, $NO_3$

**Nitrous oxide,** $N_2O$ —(*a*) *Preparation*—Nitrous oxide was prepared by Priestley in 1775 by the action of moistened iron filings on nitric oxide

$$2NO + Fe + H_2O = N_2O + Fe(OH)_2$$

It is generally made by cautiously heating ammonium nitrate in a hard glass test tube (Fig 49), and collecting the gas over hot water, since it is appreciably soluble in cold water

$$NH_4NO_3 \rightarrow N_2O + 2H_2O$$

The impurities present are moisture, nitrogen, nitric oxide and chlorine, the last is due to the presence of a little ammonium chloride in the nitrate The crude product may be purified by passing it through a solution of ferrous sulphate to remove nitric oxide, through caustic soda to remove chlorine and through concentrated sulphuric acid to remove moisture, the purified gas is then collected over mercury It is usual to stop heating when two-thirds of the nitrate has decomposed, otherwise nitrogen trichloride may be formed and cause a dangerous explosion

Very pure nitrous oxide may be obtained by mixing equimolar solutions of hydroxylamine hydrochloride and sodium nitrite

$$NH_2OH,HCl + NaNO_2 = NaCl + N_2O + 2H_2O.$$

(*b*) *Properties* —Nitrous oxide is a colourless gas with a faint but pleasant smell It liquefies at $-90°$, and dissolves in an equal volume of cold water at 6° , but the solution is neutral and the gas is recovered unchanged on warming

With the exception of its freezing-point, nitrous oxide resembles carbon dioxide very closely in its physical properties (cf p 144) This resemblance is attributed to the fact that the two compounds are ISOSTERIC, *i e* the molecules contain the same number of atoms and the same number of planetary electrons arranged in a similar manner, but differ in the distribution of the nuclear charges and masses The structure of the gas is therefore shown by the formula

$$\overset{+}{O}\quad N\quad \overset{-}{N} \text{ or } O{=}\overset{+}{N}{=}\overset{-}{N}, \text{ compare } O\quad C\quad O \text{ or } O{=}C{=}O,$$

where the central quadrivalent atom of nitrogen carries a positive charge as in $NH_4^+$, whilst the bivalent nitrogen is negative

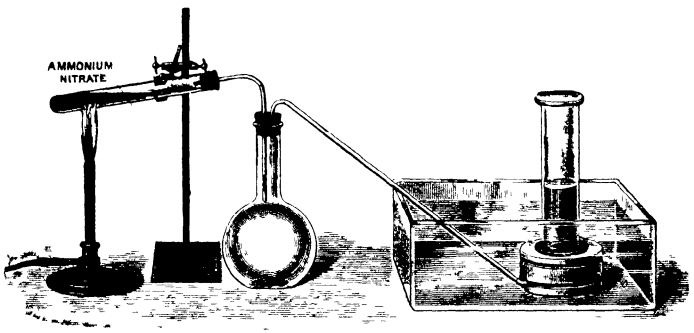



FIG 49 PREPARATION OF NITROUS OXIDE

Nitrous oxide is an endothermic compound

$$N_2 + \tfrac{1}{2}O_2 = N_2O - 20{,}600 \text{ cal}$$

It is readily decomposed above 600°, giving a mixture which is half as rich again in oxygen as air , it therefore resembles oxygen in its power of supporting combustion, and will relight a glowing splint It differs from oxygen, however, in the following respects

(i) Its density is greater in the ratio 22 16

(ii) It is much more soluble in cold water, but is not absorbed by alkaline pyrogallol

(iii) It has a faint but distinct smell

(iv) It does *not* give brown fumes of nitrogen peroxide when mixed with nitric oxide

(v) Its volume is not altered when phosphorus is allowed to burn in it

$$5N_2O + 2P = P_2O_5 + 5N_2$$

(*c*) *Composition* —(i) When an iron wire is heated electrically in nitrous oxide, oxygen is removed and the volume of gas remains unaltered,

showing that the gas contains its own volume of nitrogen, *i e* the formula is $N_2O_x$

(ii) If a mixture of nitrous oxide and electrolytic gas ($2H_2 + O_2$) is exploded in a eudiometer, the nitrous oxide is decomposed by the heat of the explosion into nitrogen and oxygen Two volumes of nitrous oxide are thus decomposed into three volumes, one of which can be shown to be oxygen by sparking with hydrogen, hence

$$2N_2O_x = 2N_2 + O_2, \qquad x = 1 \text{ and nitrous oxide} = N_2O$$

(iii) The density of nitrous oxide is 22, so that its molecular weight is about 44, in agreement with the formula $N_2O$

**Preparation of nitric oxide**, NO —(*a*) Nitric oxide is usually prepared in the laboratory by the action of copper turnings on cold dilute nitric acid

$$3Cu + 8HNO_3 = 3Cu(NO_3)_2 + 2NO + 4H_2O.$$

EXPT 18 **Preparation of nitric oxide (first method)**

Concentrated nitric acid (one part) is poured down a thistle funnel (Fig 50) into a flask containing copper turnings (one part) covered with a layer

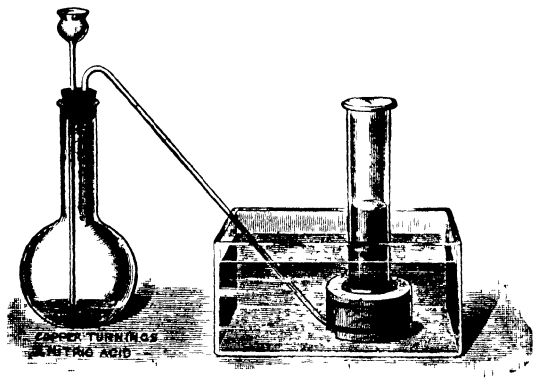



FIG 50 PREPARATION OF NITRIC OXIDE

of water The gas is collected over water, in which it is almost insoluble, whilst nitrogen peroxide (which is also formed) is dissolved The product can be freed from nitrogen, etc , by absorbing it in a strong solution of ferrous sulphate (when the dark brown compound, $FeSO_4,NO$, is formed) and separated in a pure state by heating this solution

(*b*) Pure nitric oxide can be prepared as the sole product of reduction of nitric acid by ferrous sulphate

$$2KNO_3 + 6FeSO_4 + 4H_2SO_4 = 2NO + 3Fe_2(SO_4)_3 + K_2SO_4 + 4H_2O$$

EXPT 19 **Preparation of nitric oxide (second method)**

Cold concentrated sulphuric acid is mixed with powdered potassium nitrate and a saturated solution of ferrous sulphate is poured upon the

mixture, this solution forms a separate layer on the top of the acid, and a brown ring develops between the two liquids (p 395) When the two layers are mixed together, heat is evolved and gaseous nitric oxide set free

(*c*) Quantitative yields of pure nitric oxide are obtained when mercury is shaken with potassium nitrate and concentrated sulphuric acid, as in the Lunge nitrometer (p 202)

$$6Hg + 2HNO_3 + 3H_2SO_4 = 3Hg_2SO_4 + 2NO + 4H_2O$$

(*d*) Nitric oxide was formerly prepared on a very large scale (as an intermediate stage in the manufacture of nitric acid) by the action of an electric discharge in air The oxidation is an endothermic process

$$N_2 + O_2 \rightleftharpoons 2NO - 2 \times 21{,}600 \text{ calories}$$

The proportion of nitric oxide at equilibrium therefore increases with rising temperature

TABLE 16.—OXIDATION OF NITROGEN AND DISSOCIATION OF NITRIC OXIDE

| | $N_2 + O_2$ | $\rightleftharpoons$ | 2NO |
|---|---|---|---|
| At 1500° | 99⅔% | | ⅓% |
| At 1930° | 99% | | 1% |
| At 2300° | 98% | | 2% |
| At 3000° (about) | 95% | | 5% |

In order to secure a maximum yield, it is necessary to heat the air to the highest possible temperature and then to fix the nitric oxide by cooling quickly to 1200°, below which temperature the nitric oxide is no longer liable to decompose The preparation of nitric oxide from nitrogen and oxygen is therefore in many respects analogous to the preparation of ozone from oxygen, but, as nitric oxide is far more stable than ozone, it is not necessary to chill the gas either so rapidly or to so low a temperature after heating it, and a much heavier electric discharge could therefore be employed Since the process is already obsolete, however, the furnaces used for this purpose need not be described

**Properties of nitric oxide.**—Nitric oxide is a colourless gas, when liquid it boils at −150° and freezes at −160° It is only sparingly soluble in cold water, which dissolves 6% of its volume at 8°, as compared with 4% of oxygen and 2% of nitrogen or hydrogen

It is freely soluble in solutions of ferrous salts, giving a dark brown liquid, which probably contains an unstable nitroso compound, *e g* $FeSO_4,NO$

Although nitric oxide (like nitrous oxide) is a strongly endothermic compound, it is stable up to a temperature of about 1000°, and therefore does not readily support combustion Thus burning charcoal and sulphur are extinguished when placed in the gas, but vigorously-burning phosphorus will continue to burn If a few drops of carbon disulphide are placed in a jar of the gas and the mixture is ignited with a taper, a brilliant flash is produced, which is very rich in active rays and was formerly used for "flash-light" photography

Nitric oxide is a neutral oxide like nitrous oxide, since it does not affe moist litmus or react with dilute alkalis to produce salts It readil combines with oxygen to form brown fumes of nitrogen peroxide,

$$2NO + O_2 = 2NO_2 ,$$

its smell and taste are therefore unknown Powerful oxidising agent such as potassium permanganate, oxidise nitric oxide to nitric acid

$$6KMnO_4 + 10NO + 9H_2SO_4 = 10HNO_3 + 3K_2SO_4 + 6MnSO_4 + 4H_2O$$

When the gas is heated with hydrogen in the presence of platinun reduction takes place and ammonia is formed

$$2NO + 5H_2 = 2NH_3 + 2H_2O$$

It is reduced by tin and hydrochloric acid to hydroxylamine (p 188), an to nitrous oxide by sulphurous acid

$$2NO + 3H_2 = 2NH_2 OH ,$$
$$2NO + H_2SO_3 = N_2O + H_2SO_4$$

Nitric oxide unites with chlorine in presence of charcoal to for **nitrosyl chloride,**

$$2NO + Cl_2 = 2NOCl,$$

and with bromine to form **nitrosyl bromide** and **nitrosyl tribromide**

$$2NO + Br_2 = 2NOBr, \qquad NOBr + Br_2 = NOBr_3$$

**Volumetric composition of nitric oxide** —Nitric oxide gives *half* its ow volume of nitrogen when the oxygen is removed by a red-hot iron wire

$$\underset{2 \text{ vols}}{2NO} + 2Fe = 2FeO + \underset{1 \text{ vol}}{N_2}$$

When reduced with heated charcoal it also gives half its volume of carbc dioxide

$$\underset{2 \text{ vols}}{2NO} + C = \underset{1 \text{ vol}}{N_2} + \underset{1 \text{ vol}}{CO_2}$$

The molecule of the gas therefore contains half a molecule each of nitroge and oxygen and has the formula NO This is in agreement with th density of the gas, which is 15 times as great as that of hydrogen, an is an arithmetic mean of the densities of nitrogen and oxygen

**Gravimetric composition of nitric oxide** —The gravimetric analysis nitric oxide, and hence the equivalent weight of nitrogen, was determine by Grav in 1905, by reducing the oxide with nickel and weighing bo the oxygen absorbed by the nickel and the nitrogen set free

The flask, *A* (Fig 51), was provided with a glass stopper, *B*, leadir through a stopcock to a capillary ground-glass joint, *D* A small plat num boat, *H*, containing finely-divided nickel, was surrounded by a cc of platinum wire, which could be heated to any desired temperature by a electric current, supplied through the stout platinum electrodes, *E* The bulb, *M*, containing charcoal and provided with a stopcock, could l connected with the bulb *A*, through the capillary ground-glass joints

*K* and *D* Air could be pumped out or nitric oxide admitted through the stopcock, *P*

The bulb, *A*, was weighed (i) empty, and (ii) filled with nitric oxide After burning the nickel in the boat, *H*, the nitrogen left in the bulb, *A*, was transferred to the bulb, *M*, by opening the two stopcocks (after pumping out the air between *K* and *D*) and then cooling the charcoal in *M* by

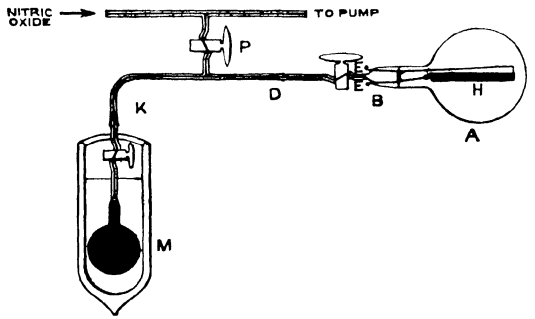



FIG 51 GRAY'S APPARATUS FOR DETERMINING THE GRAVIMETRIC COMPOSITION OF NITRIC OXIDE

liquid air The whole of the nitrogen was thus condensed on the charcoal and a vacuum was produced in the rest of the apparatus A third weighing of the bulb, *A*, gave the weight of oxygen which had been taken by the nickel from the nitric oxide, whilst the increase in the weight of the bulb, *M*, gave the weight of the nitrogen that had been set free, as shown in the equation

$$2NO + 2Ni = N_2 + 2NiO$$

In a typical experiment,

$$0.62103 \text{ gram of nitric oxide gave } \begin{cases} 0.33103 \text{ gram of oxygen,} \\ 0.28998 \text{ gram of nitrogen,} \end{cases}$$

whence 14.013 grams of nitrogen combine with 16 grams of oxygen to form 30.013 grams of nitric oxide

**Nitrous anhydride** or **nitrogen sesquioxide**, $N_2O_3$, may be prepared by distilling arsenious oxide with an equal weight of nitric acid (60%) and condensing the vapours evolved in a glass worm cooled by a mixture of ice and salt

$$As_2O_3 + 2HNO_3 = As_2O_5 + N_2O_3 + H_2O$$

Nitrogen trioxide condenses to blue crystals which melt at $-103°$, but like nitrogen peroxide (see below) it begins to dissociate as soon as it melts

$$2N_2O_3 \rightleftharpoons 2NO + N_2O_4$$

The blue colour persists almost up to 0°, after which the colourless $N_2O_4$ begins to dissociate into *brown* $NO_2$, and the *blue* colour of the liquid turns to *green* In the gaseous state dissociation appears to be complete,

so that the gas is essentially a mixture of NO, $NO_2$, and $N_2O_4$ This combines with alkalis (*e g* with dry potash) to form nitrites,

$$(NO + NO_2) + 2KOH = 2KNO_2 + H_2O,$$

but, with water, nitric acid is formed as well as nitrous acid, since some of the nitric oxide remains undissolved

**Nitrogen peroxide**, $N_2O_4 \rightleftharpoons 2NO_2$ —(*a*) *Preparation* —Nitrogen peroxide is generally prepared in the laboratory by heating lead nitrate (Fig 52)

$$2Pb(NO_3)_2 = 2PbO + 4NO_2 + O_2$$

The mixed gases are passed into a U-tube surrounded by a freezing mixture, and purified by redistilling with phosphoric oxide, when a pale yellow liquid is produced consisting mainly of dinitrogen tetroxide

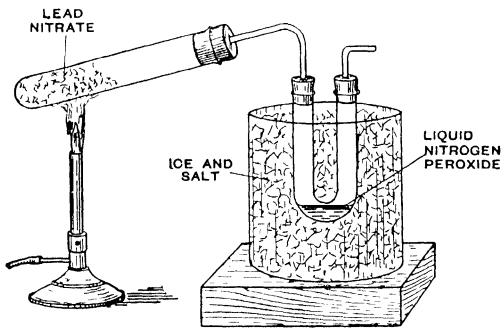



FIG 52 PREPARATION OF NITROGEN PEROXIDE

$N_2O_4$ Nitrogen dioxide, which is obtained on warming this liquid cannot be collected over water or over mercury, as it acts upon both of these liquids

(*b*) *Properties* —**Nitrogen dioxide**, $NO_2$, is a brown gas which condenses to a pale yellow liquid boiling at 22° As the liquid is cooled, the colour diminishes still further, and finally **dinitrogen tetroxide**, $N_2O_4$, separates at −10° as an absolutely colourless ice The reversible polymerisation or "association" of the gaseous dioxide is an exothermic process and is therefore favoured by a fall in temperature (Table 17A)

TABLE 17A —ASSOCIATION OF NITROGEN DIOXIDE

$2NO_2 \rightleftharpoons N_2O_4 + 12{,}900$ calories.

| | | |
|---|---|---|
| At 26 7° - | 20% | 80% (approximately) |
| At 49 6° - | 40% | 60% |
| At 100 1° - | 89% | 11% |
| At 154 0° - | 100% | 0% |

In accordance with le Chatelier's principle, the polymerisation is also favoured by increase of pressure

When nitrogen peroxide is heated above 154° it begins to dissociate into

nitric oxide and oxygen Since the dissociation is endothermic, it is promoted by raising the temperature (Table 17B)

TABLE 17B —DISSOCIATION OF NITROGEN DIOXIDE

| | $2NO_2 \rightleftharpoons 2NO + O_2 - 26{,}900$ calories | |
|---|---|---|
| At 223° - | 94 7% | 5 3% |
| At 390° - | 64 9% | 35 1% |
| At 490° - | 45 0% | 55% |
| At 620° - | — | 100% |

Nitrogen peroxide behaves as a mixed acid-anhydride since it interacts with alkalis to give equivalent quantities of nitrate and nitrite

$$2KOH + 2NO_2 = KNO_3 + KNO_2 + H_2O$$

A similar action takes place with water, but the nitrous acid thus formed is unstable and decomposes into nitric oxide and nitrogen peroxide, so that the ultimate products are nitric acid and nitric oxide

$$H_2O + 3NO_2 = 2HNO_3 + NO$$

Although nitrogen peroxide contains twice as much oxygen as nitric oxide, it does not readily support combustion, but vigorously-burning phosphorus and charcoal will continue to burn in the gas, which is thus reduced to nitrogen Potassium ignites in the gas and reduces it to nitric oxide,

$$K + 2NO_2 = KNO_3 + NO,$$

whilst sodium and mercury are attacked but without the production of flame Carbon monoxide burns to carbon dioxide and sulphur dioxide is oxidised to sulphur trioxide, a reaction which is used in the " lead chamber process " for the manufacture of sulphuric acid (p 256)

$$NO_2 + SO_2 = SO_3 + NO$$

Since nitric oxide is readily oxidised by air to nitrogen peroxide, the latter can be used as a means of transferring oxygen from the air to a reducing agent, and hence is called a CARRIER OF OXYGEN

**Nitric anhydride or dinitrogen pentoxide**, $N_2O_5$, can be prepared by oxidising nitrogen peroxide with ozone or by distilling a mixture of fuming nitric acid and phosphoric oxide

$$2HNO_3 + P_2O_5 = N_2O_5 + 2HPO_3.$$

Nitric anhydride forms colourless, glistening prisms, which melt with slight decomposition at about 40° It dissolves in water to form nitric acid It is a powerful oxidising agent and attacks organic substances with great violence, so that it can be handled only in apparatus composed entirely of glass, without corks or rubber connections In presence of ozone it is oxidised to a **hyperoxide**, apparently the **trioxide**, $NO_3$, which has a characteristic absorption in the red but condenses in liquid air to a colourless solid The mixture with ozone is, however, unstable and ignites below 100°, burning according to the equation

$$NO_3 + O_3 = NO_2 + 2O_2.$$

**Preparation of nitric acid.**—(*a*) *From potassium nitrate* —Nitric acid is prepared in the laboratory by distilling equal weights of potassium nitrate and concentrated sulphuric acid in a retort and collecting the distillate in a water-cooled flask (Fig 53)

$$KNO_3 + H_2SO_4 = KHSO_4 + HNO_3$$

The apparatus must be without corks, since these are rapidly attacked by nitric acid The product may be concentrated to 98% by distilling it with twice its weight of concentrated sulphuric acid, and purified from oxides of nitrogen by blowing dry air through it Absolutely pure nitric acid cannot be prepared by further distillation with sulphuric acid, since nitric anhydride, which is always present owing to dissociation, distils over first and then a constant-boiling mixture of 98 67% strength

$$2HNO_3 \rightleftharpoons N_2O_5 + H_2O$$

The pure acid may be obtained by cooling concentrated nitric acid in a freezing mixture, when colourless crystals, melting at $-41\ 3°$, separate

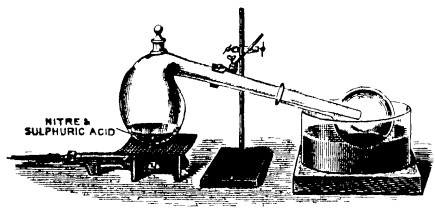



FIG 53 PREPARATION OF NITRIC ACID

(*b*) *From Chile saltpetre* —On a large scale nitric acid is prepared by the action of sulphuric acid on Chile saltpetre

$$NaNO_3 + H_2SO_4 = NaHSO_4 + HNO_3$$

The mixture is distilled in cast-iron pots, connected to condensers made of fused silica or of acid-resisting earthenware (Fig 54) The greater part of the nitric acid is of 90 to 95% strength, but in the final stages of the action, when the sulphuric acid is becoming exhausted, a weaker acid (40 to 65% $HNO_3$) distils Provision is also made for the oxidation, and absorption in water as dilute nitric acid, of gaseous oxides of nitrogen set free by the decomposition of the acid

The residue of NITRE-CAKE consists mainly of sodium hydrogen sulphate or sodium bisulphate, $NaHSO_4$, and not of the neutral sulphate, $Na_2SO_4$, since nitric acid decomposes at the temperature required to displace the second hydrogen atom of the sulphuric acid , it is also important to use sufficient acid to produce a nitre-cake which can be withdrawn from the nitre-pots as a fluid

(*c*) *From ammonia* —In the OSTWALD PROCESS, ammonia is oxidised to nitric oxide by passing a mixture of ammonia and air over red-hot platinum gauze

$$4NH_3 + 5O_2 = 4NO + 6H_2O$$

The nitric oxide thus produced is oxidised by air and absorbed in wate as in process (*d*)

$$4NO + 3O_2 + 2H_2O = 4HNO_3$$

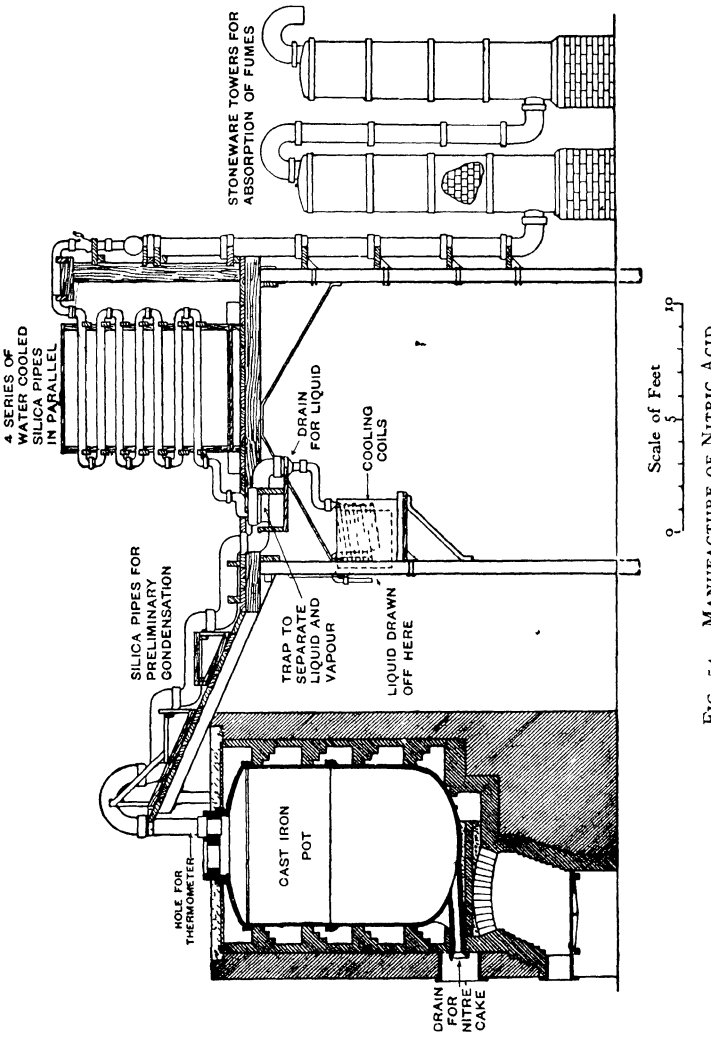



FIG 54 MANUFACTURE OF NITRIC ACID

The mixture used contains about 8% of ammonia , if richer mixture are used, or if the flow is so fast that the ammonia is not all oxidised, ther is a serious loss, owing to the interaction of ammonia with oxides of nitroge to form elementary nitrogen On the other hand, the time of contact wit the catalyst must be reduced to about 1/1000 second at 700-800°, otherwis

the nitric oxide is dissociated into its elements and the ammonia is again oxidised to elementary nitrogen

$$4NH_3 + 3O_2 = 2N_2 + 6H_2O$$

(*d*) *From air* —Before cheap synthetic ammonia was available for the above process, nitric oxide was manufactured on a very large scale by the action of an electric discharge on air (p 191)

The absorption of oxides of nitrogen from (*d*) was effected on the COUNTER-CURRENT SYSTEM, by passing the gases in an upward direction through a series of from 5 to 7 towers packed with quartz, in which the oxides of nitrogen were washed out by a downward flow of acids of progressively diminishing strength, whilst the acid, which was worked gradually in the opposite direction from tower to tower, increased progressively in strength by absorption from the gases The strength of the nitric acid produced in this way may be as high as 50% It can be increased to 98% by mixing it with two or three times its weight of 92% sulphuric acid and allowing the mixture to flow down a tower packed with quartz The heat set free on mixing the two acids causes strong nitric acid (about 98% $HNO_3$) to distil from the top of the tower, and steam is passed into the bottom to remove the last traces of nitric acid from the sulphuric acid before sending it to be concentrated again for further use Alternatively, the dilute nitric acid may be converted into **calcium nitrate**, $Ca(NO_3)_2$, by the action of chalk, and used as a fertilizer or for the preparation of ammonium nitrate (p 186) Calcium nitrate is deliquescent, but it can be converted into a non-deliquescent basic nitrate by treatment with lime, since it is much more suitable for transportation, the basic nitrate is always prepared when calcium nitrate is required for use as a fertilizer **Sodium nitrite**, $NaNO_2$, may also be prepared by absorbing the hot gases in soda at 200° to 300° when they have been oxidised to an extent corresponding with the formula $N_2O_3$

**Physical properties of nitric acid.**—When free from water and from oxides of nitrogen, nitric acid is a colourless liquid having a density of 1 52 at 15° It boils with partial decomposition at 86° and freezes to a snow-white solid at −41°

Nitric acid is miscible with water, with which it forms the hydrates, $HNO_3,H_2O$ and $HNO_3,3H_2O$ (f -pts −38° and −18°) When the dilute acid is distilled, the boiling-point rises gradually to 121°, at which temperature a mixture of constant boiling-point containing 68% $HNO_3$ distils, this is the ordinary commercial acid of density 1 414 Fuming nitric acid, of density 1 52, is prepared by distilling the ordinary commercial acid with concentrated sulphuric acid (see above)

**Chemical properties of nitric acid.**—(*a*) *Acid properties* —Pure nitric acid is without action on the metals and does not even act upon chalk When water is added, it develops all the characteristics of a monobasic acid and forms a series of salts, of which **sodium nitrate**, $NaNO_3$, is important as the principal source of nitric acid, **potassium nitrate**, $KNO_3$, as a constituent of gunpowder, **ammonium nitrate**, $NH_4NO_3$, as a constituent of military and commercial explosives, **silver nitrate**, $AgNO_3$, as a caustic and as the principal soluble salt of silver, and **lead nitrate**, $Pb(NO_3)_2$, as the principal soluble salt of lead. These can be prepared in a normal

manner by the action of nitric acid on the corresponding oxides or carbonates, but, when nitrates are prepared directly from the metals, reduction of the acid takes place (see below) and considerable loss of acid occurs Thus, it is much more economical to prepare lead nitrate from lead oxide than to make it from metallic lead

(*b*) *Decomposition* —When nitric acid is heated it decomposes according to the equation

$$4HNO_3 = O_2 + 4NO_2 + 2H_2O$$

The formation of oxygen as a decomposition product of nitric acid may be shown readily by allowing nitric acid to drip slowly through a red-hot clay pipe and collecting the oxygen over water in the usual way (Fig 55)

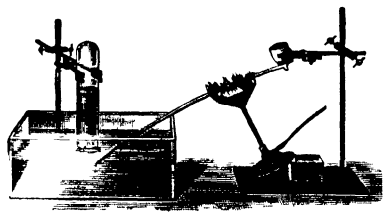


FIG 55 DECOMPOSITION OF NITRIC ACID BY HEAT

It is probable that the acid is first decomposed into water and nitric anhydride,

$$2HNO_3 = H_2O + N_2O_5,$$

and that the nitric anhydride is then decomposed according to the equation,

$$2N_2O_5 = 4NO_2 + O_2,$$

the decomposition is therefore brought about most readily in strong nitric acid Decomposition is also promoted by exposure to light, and the oxygen liberated from strong nitric acid in sunlight may produce enough pressure to burst the bottle in which the acid is contained

(*c*) *Nitric acid as an oxidising agent* —The ready liberation of oxygen from nitric acid makes it a powerful oxidising agent, especially when hot and concentrated

(i) Hot dilute or cold concentrated nitric acid will liberate sulphur from sulphuretted hydrogen and iodine from potassium iodide

$$3H_2S + 2HNO_3 = 3S + 2NO + 4H_2O,$$
$$6KI + 8HNO_3 = 3I_2 + 6KNO_3 + 2NO + 4H_2O$$

(ii) When concentrated nitric acid (1 vol ) is heated with concentrated hydrochloric acid (3 vols ), chlorine and nitrosyl chloride, NOCl, are formed

$$3HCl + HNO_3 = Cl_2 + NOCl + 2H_2O,$$

This mixture of acids is called aqua regia because it dissolves gold

$$4HCl + HNO_3 + Au = HAuCl_4 + NO + 2H_2O$$

(iii) Hot concentrated nitric acid will oxidise sulphur to sulphuric acid, phosphorus to phosphoric acid and iodine to iodic acid

$$S + 2HNO_3 = H_2SO_4 + 2NO,$$
$$3P + 5HNO_3 + 2H_2O = 3H_3PO_4 + 5NO,$$
$$3I_2 + 10HNO_3 = 6HIO_3 + 10NO + 2H_2O$$

(iv) In qualitative analysis nitric acid is used to oxidise ferrous to ferric salts, *e g*

$$3FeCl_2 + 3HCl + HNO_3 = 3FeCl_3 + 2H_2O + NO$$

(v) The reduction of nitric acid to nitrous acid, hydroxylamine, ammonia, etc , as described above under these headings, may all be regarded as illustrations of the oxidising properties of nitric acid

(vi) It will oxidise many organic compounds, *e g* sugar to oxalic acid

(*d*) *Action of nitric acid on the metals* —In its action on metals nitric acid plays a double part, as an acid and as an oxidising agent , it is therefore able to dissolve copper, mercury and silver, which are usually insoluble in dilute acids, although it will not dissolve gold and platinum, which are, however, soluble in chlorinating acids The action on copper, silver and mercury can be delayed by blowing air through the dilute acid, or by adding urea, to remove nitrous acid from the solution

When metals are dissolved in nitric acid, a large number of reduction-products are formed by parallel reactions, which cannot be covered by a single equation

(i) Magnesium will liberate hydrogen from nitric acid, provided that the acid is very dilute

$$Mg + 2HNO_3 = Mg(NO_3)_2 + H_2$$

Ammonia, hydroxylamine and nitrous oxide are also formed owing to secondary reactions between hydrogen and nitric acid

(ii) Zinc and other easily oxidised metals dissolve in dilute nitric acid with liberation of nitrous oxide, but nitrogen, ammonia and hydroxylamine are also produced

$$4Zn + 10HNO_3 = 4Zn(NO_3)_2 + N_2O + 5H_2O$$

In alkaline solution reduction to ammonia takes place, *e g*

$$NaNO_3 + 4Zn + 7NaOH = NH_3 + 4Na_2ZnO_2 + 2H_2O$$

(iii) Copper with cold dilute nitric acid gives mainly nitric oxide,

$$3Cu + 8HNO_3 = 3Cu(NO_3)_2 + 2NO + 4H_2O,$$

but with the concentrated acid nitrogen peroxide is the chief product

$$Cu + 4HNO_3 = Cu(NO_3)_2 + 2NO_2 + 2H_2O$$

(iv) In the case of tin, strong nitric acid acts mainly as an oxidising agent, converting the tin into metastannic acid, $H_2Sn_5O_{11},4H_2O$, a hydrated form of the oxide $SnO_2$

The complex nature of the reactions of nitric acid with metals may be accounted for by assuming that the first product is hydrogen and that

secondary and tertiary reactions then take place as shown by the following equations

$$HNO_3 + 2H = HNO_2 + H_2O,$$
$$2HNO_3 + 8H = \underset{\text{Hyponitrous acid}}{H_2N_2O_2} + 4H_2O,$$
$$HNO_3 + 6H = \underset{\text{Hydroxylamine}}{NH_2OH} + 2H_2O,$$
$$HNO_3 + 8H = NH_3 + 3H_2O,$$
$$3HNO_2 = HNO_3 + 2NO + H_2O$$
$$H_2N_2O_2 = N_2O + H_2O,$$
$$HNO_2 + NH_2OH = N_2O + 2H_2O,$$
$$HNO_2 + NH_3 = N_2 + 2H_2O$$

The extent to which any of these reactions takes place depends upon the metal, the concentration of the acid and the temperature

(*e*) *Nitration* —Nitric acid is used extensively in organic chemistry to effect NITRATION, *i e* to replace hydrogen by the NITRO-GROUP, $-NO_2$ This process is usually effected by the action of a mixture of nitric and sulphuric acid, the sulphuric acid serving to remove the water formed in the action, and apparently diminishing also the tendency of the nitric acid to act as an oxidising agent Two typical actions are shown in the equations

$$\underset{\text{Benzene}}{C_6H_6} + HNO_3 = \underset{\text{Nitrobenzene}}{C_6H_5NO_2} + H_2O,$$
$$\underset{\text{Glycerine}}{C_3H_5(OH)_3} + 3HNO_3 = \underset{\text{Nitroglycerine}}{C_3H_5(ONO_2)_3} + 3H_2O$$

Nitrations of the above type are of great importance in the synthetic dye and explosives industries Thus nitrobenzene (p 777) is the intermediate product in the manufacture of aniline, $C_6H_5NH_2$ (p 796), which is used to prepare important dyes such as indigo, whilst trinitrotoluene, $CH_3C_6H_2(NO_2)_3$ (p 779), and nitroglycerine (p 736) are powerful explosives

**Action of heat on nitrates.**—(*a*) Sodium and potassium nitrates are decomposed by heat into a nitrite and oxygen

$$2KNO_3 = 2KNO_2 + O_2$$

(*b*) Nitrates of heavy metals are decomposed into the oxide, whilst oxygen and nitrogen peroxide are evolved

$$Pb(NO_3)_2 = PbO + 2NO_2 + \tfrac{1}{2}O_2$$

Mercury and silver nitrates, however, give the metal, since their oxides are readily decomposed by heat

$$Hg(NO_3)_2 = Hg + 2NO_2 + O_2$$

(*c*) Ammonium nitrate is completely decomposed into nitrous oxide and steam

$$NH_4NO_3 = N_2O + 2H_2O$$

**Estimation of nitric acid, nitrates and nitrites.**—(1) In the absence of other acids, free nitric acid may be estimated by direct titration with standard alkali (p 414)

(ii) Small quantities (*e g* 0 1 gm ) of nitrates and nitrites may be estimated by means of Lunge's nitrometer (Fig 56), which makes use of the fact that nitric and nitrous acids are reduced quantitatively to nitric oxide by mercury in the presence of concentrated sulphuric acid, according to the equations

$$6Hg + 2HNO_3 + 3H_2SO_4 = 3Hg_2SO_4 + 2NO + 4H_2O,$$
$$2Hg + 2HNO_2 + H_2SO_4 = Hg_2SO_4 + 2NO + 2H_2O$$

EXPT 20 **Estimation of nitrogen as nitric oxide**

About 0 1 gram of the nitrate or nitrite is shaken from a weighing bottle into the cup *A*, of the nitrometer (Fig 56) and dissolved in about 3 c c of distilled water The solution is carefully drawn into the limb, *B*, followed by 2 c c of water and 6 c c of concentrated sulphuric acid, which wash down the traces of nitrate left in *A* The tube, *B*, is held in a nearly horizontal position, so that a large surface of mercury may be exposed and is agitated gently since the action is very slow

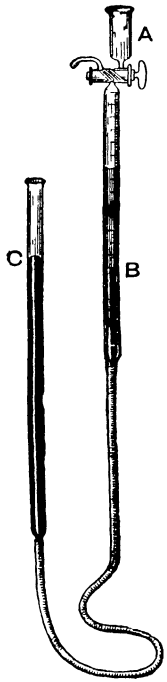


FIG 56 THE LUNGE NITROMETER

The volume of nitric oxide is read off and reduced to N T P after levelling *B* and *C* (10 cms of the acid solution may be taken as equivalent to 1 cm of mercury)

(iii) Nitrates and nitrites in alkaline solutions are reduced quantitatively by Devarda's alloy to ammonia, which can be estimated by means of standard acid (p 418)

(iv) Nitrites can be estimated by oxidation with a standard solution of potassium permanganate (p 428)

**Nitrous acid and nitrites.**—Nitrous acid, $HNO_2$ has never been isolated, since it is very unstable breaking down into water and nitrous anhydride which in its turn decomposes into nitric oxide and nitrogen peroxide

$$2HNO_2 = H_2O + N_2O_3 = H_2O + NO + NO_2$$

A very dilute solution of nitrous acid may be obtained by adding the theoretical quantity of ice cold dilute sulphuric acid to a solution of barium nitrite and filtering from barium sulphate,

$$Ba(NO_2)_2 + H_2SO_4 = BaSO_4 + 2HNO_2 ,$$

but at room temperatures this solution rapidly loses oxides of nitrogen

The salts of nitrous acid are more stable and are easily prepared Thus **sodium nitrite** and **potassium nitrite** may be obtained in the laboratory by heating the corresponding nitrates, either alone or preferably with lead when loss of oxygen takes place at a lower temperature ·

$$KNO_3 + Pb = KNO_2 + PbO.$$

The product is extracted with water and the resulting solution is made just acid with nitric acid before it is evaporated to crystallisation

Nitrites are now manufactured by passing into the appropriate alkali an equimolecular mixture of NO and $NO_2$, the latter being obtained by the catalytic oxidation of ammonia (see p 196)

$$2KOH + N_2O_3 = 2KNO_2 + H_2O$$

Unlike nitric acid, nitrous acid is a very weak acid and can be liberated from its salts even by acetic acid The addition of an acid to a nitrite therefore leads to effervescence, with liberation of brown fumes of nitrogen peroxide and nitric oxide

Nitrous acid is a more powerful oxidising agent than nitric acid , but this is perhaps due to the nitrogen peroxide which is produced by the spontaneous decomposition of nitrous acid Thus iodine is immediately liberated when a nitrite is added to an acidified solution of potassium iodide, while it is only liberated very slowly by the addition of a nitrate

$$2KNO_2 + 2KI + 2H_2SO_4 = 2K_2SO_4 + I_2 + 2NO + 2H_2O$$

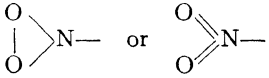
Nitrous acid also more readily oxidises stannous chloride to stannic chloride, ferrous salts to ferric salts, sulphurous acid to sulphuric acid and hydrogen sulphide to water and sulphur

$$SnCl_2 + 2HCl + 2HNO_2 = SnCl_4 + 2NO + 2H_2O,$$
$$2FeSO_4 + H_2SO_4 + 2HNO_2 = Fe_2(SO_4)_3 + 2NO + 2H_2O,$$
$$H_2SO_3 + 2HNO_2 = H_2SO_4 + 2NO + H_2O,$$
$$H_2S + 2HNO_2 = S + 2NO + 2H_2O$$

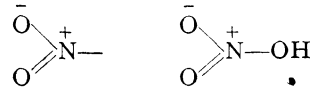
Unlike nitric acid, nitrous acid and nitrites also act as *reducing agents*, *e g* they reduce permanganate and bromine water

$$2KMnO_4 + 3H_2SO_4 + 5HNO_2 = K_2SO_4 + 2MnSO_4 + 5HNO_3 + 3H_2O,$$
$$HNO_2 + Br_2 + H_2O = HNO_3 + 2HBr$$

**Constitution of nitric and nitrous acids** —Nitric acid is universally regarded as formed by the union of a nitro-group, $NO_2$, with a hydroxyl-group, OH, as shown in the formula $NO_2$ OH The NITRO-GROUP was formerly represented by formulae in which the nitrogen was shown as a tervalent or quinquevalent element,

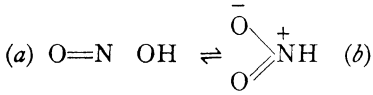


but it is now represented by a formula (see also p 782) which contains one non-polar and one semi-polar double bond



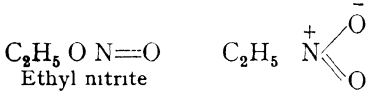
Nitro-group Nitric acid

Nitrous acid, on the other hand, possibly exists in two forms




Formula (*a*) represents nitrous acid as formed by the union of a nitroso-group, $-N{=}O$, with a hydroxyl-group, whilst (*b*) assumes the union of a nitro-group with a hydrogen atom

Both forms of the acid would yield the same nitrite ion, $O{=}N{-}\bar{O}$, so that the ionised salts can only exist in one form, as in sodium nitrite, $O{=}N{-}\bar{O}\ \overset{+}{Na}$, but when distilled with ethyl iodide (p 768), this salt yields **ethyl nitrite,** corresponding with the acid (*a*), and **nitroethane,** corresponding with the acid (*b*)




Ethyl nitrite

Nitroethane

# CHAPTER XVII

## PHOSPHORUS

### 15 PHOSPHORUS P = 31 02

**Occurrence of phosphorus** —Phosphorus is not found in the free state, ut occurs in the form of mineral phosphates, such as APATITE,

$$3Ca_3(PO_4)_2,CaF_2 \quad \text{or} \quad Ca_5(PO_4)_3F,$$

**rric phosphate,** $FePO_4$, and **aluminium phosphate,** $AlPO_4$ PHOSPHATITE, n important source of phosphorus for agriculture, contains calcium hosphate and is believed to have been formed by the decay of animal xcrements in the presence of lime Phosphorus is a normal constituent f plant and animal tissues and is essential to their growth It is partiularly abundant in bones, which, when calcined, yield a residue conisting almost entirely of **calcium phosphate,** $Ca_3(PO_4)_2$

**Preparation of phosphorus** —Phosphorus was first obtained about 1674 y Brand, who distilled evaporated urine (which contains excreted phosphorus in combination with other elements) with sand Scheele in 1775 repared it by distilling phosphoric acid with charcoal, and this method f preparation was subsequently developed on a large scale Orthophosphoric acid was prepared by the action of concentrated sulphuric acid on alcium phosphate, usually in the form of bone-ash

$$Ca_3(PO_4)_2 + 3H_2SO_4 = 3CaSO_4 + 2H_3PO_4$$

The acid was drained off on filter-beds from the insoluble residue of alcium sulphate, which was dried for use in manures , the solution was oncentrated to a syrup, mixed with coke or charcoal, and ignited until t was converted into metaphosphoric acid, $HPO_3$

$$H_3PO_4 = HPO_3 + H_2O$$

The reduction of the metaphosphoric acid was carried out by distilling in ireclay retorts (arranged rather like those in a zinc furnace (Fig 91, ) 333)), when phosphorus vapour passed over and was condensed under vater

$$4HPO_3 + 12C = P_4 + 2H_2 + 12CO$$

At the present time phosphorus is manufactured by heating a mixture of sand, coke and phosphatic mineral in an electric furnace (Fig 57) At the high temperature of the furnace, silicon dioxide displaces the more trongly acidic phosphoric oxide, owing to the volatility of the latter

$$Ca_3(PO_4)_2 + 3SiO_2 = 3CaSiO_3 + P_2O_5$$

The coke then reduces the phosphoric oxide to phosphorus, which distills over and is condensed under water to give **white phosphorus**

$$P_2O_5 + 5C = 2P + 5CO$$

The advantages of this process are that mineral phosphates can be used, which are insoluble or difficultly soluble in acids, and that sand replaces the much more expensive sulphuric acid

The crude phosphorus is melted under hot water in order to separate it from clay and sand, purified by oxidation with chromic acid, filtered through a canvas bag to remove mechanical impurities, cast into wedges or sticks, and packed with water in soldered tins

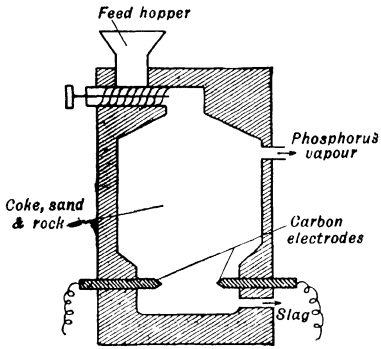



FIG 57 ELECTRIC FURNACE FOR MANUFACTURE OF PHOSPHORUS

**Properties of phosphorus.**—(*a*) *Classification* — Although phosphorus is classified with nitrogen and arsenic, the resemblance between them is so remote that no one would have dreamed of grouping them together as a result of studying the elements themselves, and even the compounds resemble one another mainly because the similar valencies of the elements lead in certain cases to similarity of formulae, which is sometimes accompanied by isomorphism Thus, a consideration of the physical properties and general behaviour of the elements would certainly lead us to classify nitrogen with oxygen, as the principal gases of the atmosphere, phosphorus with sulphur as easily-melted and highly inflammable solids, whilst arsenic would be grouped with antimony and bismuth as brittle, easily oxidised and mechanically almost-useless metals

This wide contrast between the first three elements of the nitrogen family is confirmed by a more detailed study of the elements Thus gaseous nitrogen forms diatomic molecules which are adequately represented by the formula $N \equiv N$, whilst the vapours of phosphorus and arsenic contain complex molecules, $P_4$, $As_4$, of unknown structure, but, whilst solid white phosphorus probably contains the same molecules as the vapour, the quasi-metallic properties of arsenic (which are only remotely imitated by metallic phosphorus) are associated with the formation of layer-lattices, in which twin sheets of atoms are united by bonds to form giant molecules like those of graphite (p 140)

A somewhat similar state of affairs prevails amongst the *compounds* of the elements now under consideration, although valency plays a more important part than it does amongst the elements themselves. Thus, the formation of pungent, water-soluble fumes on setting fire to *sulphur* and *phosphorus*, and the production in each case of two common acids, finds no analogy in the case of nitrogen, although compounds with similar

formulae to those produced from phosphorus can be prepared (under dissimilar conditions) from arsenic, thus

| | |
|---|---|
| Sulphurous acid, $H_2SO_3$ | Sulphuric acid, $H_2SO_4$ |
| Phosphorous acid, $H_3PO_3$ | Phosphoric acid, $H_3PO_4$ |
| Arsenious acid, $H_3AsO_3$ | Arsenic acid, $H_3AsO_4$ |

The hydrides of these three elements are all gases, but they differ in acidity and basicity, thus

Ammonia, $NH_3$, *basic*, *e g* in ammonium chloride, $NH_4Cl$
Phosphine, $PH_3$, *feebly basic* in phosphonium iodide, $PH_4I$
Arsine, $AsH_3$, *neutral*
Sulphuretted hydrogen, $SH_2$, *acidic*

Nitrides, phosphides, and arsenides are, however, easily prepared by other methods, although they are not formed (like the sulphides) by neutralising an acidic hydride

It is also of interest to notice that, whereas nitrogen is not acted on by alkalis and arsenic only with difficulty, both sulphur and phosphorus undergo simultaneous oxidation and reduction

$$3S + 6KOH = 2K_2S + K_2SO_3 + 3H_2O,$$
$$P_4 + 3KOH + 3H_2O = PH_3 + 3KH_2PO_2$$

In the case of sulphur, the hydride, $SH_2$, and the oxide, $SO_2$, are both retained in the form of salts, in the case of phosphorus, however, the hydride escapes as a gas, since it has no acidic properties, whilst the oxide is retained as a salt

In its behaviour towards the halogens, nitrogen differs from sulphur, phosphorus and arsenic in being completely inert The other three elements, however, form halogen compounds as follows

$$S_2Cl_2,\ SCl_2,\ SCl_4,\quad PCl_3,\ PCl_5,\quad AsCl_3,\ AsCl_5$$

The formulae of these compounds serve to bring phosphorus and arsenic together, but sulphur shares with these elements the property of forming (i) a chloride with similar structure to the hydride, and (ii) a less stable perchloride, in which two additional atoms of chlorine are united with the element In general, therefore, the formal chemistry of phosphorus can be correlated with that of arsenic and much more remotely with that of nitrogen, but the similarity of phosphorus and sulphur is too important to be overlooked, in spite of its failure to secure equal recognition in the classification of the elements

(*b*) *Allotropy* —Condensation of the vapour yields "yellow" or **white phosphorus**, a colourless waxy solid of density 1 83, which melts at 44° and boils at 280°, but when exposed to light, or heated at 240° (either alone or with a small quantity of iodine), it is converted into **red phosphorus**, of density 2 34 This melts at 590°, boils at 725°, and is insoluble in carbon disulphide It is much less active, since it is formed from white phosphorus with the liberation of 3,700 calories per gram-atom.

$$P_4(\text{white}) \rightleftharpoons P_4(\text{red}) + 4 \times 3{,}700 \text{ calories}$$

Thus white phosphorus ignites in air at 35° and red phosphorus at 260° Again, only white phosphorus is attacked by hot dilute alkali to give phosphine (p 209) Both allotropes combine with sulphur, halogens and some metals, but the action is more vigorous with white phosphorus

When phosphorus is heated strongly with lead in a sealed tube, and the metal removed with acid, it is converted into an opaque **violet** or **metallic phosphorus** (density 2 33), which is perhaps identical with red phosphorus When, however, white phosphorus is compressed under 35,000 atmospheres, or heated to 200° under 12,000 atmospheres, it is converted into **black phosphorus** (density 2 70) When distilled, red and black phosphorus are reconverted into white phosphorus, but red phosphorus can be sublimed unchanged in a vacuum at 100°

**The glow of phosphorus** —White phosphorus emits a greenish glow when exposed to air at room temperatures, provided that the partial pressure of oxygen is more than 1 mm and less than 600 mm The glow is inhibited by traces of certain substances, *e g* in presence of 0 7% by volume of iodobenzene it only occurs when the partial pressure of oxygen has been reduced to 350 mm The glow is supposed to be due to a chain reaction (p 590) in which phosphorus molecules are oxidised to phosphorous oxide

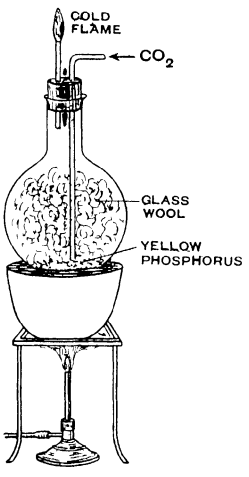



FIG 58 THE GLOW OF PHOSPHORUS

EXPT 21 **The glow of phosphorus**

A flask containing a few pieces of white phosphorus and packed with glass wool is fitted with a cork and two tubes (Fig 58), and heated on a water bath When carbon dioxide is passed through the flask, a luminous flame of glowing phosphorus vapour is produced at the mouth of the exit tube, and is clearly visible in a darkened room The flame is quite cold to the hand

**Uses of phosphorus.**—Phosphorus is used in the manufacture of matches The " heads " of the matches were formerly rendered inflammable by the presence of white phosphorus, but this was replaced by red phosphorus in order to avoid phosphorus-poisoning (" phossy-jaw ") At the present time the " head " usually contains **tetraphosphorus trisulphide,** $P_4S_3$, with potassium chlorate and manganese dioxide as oxidising agents, glue to act as a " binder," powdered glass or some similar inert material to increase friction, and Prussian blue, chrome yellow, etc , as a colouring matter In safety matches, the head of the match contains the oxidising substances (usually potassium chlorate, potassium dichromate, and red lead) together with antimony sulphide, and sometimes sulphur and charcoal, whilst the composition on the box usually includes red phosphorus

The halides, prepared directly from phosphorus, are used in chemical industry, but the principal use of the element is in the manufacture of

phosphatic manures The more concentrated forms are made from the element, whilst the less concentrated are made by the action of sulphuric acid on rocks containing calcium phosphate (p 215)

## Compounds of Phosphorus

**Phosphine**, $PH_3$ —Impure phosphine may be prepared as a spontaneously inflammable gas by heating white phosphorus with aqueous sodium hydroxide

$$P_4 + 3NaOH + 3H_2O = PH_3 + 3NaH_2PO_2$$

Sodium dihydrogen hypophosphite

This action is analogous to the action of caustic soda on sulphur,

$$3S + 6NaOH = 2Na_2S + Na_2SO_3 + 3H_2O,$$

but since hydrogen sulphide, unlike phosphine, is acidic, it is retained by the alkali as sulphide

Expt 22 **Preparation of phosphine**

A few pieces of white phosphorus and 200 c c of 30% caustic soda are placed in a 500 c c flask (Fig 59) and the air is swept out by a current

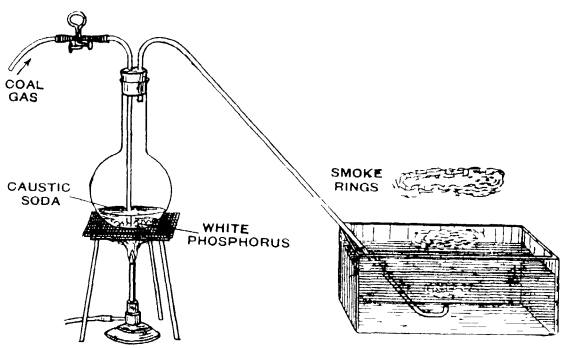



Fig 59 Preparation of Phosphine

of coal gas Phosphine is evolved on heating and catches fire as soon as it rises up out of the water, producing rings of white smoke

Pure phosphine may be prepared by warming phosphonium iodide, $PH_4I$, with caustic soda

$$PH_4I + NaOH = PH_3 + NaI + H_2O$$

Phosphine is a colourless gas, with a garlic-like odour, which condenses to a liquid boiling at $-86°$ It is extremely inflammable, burning to water and phosphoric oxide, but when pure it does not inflame spontaneously It cannot be formed by the direct union of phosphorus with

hydrogen and is readily decomposed into its elements, *e g* by sparking or heating to 440° (cf ammonia) For this reason phosphine is a powerful reducing agent, thus it will precipitate copper, silver and gold from solutions of their salts

Although its formula is analogous to that of ammonia, phosphine is insoluble in water and does not impart to it an alkaline reaction It is also devoid of acid properties, and is not absorbed by aqueous potash, soda, or ammonia It combines, however, with the halogen acids to form salt-like compounds, such as **phosphonium chloride**, $PH_4Cl$, melting-point 26°, **phosphonium bromide**, $PH_4Br$, and **phosphonium iodide**, $PH_4I$ The last compound can be prepared directly by the action of water on iodine and phosphorus, as shown in the empirical equation

$$5I + 9P + 16H_2O = 5PH_4I + 4H_3PO_4$$

The iodine is here reduced to hydrogen iodide, whilst part of the phosphorus is reduced to phosphine and another part is oxidised to phosphoric acid

EXPT 23 **Preparation of phosphonium iodide**

White phosphorus is mixed with twice its weight of iodine in a retort in the presence of carbon disulphide, which is then removed by distillation in a current of carbon dioxide The residue is decomposed with the calculated quantity of water, and heated in a stream of carbon dioxide to sublime the phosphonium iodide

**Liquid hydrogen phosphide**, $P_2H_4$, is formed as an impurity when phosphine is prepared by the action of caustic soda on white phosphorus, and is responsible for its spontaneous inflammability It may be prepared in quantity by the action of warm water on calcium diphosphide

$$Ca_2P_2 + 4H_2O = 2Ca(OH)_2 + P_2H_4$$

Unlike hydrazine, $N_2H_4$, it is spontaneously inflammable in air and has no basic properties It decomposes slowly on exposure to light into phosphine and a yellow solid hydride, $P_{12}H_6$

**Oxides and oxy-acids** —The principal oxides and oxy-acids of phosphorus are

Phosphorous oxide, $P_4O_6$ — Hypophosphorous acid, $H_3PO_2$ ($P_2O + 3H_2O$); Phosphorous acid, $H_3PO_3$ ($P_2O_3 + 3H_2O$)

Phosphorus dioxide, $(PO_2)_n$ — Hypophosphoric acid, $H_4P_2O_6$ ($PO_2 + H_2O$)

Phosphoric oxide, $P_4O_{10}$ —
- *ortho*-Phosphoric acid, $H_3PO_4$ ($P_2O_5 + 3H_2O$)
- *meta*-Phosphoric acid, $HPO_3$ ($P_2O_5 + H_2O$)
- *pyro*-Phosphoric acid, $H_4P_2O_7$ ($P_2O_5 + 2H_2O$).

The empirical formulae of the oxides derived by subtracting water from the acids are shown in brackets in order to indicate their degree of oxidation.

**Phosphorous oxide**, $P_4O_6$, can be prepared by burning phosphorus in a limited supply of air

EXPT 24 **Preparation of phosphorous oxide**

A slow stream of air is drawn over white phosphorus heated gently in the tube, *a* (Fig 60), and the less volatile phosphoric oxide, which is also formed, is condensed in the metal condenser, *b*, which is surrounded by water at about 60° The vapour passes through a plug of glass wool at *c*, which removes floating particles of the phosphoric oxide, and is condensed to a solid in the U-tube, *d*, which is surrounded by ice The wash-bottle *e*

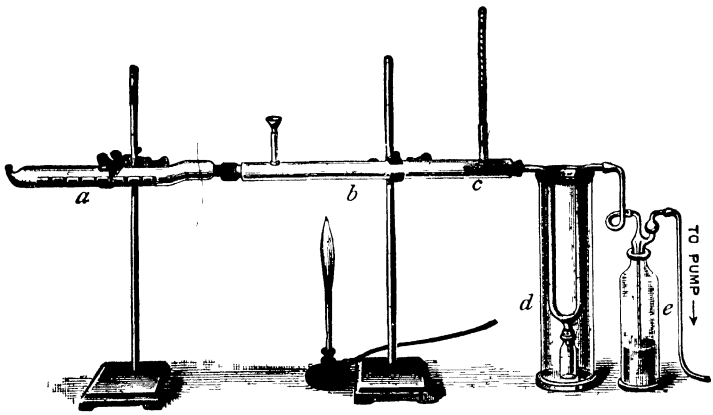



FIG 60 PREPARATION OF PHOSPHOROUS OXIDE

contains concentrated sulphuric acid and indicates the rate of the stream of air, it must be connected to the water pump through an empty wash-bottle in case the water should be sucked back At the end of the experiment the U-tube and bottle are immersed in hot water, when the phosphorous oxide melts and runs into the bottle The product can be purified by crystallisation from carbon disulphide

Phosphorous oxide is a transparent crystalline solid, which melts at 23 8° and boils at 173° in an inert atmosphere Measurements of vapour density and determinations of the freezing-points of solutions in benzene are in harmony with the formula $P_4O_6$

Phosphorous oxide dissolves slowly in cold water and is converted gradually into phosphorous acid, $H_3PO_3$, of which it is the anhydride

$$P_4O_6 + 6H_2O = 4H_3PO_3$$

With hot water, inflammable phosphoretted hydrogen and phosphoric acid are formed, perhaps according to the equation

$$P_4O_6 + 6H_2O = PH_3 + 3H_3PO_4$$

The oxide decomposes when heated above 300°, and (unless completely pure) also becomes red, and decomposes in a similar manner when

exposed to light The crude product oxidises with a luminous glow in contact with oxygen, it ignites at about 40° and burns to phosphoric oxide

$$P_4O_6 + 2O_2 = P_4O_{10}$$

The purified material, on the other hand, does not glow or fume below 200°, and oxidises only slowly in a sealed tube at 220°

**Phosphorus dioxide,** $(PO_2)_n$, is formed when phosphorous oxide is heated in a sealed tube to 440°, possibly according to the equation

$$P_4O_6 = 3PO_2 + P$$

It is a colourless solid of unknown molecular weight which dissolves in water, giving an acid solution containing phosphorous and phosphoric acids (cf $N_2O_4$)

$$2PO_2 + 3H_2O = H_3PO_3 + H_3PO_4$$

It can, however, also be formulated as an anhydride of the tetrabasic **hypophosphoric acid,** $H_4P_2O_6$, which is formed (with $H_2PO_3$) as the principal product of the smouldering of phosphorus

**Phosphoric oxide,** $P_4O_{10}$, is sometimes called "phosphorus pentoxide" since its empirical formula is $P_2O_5$ It is prepared by burning white phosphorus in a plentiful supply of air

EXPT 25 **Preparation of phosphoric oxide**

A lump of white phosphorus in an iron "deflagrating spoon" is placed in a large bottle and is ignited by touching it with a hot piece of iron wire Alternatively, the phosphorus may be burnt in a crucible standing on a tile under a bell-jar, which is lifted from time to time to admit fresh air to the burning phosphorus The product, which settles down like snow, can be purified by distillation in an iron tube in a stream of air or oxygen, and condensed in a wide glass tube

The complete combustion of phosphorus is a strongly exothermic action

$$P_4 + 5O_2 = P_4O_{10} + 740{,}000 \text{ calories},$$

*i e* 74,000 calories are liberated for each atom of oxygen as compared with

48,000 calories for $\frac{1}{2}C$ burning to $\frac{1}{2}CO_2$,

68,360 ,, ,, $H_2$ ,, ,, $H_2O$,

and 127,000 ,, ,, 2/3 Al ,, ,, $1/3\ Al_2O_3$

The oxide is a colourless powder which dissolves in water with great liberation of heat, forming **metaphosphoric acid,** $HPO_3$, and then **phosphoric acid,** $H_3PO_4$

$$P_4O_{10} + 6H_2O = 4H_3PO_4 + 70{,}000 \text{ calories}$$

It is deliquescent, and is one of the best agents known for drying gases and liquids, or for the removal of the elements of water from compounds (see nitric anhydride, p 195). Its vapour density at 1400° is a little higher than that required for the formula $P_4O_{10}$

**Hypophosphorous acid**, $H_3PO_2$, is a weak monobasic acid Salts of hypophosphorous acid are formed by heating white phosphorus with an alkali, *e g*

$$3Ba(OH)_2 + 2P_4 + 6H_2O = 3Ba(H_2PO_2)_2 + 2PH_3$$

The free acid may be prepared by adding dilute sulphuric acid to a solution of **barium hypophosphite**, filtering from the precipitate of barium sulphate, and evaporating to crystallisation

$$Ba(H_2PO_2)_2 + H_2SO_4 = BaSO_4 + 2H_3PO_2$$

When heated, the acid decomposes into phosphine and phosphoric acid (compare phosphorous acid) It is a powerful reducing agent, *e g* it reduces mercuric chloride to mercurous chloride or to mercury

$$2HgCl_2 + H_3PO_2 + 2H_2O = H_3PO_4 + 2Hg + 4HCl$$

**Phosphorous acid**, $H_3PO_3$, is formed when phosphorous oxide is dissolved in water It can be prepared by decomposing phosphorus trichloride with water and concentrating the solution until the temperature rises to 180°, and then cooling, when crystals separate

$$PCl_3 + 3H_2O = H_3PO_3 + 3HCl$$

When heated strongly, phosphorous acid (like hypophosphorous acid) gives phosphine and phosphoric acid

$$4H_3PO_3 = PH_3 + 3H_3PO_4$$

Phosphorous acid is also oxidised to phosphoric acid when exposed to air, or when used as a reducing agent to precipitate gold and silver from their solutions, or to reduce mercuric chloride to mercurous chloride or to mercury :

$$H_3PO_3 + 2HgCl_2 + H_2O = H_3PO_4 + Hg_2Cl_2 + 2HCl$$

Phosphorous acid is a tribasic acid, but usually only two of the three hydrogen atoms are replaced by metals

**Phosphoric acid and the phosphates.**—Phosphoric acid, $H_3PO_4$, is usually manufactured by the action of sulphuric acid on calcium phosphate as described above (p 205) It can be prepared in the laboratory by heating red phosphorus with concentrated nitric acid

$$3P + 5HNO_3 + 2H_2O = 3H_3PO_4 + 5NO.$$

EXPT 26 **Preparation of phosphoric acid**

Red phosphorus (20 grams) is added cautiously to nitric acid (100 c c. conc + 100 c c water) in a litre flask and the mixture is heated on a water-bath in a fume-chamber until oxides of nitrogen cease to be evolved If necessary, the solution is filtered, after dilution with its own volume of water, and evaporated carefully in a porcelain dish until the temperature reaches 180°, since at higher temperatures pyrophosphoric acid is formed A trace of iodine is sometimes added to assist the oxidation

(*a*) **Orthophosphoric acid**, $H_3PO_4$ —Phosphoric acid exists in several forms containing different proportions of water; but, unlike the hydrates

of sulphur trioxide, these are converted into one another only slowly and may even give different salts when neutralised By evaporating the aqueous acid in a vacuum over sulphuric acid, **orthophosphoric acid,** $H_3PO_4$, can be crystallised out in transparent prisms melting at 42° It is a tribasic acid and forms three series of orthophosphates, *e g*

| Salt | Formula | Reaction |
|---|---|---|
| Trisodium phosphate - - | - $Na_3PO_4,2H_2O$ | Alkaline |
| Disodium hydrogen phosphate | - $Na_2HPO_4,12H_2O$ | Neutral |
| Sodium dihydrogen phosphate | - $NaH_2PO_4,H_2O$ | Acid |

The first of these is strongly alkaline in solution owing to hydrolysis, and is completely decomposed by carbon dioxide

$$Na_3PO_4 + H_2O \rightleftharpoons Na_2HPO_4 + NaOH ,$$
$$Na_3PO_4 + H_2O + CO_2 = Na_2HPO_4 + NaHCO_3$$

The second is neutral to phenolphthalein, but alkaline to methyl orange , with silver nitrate, however, it gives a strongly acid solution, owing to the partial precipitation of yellow **trisilver phosphate**

$$Na_2HPO_4 + 3AgNO_3 \rightleftharpoons Ag_3PO_4 + 2NaNO_3 + HNO_3$$

The third salt is acid to litmus but neutral to methyl orange If, therefore, the volume, $V$, of caustic soda required to neutralize a given volume of phosphoric acid is determined, using methyl orange as indicator, then the above three sodium salts can be prepared by adding $3V$, $2V$, and $V$ volumes of caustic soda to three separate portions of the phosphoric acid

(*b*) **Pyrophosphoric acid**, $H_4P_2O_7$, is prepared by heating phosphoric acid to 215°

$$2H_3PO_4 = H_4P_2O_7 + H_2O$$

The acid melts at 61°, and does not at once revert to phosphoric acid when dissolved in cold water

It forms a series of PYROPHOSPHATES which differ from the orthophosphates in giving a *white* precipitate with silver nitrate, consisting presumably of **silver pyrophosphate**, $Ag_4P_2O_7$, and from the metaphosphates (see below) in not coagulating albumen They are prepared most readily by heating the mono-hydrogen phosphates , *e g* **sodium pyrophosphate,** $Na_4P_2O_7$, is formed from disodium hydrogen phosphate

$$2Na_2HPO_4 = Na_4P_2O_7 + H_2O.$$

(*c*) **Metaphosphoric acid**, $HPO_3$, compare $HNO_3$, is obtained as a transparent, deliquescent glass, to which the name of GLACIAL PHOSPHORIC ACID is given, by igniting orthophosphoric acid It volatilises at a bright red heat, and the appearance of a white fume is an indication that the removal of water from the phosphoric acid is complete It is the first product formed when phosphoric oxide is exposed to moist air,

$$P_4O_{10} + 2H_2O = 4HPO_3,$$

but it is left behind when the oxide is resublimed The acid is reconverted into ordinary phosphoric acid by boiling water and more slowly by cold

water Metaphosphoric acid differs from the ortho- and pyro-acids in coagulating a solution of egg albumen (white of egg) in water

METAPHOSPHATES can be prepared either directly from the acid, or by heating the dihydrogen phosphates Thus, **sodium metaphosphate,** $NaPO_3$, can be made by heating sodium dihydrogen phosphate,

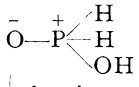
$$NaH_2PO_4 = NaPO_3 + H_2O,$$

or microcosmic salt (p 444),

$$Na(NH_4)HPO_4 = NaPO_3 + NH_3 + H_2O$$

The product is a glass, which readily takes up metallic oxides when melted, forming coloured beads (compare borax beads, p 397)

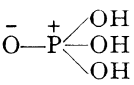
(*d*) The structural formulae of these acids are perhaps as follows



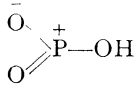
Hypophosphorous acid



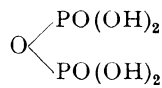
Phosphorous acid



*ortho*-Phosphoric acid



*meta*-Phosphoric acid



*pyro*-Phosphoric acid

**Phosphatic fertilizers.**—Phosphorus is essential for the growth of plants, but can only be assimilated when it is in the soil in a soluble form The phosphorus absorbed by the plant is largely concentrated in the seed and is therefore removed from the soil with the crops When the crops are eaten in the fields, or on the farm, by cattle, sheep or horses, much of the phosphorus is excreted and returned to the soil as liquid or solid farmyard manure , but phosphorus is also present in dairy produce, such as milk and cheese, as well as in meat and in bones, and is therefore constantly being sent away, even when the crops are mainly consumed on the farm This removal of phosphorus resulted in a most serious loss of fertility in the English pasture lands during the early part of the nineteenth century , their fertility was, however, restored by manuring with bones At the present time insoluble phosphatic rocks, such as apatite, are converted into soluble phosphates by mixing the finely powdered rock with 70% sulphuric acid from the lead chamber process The damp product, after maturing for several weeks, becomes dry and granular and is sold under the name of SUPERPHOSPHATE It consists of calcium sulphate together with about 15% of phosphoric oxide in the form of **calcium acid phosphate,** $Ca(H_2PO_4)_2$ **Mono-ammonium phosphate,** $(NH_4)H_2PO_4$, manufactured by treating phosphatic rock with sulphuric acid and ammonium sulphate, is used in concentrated garden fertilizers Guano, the excrements of birds, collected from islands in the Pacific Ocean, is also an important source of phosphorus for agriculture

**Phosphorus and the halogens.**—Phosphorus combines with the halogens to form two principal series of compounds, $PX_3$ and $PX_5$ These are

hydrolysed completely by water to phosphorous and phosphoric acid respectively

$$PX_3 + 3H_2O \rightarrow H_3PO_3 + 3HX,$$
$$PX_5 + 4H_2O \rightarrow H_3PO_4 + 5HX$$

In this respect they differ from the non-metallic halides, $CCl_4$ and $SF_6$, which are not decomposed by water, as well as from the salt-like halides of the alkali-metals, which are ionised without hydrolysis in aqueous solutions

**Phosphorus trichloride**, $PCl_3$, is formed by the direct combination of chlorine with red or white phosphorus

$$P_4 + 6Cl_2 = 4PCl_3$$

EXPT 27 **Preparation of phosphorus trichloride**

Chlorine, prepared by dropping concentrated hydrochloric acid on permanganate and dried by concentrated sulphuric acid, is passed over white phosphorus in a retort heated on a water bath (Fig 61) Phosphorus

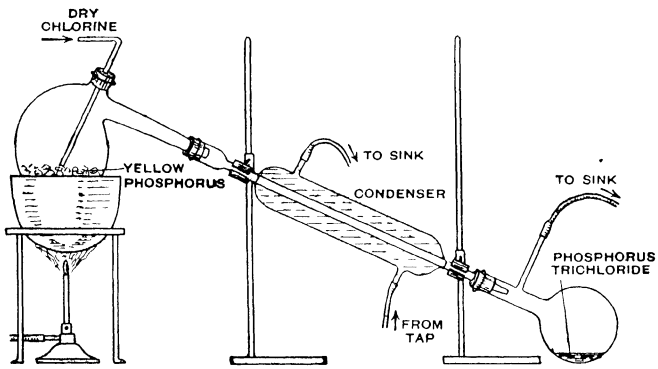



FIG 61 PREPARATION OF PHOSPHORUS TRICHLORIDE

trichloride is condensed and collected in a flask The white phosphorus must be cut into small pieces under water, dried hurriedly with filter paper and placed in the retort after the air in the whole apparatus has been displaced by carbon dioxide These precautions are necessary because white phosphorus readily ignites at atmospheric temperatures. The delivery tube must be close to the surface of the phosphorus and the stream of chlorine not too rapid, otherwise much of the trichloride will be further chlorinated before it passes over The trichloride is purified from pentachloride by distilling it with white phosphorus.

Phosphorus trichloride is a mobile, colourless liquid of density 1 6 It boils at $+76°$ and freezes at $-112°$ It has a pungent smell, and fumes in moist air It is decomposed violently by water, giving hydrochloric and phosphorous acids,

$$PCl_3 + 3H_2O = 3HCl + H_3PO_3,$$

it is thus a convenient material for the preparation of phosphorous acid It combines with chlorine to form a pentachloride, but will also dissolve phosphorus It is used extensively in organic chemistry as an agent for replacing hydroxyl by chlorine, *e g* in converting acetic acid into acetyl chloride (p 711)

$$\underset{\text{Acetic acid}}{3CH_3\,CO\,OH} + PCl_3 = \underset{\text{Acetyl chloride}}{3CH_3\,CO\,Cl} + \underset{\text{Phosphorous acid}}{H_3PO_3}$$

In this action it is converted into phosphorous acid, just as it is by the action of water

**Phosphorus pentachloride**, $PCl_5$, is prepared by the action of an excess of chlorine on the trichloride

$$PCl_3 + Cl_2 \rightleftharpoons PCl_5 + 30{,}000 \text{ calories}$$

EXPT 28 **Preparation of phosphorus pentachloride**

Dry chlorine, prepared as above, is passed into a flask (Fig 62), cooled in ice, whilst phosphorus trichloride is run in drop by drop from a funnel A solid yellow mass of pentachloride is formed on the bottom of the flask

Phosphorus pentachloride forms yellowish-white crystals which sublime below 100°, but melt under pressure at 148° When vaporised, it dissociates reversibly into phosphorus trichloride and chlorine , the vapour is therefore coloured by free chlorine The dissociation is endothermic and hence increases with rising temperature, becoming almost complete at 300°

Phosphorus pentachloride fumes strongly in moist air and is decomposed by water, giving the oxychloride, $POCl_3$, and then phosphoric acid, $H_3PO_4$

$$PCl_5 + H_2O = POCl_3 + 2HCl,$$
$$POCl_3 + 3H_2O = H_3PO_4 + 3HCl$$

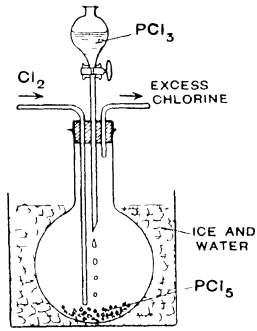



FIG 62 PREPARATION OF PHOSPHORUS PENTACHLORIDE

It is used extensively as a more powerful agent than the trichloride for replacing oxygen or hydroxyl by chlorine, *e g*

$$SO_3 + PCl_5 = POCl_3 + SO_2Cl_2 \text{ (Sulphuryl chloride)}$$

It also converts many metals into their chlorides and is itself reduced to the trichloride, *e g*

$$Zn + PCl_5 = ZnCl_2 + PCl_3$$

**Phosphorus tribromide**, $PBr_3$, is prepared by adding bromine gradually to *red* phosphorus, covered with a layer of benzene, since the reaction with *white* phosphorus is explosively violent The mixture is distilled and the tribromide collected in the last fraction It is a colourless liquid which boils at 172° and is very similar to the trichloride in its chemical properties. By further combination with bromine it yields yellow crystals of **phosphorus pentabromide**, $PBr_5$

**Phosphorus tri-iodide**, $PI_3$, can be prepared by the direct combination of red phosphorus with excess of iodine in the presence of carbon disulphide. It separates from solution in red crystals which melt at 61°

**Phosphorus oxychloride**, $POCl_3$, is the first product of the action of water on phosphorus pentachloride

$$PCl_5 + H_2O = POCl_3 + 2HCl$$

It can be prepared conveniently by adding the calculated quantity of powdered potassium chlorate to phosphorus trichloride and distilling

$$KClO_3 + 3PCl_3 = KCl + 3POCl_3$$

It is a colourless fuming liquid which boils at 107° and reacts like the pentachloride with compounds containing hydroxyl groups

**Sulphides of phosphorus.**—**Phosphorus pentasulphide**, $P_2S_5$, and **tetraphosphorus trisulphide**, $P_4S_3$, may be prepared by heating red phosphorus with sulphur, and purified by crystallising from carbon disulphide The pentasulphide is a yellow crystalline solid which is analogous to the pentachloride in some of its reactions, *e g*

$$P_2S_5 + 8H_2O = 2H_3PO_4 + 5H_2S.$$

**Estimation of phosphorus** —Phosphorus is generally estimated by precipitating as **magnesium ammonium phosphate**, $MgNH_4PO_4,6H_2O$, this can be dried at 100° and weighed as such, or converted by strong ignition into **magnesium pyrophosphate**, $Mg_2P_2O_7$ (p 443) The phosphorus must first be converted into a phosphate, if it is not initially present in this form Thus, phosphorus trichloride is converted into ammonium phosphate by hydrolysing the chloride, oxidising the resulting phosphorous acid with nitric acid, and then neutralising with ammonia

# CHAPTER XVIII

## ARSENIC, ANTIMONY, AND BISMUTH

| Atomic number | Element | Symbol | Atomic weight |
|---|---|---|---|
| 7 | NITROGEN | N | 14 008 |
| 15 | PHOSPHORUS | P | 31 02 |
| 33 | ARSENIC | As | 74 91 |
| 51 | ANTIMONY | Sb | 121 76 |
| 83 | BISMUTH | Bi | 209 00 |

**Classification.**—The three elements,

33 ARSENIC, 51 ANTIMONY, 83 BISMUTH,

which lie near the ends of the *long* periods differ in almost every respect (except valency) from the two elements, nitrogen and phosphorus, which occupy the corresponding positions near the ends of the two *short* periods, but they show nevertheless a striking similarity to one another, and form one of the most obvious "natural families" of elements In particular, the elements are all semi-metals, which possess only in an inferior degree the characteristic properties of metallic conductivity and metallic lustre, but they are too brittle to be included amongst the useful constructional metals Their compounds also are intermediate in character between the ionised salts of the typical metals and the covalent compounds of the typical non-metals The properties of these elements and of their compounds are summarised in Table 18 (p 220)

### 33 ARSENIC As = 74 91

**Occurrence of arsenic.**—Arsenic is widely distributed in the combined state and occurs in many metallic ores The most important mineral is ARSENICAL PYRITES or MISPICKEL, FeSAs, whilst less important minerals are the sulphides REALGAR, AsS, and ORPIMENT, $As_2S_3$

**Preparation and properties of arsenic.**—(*a*) *Preparation*—Metallic arsenic is prepared by reducing arsenious oxide with carbon

$$As_4O_6 + 3C = As_4 + 3CO_2$$

The metal is obtained as a crystalline sublimate in the upper part of the crucible It can also be prepared on a large scale by distilling arsenical pyrites

$$FeSAs = FeS + As$$

TABLE 18.—PROPERTIES OF ARSENIC, ANTIMONY AND BISMUTH *

| | ARSENIC | ANTIMONY | BISMUTH |
|---|---|---|---|
| **Physical properties** | | | |
| Density | 5 72 | 6 68 | 9 80 |
| Melting-point | 814° (under pressure), | 630°. | 271° |
| Boiling-point | 616° (sublimes) | 1380° | 1450° |
| Molecule in vapour | $As_4$ | $Sb_2$ | $Bi_2$ |
| Electrical conductivity | 4% of that of Cu | 4% of that of Cu | 1% of that of Cu |
| | Grey metallic lustre | White metallic lustre | White metallic lustre |
| | Exhibits allotropy | Exhibits allotropy | Exhibits allotropy |
| **Chemical properties** | Untarnished in air, but when heated burns to $As_4O_6$ | Untarnished in air, but when heated burns to $Sb_4O_6$ | Untarnished in air, but when heated burns to $Bi_2O_3$ |
| | Unaffected by dilute acids | Unaffected by dilute acids | Unaffected by dilute acids |
| | Concentrated nitric acid gives oxide, $As_2O_5$ | Concentrated nitric acid gives oxide, $Sb_2O_5$ | Concentrated nitric acid gives salt, $Bi(NO_3)_3$ |
| **Compounds** | | | |
| Hydrides | $AsH_3$, gas with no basic properties | $SbH_3$, gas with no basic properties | $BiH_3$ is so unstable that its formula has not been verified |
| Oxides | $As_4O_6$, amphoteric, acid not isolated, but forms salts, *e g* $NaAsO_2$ | $Sb_4O_6$, amphoteric, forms acid and salts, *e g* $H_3SbO_3$, $NaSbO_2$ | BiO, basic |
| | | | $Bi_2O_3$, basic, but also shows feeble acidic properties |
| | $As_2O_4$, mixed anhydride | $Sb_2O_4$, mixed anhydride | $Bi_2O_4$, mixed oxide |
| | $As_2O_5$, acidic, acids not isolated, but many salts isomorphous with those of phosphorus are known, *e g* $NaAsO_3$, $NaH_2AsO_4 12H_2O$ | $Sb_2O_5$, acidic, forms acid and salts, *e g* $H_3SbO_4$, $NaSbO_3$, etc | $Bi_2O_5$, acidic, acid not isolated, but forms salts, *e g* $NaBiO_3$ |
| Sesquisulphides | Precipitated by $H_2S$ in acid solution, soluble in yellow ammonium sulphide | Precipitated by $H_2S$ in acid solution, soluble in yellow ammonium sulphide | Precipitated by $H_2S$ in acid solution, insoluble in yellow ammonium sulphide |
| Halides | Stable trihalides, reversibly hydrolysed by water | Stable trihalides, reversibly hydrolysed by water | BiCl, $BiCl_2$(?) $BiCl_3$, $BiCl_4$ |
| | $2AsCl_3 + 3H_2O \rightleftharpoons As_2O_3 + 6HCl$ | $SbCl_3 + H_2O \rightleftharpoons SbOCl + 2HCl$ | $BiCl_3 + H_2O \rightleftharpoons BiOCl + 2HCl$ |
| | Unstable pentahalides | Unstable pentahalides | None |
| Compounds with metals | Combines with metals, *e g* NiAs (apparently bivalent As) $Ag_3As_6$ | Combines with metals, *e g* NiSb (apparently bivalent Sb) $Ag_3Sb$ | Combines with some metals, *e g* LiBi and $Li_3Bi$, NaBi and $Na_3Bi$ — |

* See also p 164 for comparison of antimony and bismuth with tin and lead

(*b*) *Physical properties*—Arsenic is a crystalline element of density 5·7, with a dull metallic lustre and marked metallic conductivity. It melts at 814° when heated under pressure or in a sealed tube, but usually sublimes without melting. The density of the yellow vapour corresponds with the formula $As_4$, just as in the case of phosphorus, the gaseous molecules of which are represented by the formula $P_4$.

(*c*) *Allotropy*—An unstable non-metallic form of arsenic can be obtained by the rapid condensation of the vapour from a stream of hydrogen or carbon dioxide. It is yellow in colour, dissolves in carbon disulphide, and is much lighter than metallic arsenic, to which it reverts readily under the influence of light, or when heated. Its molecular weight in solution corresponds with the formula $As_4$. The similarity of this form of arsenic to white phosphorus provides some justification for the classification of these elements in the same family.

(*d*) *Chemical properties*—Arsenic is stable in air at atmospheric temperatures, but when heated burns readily to the oxide, $As_4O_6$. It combines directly with chlorine to form arsenious chloride, $AsCl_3$, and is converted into arsine, $AsH_3$, when hydrogen is generated in contact with the metal or its compounds.

Arsenic behaves as a non-metal towards acids, since it is only attacked by oxidising acids, which convert it into the oxides, $As_4O_6$ or $As_2O_5$, instead of salts.

(*e*) *Valency*—Arsenic exhibits important variations of valency. In its principal compounds it is *tervalent*, as in $AsH_3$, $AsCl_3$, $As_4O_6$, etc. It is, however, *quinquevalent* in the pentoxide, $As_2O_5$, and in the arsenates derived from it, *e.g.* $Na_3AsO_4$, which are isomorphous with the phosphates. Quinquevalent halogen derivatives, such as the iodide, $AsI_5$, compare $PCl_5$, have also been prepared. In realgar, AsS, and in arsenical pyrites, FeSAs, arsenic is probably *bivalent*.

**Arsine**, $AsH_3$—Metallic arsenic does not combine directly with hydrogen, but arsine, $AsH_3$, is formed when hydrogen is generated, either by the action of acids on metals or by electrolysis, in contact with solutions containing arsenic. Pure arsine may be prepared by the action of dilute hydrochloric acid on zinc arsenide, which is formed by heating arsenic and zinc together in a crucible.

$$Zn_3As_2 + 6HCl = 3ZnCl_2 + 2AsH_3$$

It is a colourless gas with highly poisonous properties. It is decomposed by heating, depositing metallic arsenic as in MARSH'S TEST for arsenic.

$$4AsH_3 = As_4 + 6H_2$$

EXPT 29 **Marsh's test for arsenic**

In Marsh's test the substance to be examined is placed in a flask (Fig. 63) with arsenic-free zinc. On the addition of pure dilute sulphuric acid "nascent" hydrogen is evolved and converts any arsenic present into arsine. The gases are freed from traces of hydrogen sulphide by a roll of lead acetate paper, and dried by calcium chloride. The arsine is decomposed into arsenic and hydrogen by heating the delivery tube to dull redness at *A*, and a black stain of metallic arsenic is formed at *B*. After a

time all the arsenic will be volatilised and deposited, and the amount present may be determined by comparison with the stains produced by known amounts of arsenic Antimony gives a similar stain, but it may be distinguished from the arsenic stain as it is not dissolved by a solution of sodium hypochlorite or bleaching powder

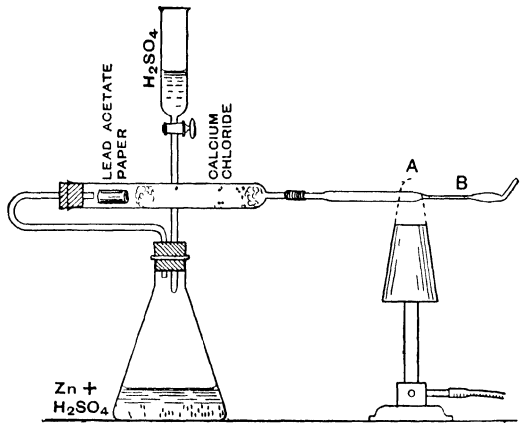



FIG 63 MARSH'S TEST FOR ARSENIC

In a limited supply of air, arsine burns to metallic arsenic and water, but in an excess of air arsenious oxide and water are formed It can be removed from a gas by passing it through a solution of a soluble silver salt

$$4AsH_3 + 24AgNO_3 + 6H_2O = As_4O_6 + 24Ag + 24HNO_3$$

**Arsenious chloride**, $AsCl_3$, is prepared by the direct action of chlorine on metallic arsenic

$$As_4 + 6Cl_2 = 4AsCl_3$$

It is also formed by the action of strong hydrochloric acid, or of a mixture of sulphuric acid and common salt, on arsenious oxide

$$As_4O_6 + 12HCl \rightleftharpoons 4AsCl_3 + 6H_2O$$

The anhydrous compound is a liquid, which boils at 130° and when frozen melts at −18° In presence of an excess of water, arsenious oxide is precipitated, the action shown in the last equation is therefore reversible

Arsenious chloride reacts with chlorine at low temperatures to form **arsenic pentachloride**, $AsCl_5$, which is very unstable and begins to decompose even at −25° (cf $PCl_5$)

$$AsCl_3 + Cl_2 \rightleftharpoons AsCl_5$$

**Arsenious oxide** or **white arsenic**, $As_4O_6$, is prepared by roasting arsenical ores, such as pyrites, and condensing the volatile arsenious oxide in a series of chambers or flues, which are cleared at intervals of a few weeks The crude product can be purified by resubliming it from a reverberatory furnace (p. 169) heated by means of anthracite or coke

Arsenious oxide can exist in three forms, viz amorphous or *vitreous* arsenious oxide, *rhombic* arsenious oxide, and *octahedral* arsenious oxide, but only the latter form is stable The oxide is sparingly soluble in water ($1\frac{1}{2}\%$ at 15°), to which it imparts a slight acid reaction, due presumably to the formation of a weak acid, $H_3AsO_3$, which has never been isolated It sublimes at about 200° without melting, and the density of the vapour corresponds with the formula $As_4O_6$

Arsenious oxide is amphoteric in character, since it dissolves in solutions of alkalis or carbonates to form arsenites (cf nitrites), and in concentrated hydrochloric acid to form arsenious chloride

$$As_4O_6 + 4NaOH = 4NaAsO_2 + 2H_2O,$$
$$As_4O_6 + 12HCl = 4AsCl_3 + 6H_2O$$

It acts as a *reducing agent*, since it is oxidised to arsenic oxide, $As_4O_{10}$, by concentrated nitric acid, by chlorine, and also by iodine, if the hydriodic acid is removed, otherwise the oxidation is not complete

$$As_4O_6 + 4I_2 + 4H_2O \rightleftharpoons As_4O_{10} + 8HI$$

It also acts sometimes as an *oxidising agent*, since it is reduced to arsenic by heating with charcoal, and in solution by stannous chloride

$$As_4O_6 + 6SnCl_2 + 12HCl = As_4 + 6SnCl_4 + 6H_2O$$

Arsenious oxide is highly poisonous and is used for this purpose in sheep-dips Less than one-third of a gram is fatal to man, but small doses gradually produce immunity, and the oxide can then be taken as a drug to improve the wind and beautify the skin The oxide is also used in the preparation of pigments and enamels, and as a preservative, especially for wood

In view of the wide distribution of arsenic in coal and coke, as well as in sulphuric acid prepared by the chamber process, traces of arsenic are present in many products, and may find their way into substances which are used as foodstuffs , the detection and estimation of small quantities of arsenic are therefore of exceptional importance

**Arsenic oxide**, $As_2O_5$ (or perhaps $As_4O_{10}$ to correspond with $P_4O_{10}$), prepared by oxidising white arsenic with concentrated nitric acid, is obtained as a deliquescent solid by evaporating the solution It dissolves in water to give an acid solution containing arsenic acid, $H_3AsO_4$

Arsenic acid is a mild oxidising agent, since it is reduced to arsenious acid by hydrogen iodide

$$H_3AsO_4 + 2HI \rightleftharpoons H_3AsO_3 + I_2 + H_2O$$

The balanced action can be reversed completely by the addition of sodium bicarbonate, as in the estimation of arsenious acid by titration with iodine (p 421) The acid also oxidises sulphuretted hydrogen, in addition to undergoing double decomposition with it

$$As_4O_{10} + 10H_2S \begin{cases} \nearrow 2As_2S_5 + 10H_2O \\ \searrow 2As_2S_3 + 4S + 10H_2O \end{cases}$$ (cf p. 386)

The acid reacts with alkalis to form a series of ARSENATES, which are isomorphous with the corresponding phosphates, *e g*

$Na_3AsO_4,12H_2O$, $Na_4As_2O_7$, $NaAsO_3$
$Na_3PO_4,12H_2O$, $Na_4P_2O_7$, $NaPO_3$

The most important arsenate is **sodium arsenate**, $Na_2HAsO_4$, which is used in calico-printing

**Arsenic monosulphide**, AsS, is found as the mineral REALGAR, and was at one time used as a pigment and in pyrotechny

**Arsenic sesquisulphide**, $As_2S_3$, is found as the mineral ORPIMENT It can be prepared by subliming a mixture of arsenic and sulphur, or can be precipitated as a yellow powder by passing sulphuretted hydrogen into an acid solution of arsenious oxide, *e g*

$$2AsCl_3 + 3H_2S = As_2S_3 + 6HCl$$

Unlike antimony sulphide, $Sb_2S_3$, and stannic sulphide, $SnS_2$, it does not dissolve in concentrated hydrochloric acid, but it is oxidised by and dissolves in concentrated nitric acid It readily dissolves in alkaline sulphides, forming THIOARSENITES,

$$As_2S_3 + K_2S = 2KAsS_2 \text{ (Potassium thioarsenite)},$$

and in polysulphides such as yellow ammonium, sulphide, forming THIOARSENATES

$$As_2S_3 + 3(NH_4)_2S + 2S = 2(NH_4)_3AsS_4 \text{ (Ammonium thioarsenate)}$$

It also dissolves in alkalis, giving a mixture of arsenite and thioarsenite, from which it is reprecipitated by the addition of acids

$$2As_2S_3 + 4KOH = KAsO_2 + 3KAsS_2 + 2H_2O ,$$
$$KAsO_2 + 3KAsS_2 + 4HCl = 2As_2S_3 + 4KCl + 2H_2O$$

**Arsenic pentasulphide**, $As_2S_5$, is precipitated by the action of hydrogen sulphide on acid solutions of an arsenate , but the product contains variable quantities of arsenic trisulphide and free sulphur, arising from the reduction of arsenic acid to arsenious acid and oxidation of hydrogen sulphide to sulphur A purer product is obtained as a yellow powder by the action of hydrochloric acid on a thioarsenate, *e g*

$$2Na_3AsS_4 + 6HCl = As_2S_5 + 6NaCl + 3H_2S$$

It is insoluble in water and dilute acids but dissolves in alkali sulphides, forming a thioarsenate

**Estimation of arsenic** —Arsenic is estimated gravimetrically by precipitating it as **magnesium ammonium arsenate**, $MgNH_4AsO_4,6H_2O$, which may be weighed as such by drying at atmospheric temperatures, or ignited and weighed as **magnesium pyroarsenate**, $Mg_2As_2O_7$ (compare p 443)

The volumetric estimation of arsenic (p 421) depends upon the oxidation of arsenite to arsenate by means of iodine *in the presence of sodium*

*bicarbonate*, which maintains the neutrality of the solution, and so enables the oxidation reaction to proceed to completion

$$As_4O_6 + 4H_2O + 4I_2 \rightleftharpoons As_4O_{10} + 8HI,$$
$$HI + NaHCO_3 \rightarrow NaI + H_2O + CO_2$$

It is noteworthy that arsenates may be estimated by the converse reaction, viz the liberation of iodine from acidified potassium iodide solution In this case excess of potassium iodide is added to a measured volume of the acidified arsenate solution, and the liberated iodine is titrated with standard thiosulphate The reaction proceeds to completion because the equilibrium is upset by the continuous removal of iodine

## 51 ANTIMONY Sb = 121 76

**Occurrence of antimony.**—The most important source of antimony is **antimony sesquisulphide** or STIBNITE, $Sb_2S_3$, a grey or black mineral with a brilliant metallic lustre, which has been known for many centuries and used for blackening the eyebrows **Cuprous thioantimonite,** $Cu_3SbS_3$, and **silver thioantimonite,** $Ag_3SbS_3$, are of some importance as ores of copper and silver respectively

**Metallic antimony.**—(*a*) *Preparation* —Metallic antimony is prepared by heating stibnite with scrap iron

$$Sb_2S_3 + 3Fe = 2Sb + 3FeS$$

The crude molten metal is tapped from the upper layer of ferrous sulphide, and purified by fusion with a little sodium carbonate and nitre It can also be prepared, like arsenic, by the reduction of the oxide with carbon

(*b*) *Physical properties* —Antimony is a coarsely crystalline metal with a silver white lustre, which melts at 630° and has a density of 6 62 It boils at 1380°, and the density of the vapour is rather more than that required by the formula $Sb_2$ (cf $As_4$ and $Bi_2$) A yellow non-metallic allotrope has been described

(*c*) *Alloys of antimony* —Antimony forms a large number of intermetallic compounds, in which it exhibits a valence of 2, 3 or 5, *e g* CaSb, $NiSb$, $Ag_3Sb$, $Ni_5Sb_2$ In its alloys it is generally used, like carbon in iron, as a hardening element Metallic antimony possesses the property of expanding when it crystallises , this property, which is shared by the alloys of antimony, is of considerable value in casting The most important alloys are those which are used for printing, *e g* TYPE METAL (lead, antimony and tin or bismuth), and for bearings, *e g* BABBIT'S METAL (Sn 85%, Sb 10%, Cu 5%)

(*d*) *Chemical properties* —Metallic antimony is stable in air, but burns when heated, yielding the oxides $Sb_4O_6$ and $Sb_2O_4$ , it also burns in chlorine gas to the trichloride, $SbCl_3$, and combines with sulphur and phosphorus when heated It does not unite directly with hydrogen, nitrogen, or carbon, but the hydride, $SbH_3$, can be prepared by generating hydrogen in contact with the metal Dilute hydrochloric and dilute sulphuric acids have no action upon it, but it is oxidised by steam at a red heat and by nitric acid It dissolves in hot strong hydrochloric acid when

air is present, forming the chloride, it also dissolves in concentrated sulphuric acid, forming the sulphate Its metallic character is therefore more pronounced than that of arsenic

## Compounds of Antimony

**Stibine**, $SbH_3$, is formed like arsine, by generating hydrogen in contact with metallic antimony or its compounds A pure product is obtained by the action of dilute hydrochloric acid on an alloy of magnesium containing 33% of antimony

$$Mg_3Sb_2 + 6HCl = 3MgCl_2 + 2SbH_3$$

It is a colourless gas which is readily decomposed by heating, depositing a mirror of the metal, which differs from arsenic in that it is not dissolved by solutions of sodium hypochlorite or of bleaching powder The gas is very poisonous, and burns in air with liberation of white fumes of the oxide Like arsine it has no basic properties With silver nitrate solution it gives a black precipitate of silver antimonide which is rapidly decomposed by excess of silver nitrate into silver and antimonious acid

$$SbH_3 + 3AgNO_3 = Ag_3Sb + 3HNO_3,$$

compare $4AsH_3 + 24AgNO_3 + 6H_2O = 24Ag + As_4O_6 + 24HNO_3$

**Antimonious oxide**, $Sb_4O_6$, is the principal product when metallic antimony or its sulphide is burnt in air

$$2Sb_2S_3 + 9O_2 = Sb_4O_6 + 6SO_2$$

It is a colourless compound, which melts when heated and solidifies to a crystalline mass It is more volatile than the higher oxides and can be separated from them by sublimation, its vapour density corresponds with the formula $Sb_4O_6$

Antimonious oxide is almost insoluble in water but readily dissolves in hydrochloric acid to form the trichloride, and in solutions of potassium hydrogen tartrate, $KH(C_4H_4O_6)$ (p 754), to form **potassium antimonyl tartrate**, $K(SbO)(C_4H_4O_6)$, a compound which has long been known and used in medicine under the name of TARTAR EMETIC The oxide will also dissolve in fuming nitric acid and in fuming sulphuric acid to form a basic nitrate and sulphate respectively, the normal **sulphate**, $Sb_2(SO_4)_3$, has also been prepared

Antimonious oxide also dissolves in alkalis, forming a series of ANTIMONITES, *e g* **sodium metantimonite**, $NaSbO_2,3H_2O$, which crystallises out from the aqueous solutions obtained by dissolving the oxide in sodium hydroxide The meta-acid, $HSbO_2$, has not been prepared, but a hydrated form of the oxide having the composition of **orthoantimonious acid**, $H_3SbO_3$, has been prepared (compare phosphorous acid, $H_3PO_3$).

**Diantimony tetroxide**, $Sb_2O_4$, is formed by heating antimonious oxide above 400° in air It imparts an acid reaction to water, and combines with bases to form salts of the type $K_2Sb_2O_5$; but it has no obvious basic properties.

**Antimonic oxide**, $Sb_2O_5$, is obtained by the action of concentrated nitric acid on the metal or on the lower oxides, the product being heated gently to decompose any traces of basic antimonious nitrate that may be formed It is a yellow powder with an acid reaction to litmus Hydrates corresponding with the formulae of **orthoantimonic acid**, $H_3SbO_4$, **pyroantimonic acid**, $H_4Sb_2O_7,2H_2O$, and **metantimonic acid**, $HSbO_3$, have been prepared, but only salts of the last two acids are known

**Potassium pyroantimonate**, $K_2H_2Sb_2O_7$ (or $2KSbO_3,H_2O$) is used as a qualitative reagent for sodium, since the sodium salt is only sparingly soluble in water, one part dissolving in 350 parts of water

**Antimony trichloride**, $SbCl_3$, can be prepared by the action of chlorine on antimony, or by heating the sulphide with concentrated hydrochloric acid and evaporating

$$Sb_2S_3 + 6HCl = 2SbCl_3 + 3H_2S$$

It is a crystalline compound melting at 73° and boiling at 223°, and was formerly known as "butter of antimony" It dissolves in a small quantity of water, but on dilution is precipitated as a basic chloride, the principal constituent of which is **antimony oxychloride**, SbOCl

$$SbCl_3 + H_2O \rightleftharpoons SbOCl + 2HCl$$

**Antimony pentachloride**, $SbCl_5$, is formed by passing chlorine into the molten trichloride It melts at 4°, and breaks down, when heated, into the trichloride and chlorine, but it can be distilled under reduced pressure without decomposition It is decomposed by hot water, giving the hydrated oxide, **antimonic acid**, $Sb_2O_5$ aq

**Antimony trisulphide**, $Sb_2S_3$, occurs naturally as STIBNITE It is thrown down as an *orange red* precipitate (perhaps hydrated) by the action of sulphuretted hydrogen on acid solutions of antimony trichloride, when heated to 200° it loses water and becomes *black*

Antimony trisulphide is analogous to arsenic trisulphide in forming THIOANTIMONITES, *e g* $KSbS_2$, and THIOANTIMONATES, *e g* $K_3SbS_4$, with sulphides and polysulphides respectively, and in its reaction with caustic alkalis (p 224) The pentasulphide, $Sb_2S_5$, has not been isolated, but the **tetrasulphide**, $Sb_2S_4$ (compare $Sb_2O_4$), is known

## 83 BISMUTH Bi = 209 0

**Occurrence.**—Bismuth is found as native metal, which may be contaminated with isomorphous antimony and arsenic The **sesquisulphide**, $Bi_2S_3$, or BISMUTHITE, is a rare mineral, isomorphous with stibnite and possessing a similar brilliant metallic lustre

**Metallic bismuth.**—(*a*) *Preparation* —Native bismuth is separated from non-metallic impurities by melting and running off the metal It can be refined by melting it under fused potassium nitrate, in order to eliminate arsenic and antimony in the form of potassium arsenate or antimonate The pure metal can be prepared by refining the metal formed by reduction of the precipitated oxide

(*b*) *Physical properties*—Bismuth is a silvery metal (Fig 64), which melts at 271° and has a density of 9 8

(*c*) *Alloys of bismuth*—Bismuth is used mainly in the manufacture of FUSIBLE ALLOYS, including

| | Bi | Pb | Sn | Cd | Melting-point |
|---|---|---|---|---|---|
| Rose's alloy | 2 | 1 | 1 | — | 94° |
| Wood's alloy | 4 | 2 | 1 | 1 | 71° |

These alloys are used for closing automatic sprinklers in fire-protection systems

(*d*) *Chemical properties*—When heated, bismuth burns in air to the oxide, $Bi_2O_3$, and combines with sulphur and the halogens to form compounds in which the metal exhibits a valency of three Traces of the

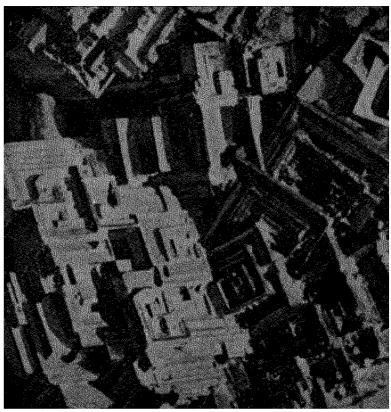


FIG 64 METALLIC BISMUTH

hydride, presumably $BiH_3$, have been detected by preparing hydrogen in contact with bismuth The metal decomposes steam at a red heat, but is insoluble in dilute acids, except nitric acid, which converts it into the nitrate, $Bi(NO_3)_3$ It reacts with boiling concentrated sulphuric acid to give the sulphate, $Bi_2(SO_4)_3$

**Bismuth monoxide**, BiO, is obtained as a black powder by heating **basic bismuth oxalate**

$$(BiO)_2C_2O_4 = 2BiO + 2CO_2$$

It is oxidised to the sesquioxide, $Bi_2O_3$, by heating in air, with acid it gives metallic bismuth and a tervalent salt (compare $Cu_2O$)

$$3BiO + 6HCl = 2BiCl_3 + Bi + 3H_2O$$

**Bismuth sesquioxide**, $Bi_2O_3$, is found as a yellow powder under the name of BISMUTH OCHRE It can be prepared by heating the metal in air, or by igniting the nitrate or carbonate It is easily reduced to the metal by heating with carbon Unlike the corresponding oxides of arsenic and

antimony, it is definitely basic in its properties and does not possess any marked acid properties **Bismuth hydroxide,** $Bi(OH)_3$, is obtained as a white amorphous precipitate by the action of ammonia or caustic alkali on a solution of a tervalent bismuth salt A black higher oxide is produced by the action of oxidising agents such as sodium hypochlorite upon tervalent bismuth compounds

**Bismuth sesquisulphide,** $Bi_2S_3$, as BISMUTHITE, is isomorphous with stibnite, $Sb_2S_3$ It can be prepared artificially by the direct combination of bismuth and sulphur, or as a brownish-black precipitate by the action of sulphuretted hydrogen on acid solutions of the chloride The precipitated sulphide is readily soluble in nitric acid and dissolves more slowly in boiling concentrated hydrochloric acid, unlike the sulphides of arsenic, antimony, and tin, it does not dissolve in alkalis or in yellow ammonium sulphide, although it is soluble in concentrated solutions of potassium sulphide Higher sulphides of bismuth do not appear to be known

**Bismuth trichloride,** $BiCl_3$, is prepared as a white crystalline solid by heating bismuth in chlorine By dissolving the oxide or carbonate in hydrochloric acid, the hydrate, $BiCl_3,H_2O$, can be crystallised out It is hydrolysed by much water to an insoluble **bismuth oxychloride,** BiOCl, which is, however, redissolved on the addition of hydrochloric acid

$$BiCl_3 + H_2O \rightleftharpoons BiOCl + 2HCl$$

A **monochloride,** BiCl, and a **tetrachloride,** $BiCl_4$, have also been prepared, but a pentachloride has not yet been isolated

**Bismuth trinitrate,** $Bi(NO_3)_3, 5H_2O$, prepared by the action of nitric acid on the metal, is a soluble deliquescent salt It is converted by the action of water into a basic nitrate, $Bi(OH)_2NO_3$, which is used extensively as a medicine in cases of diarrhoea

**Bismuth sulphate,** $Bi_2(SO_4)_3$, is obtained, like antimony sulphate, by concentrating a solution of the metal or of its oxide in strong sulphuric acid

**Basic bismuth carbonate,** $(BiO)_2CO_3,H_2O$, is precipitated when an alkali carbonate is added to a solution of bismuth nitrate It is the only carbonate formed by the elements of this group and serves to show the superior basic properties of bismuth oxide The readiness with which bismuth forms basic salts rather than normal salts also emphasizes the fact that its oxide is not a strong base

**Estimation of bismuth.**—Bismuth is usually estimated by precipitating with ammonium carbonate, igniting, and weighing as the sesquioxide, $Bi_2O_3$.

# CHAPTER XIX

## OXYGEN

### 8 OXYGEN O = 16 000

**Occurrence of oxygen.**—Oxygen is by far the most abundant of the elements In the free state it forms 23% by weight, or 20 9% by volume, of the atmosphere, whilst in combination it forms 88 8% of water or 86% of the ocean Nearly 50% of the earth's crust, to a depth of ten miles, including the ocean and the atmosphere, consists of oxygen

**Laboratory preparation of oxygen.**—(*a*) *By the decomposition of oxides* —(i) Pure oxygen may be obtained by heating *silver oxide*, prepared by precipitating a silver salt with an alkali

$$2Ag_2O = 4Ag + O_2$$

A little caustic soda must be added to hold back any carbon dioxide that may be formed by the decomposition of silver carbonate ($Ag_2CO_3$), which occurs as an impurity owing to the presence of carbonate in the precipitating alkali *Mercuric oxide*, HgO, *red lead*, $Pb_3O_4$, and *manganese dioxide*, $MnO_2$, also give oxygen when heated, but like silver oxide are not generally used since they give poor yields of oxygen

(ii) Oxygen can be prepared conveniently by dropping water from a tap funnel on to solid sodium peroxide

$$2Na_2O_2 + 2H_2O = 4NaOH + O_2$$

Hydrogen peroxide is formed as an intermediate product, but is decomposed by the alkali and by the heat of the reaction Cubes of compressed sodium peroxide, supplied for carrying out this preparation in a Kipp's apparatus (p 70), contain small amounts of ferric oxide, copper sulphate, etc , to catalyse the evolution of oxygen

(*b*) *By the decomposition of oxy-salts* —(i) When *potassium chlorate* is heated to 370° it melts and decomposes slowly into potassium chloride and potassium perchlorate

$$4KClO_3 = KCl + 3KClO_4$$

On heating to about 400°, the perchlorate loses its oxygen and is converted into the chloride

$$KClO_4 = KCl + 2O_2$$

In the presence of small quantities of manganese dioxide, platinum black, or china clay, this decomposition takes place below 240° Thus oxygen is commonly prepared in the laboratory by heating potassium chlorate with one quarter of its weight of manganese dioxide in a hard glass test tube The manganese dioxide can be recovered unchanged at the end of the action and therefore acts merely as a catalyst The oxygen prepared in

this way contains traces of chlorine, which may be removed by passing the gas through aqueous sodium hydroxide

If potassium chlorate is heated with only a trace of manganese dioxide, the mass becomes pink (larger amounts of $MnO_2$ obscure the colour) It has therefore been suggested that potassium permanganate is formed as an intermediate compound

$$2KClO_3 + 2MnO_2 = 2KMnO_4 + Cl_2 + O_2,$$
$$2KMnO_4 = K_2MnO_4 + MnO_2 + O_2,$$
$$K_2MnO_4 + Cl_2 = 2KCl + MnO_2 + O_2$$

The presence of traces of chlorine in the oxygen is regarded as evidence in favour of this mechanism

(ii) Other oxy-salts, such as potassium nitrate and potassium permanganate, liberate oxygen when heated, but are not generally used for the preparation of oxygen

$$2KNO_3 = 2KNO_2 + O_2,$$
$$2KMnO_4 = K_2MnO_4 + MnO_2 + O_2$$

(*c*) *By electrolysis* —Pure oxygen and hydrogen may be prepared by the electrolysis of a warm solution of barium hydroxide (p 72)

**Industrial preparation of oxygen** —(*a*) Oxygen was formerly obtained from the air by making use of the fact that the decomposition of barium peroxide by heat is a balanced action

$$2BaO_2 \rightleftharpoons 2BaO + O_2$$

Thus at 800°, barium peroxide is decomposed into baryta and oxygen, since at this temperature the DISSOCIATION PRESSURE (p 540) of oxygen set free by the decomposition of the peroxide rises above one atmosphere On the other hand, when baryta is heated at a temperature of 500° in air at atmospheric pressure, barium peroxide is formed, since the dissociation pressure of the oxygen at this temperature is less than one-fifth of an atmosphere and therefore less than the partial pressure of oxygen in the air

In BRIN'S PROCESS, the temperature of the baryta was kept constant at 700° and the absorption and expulsion of oxygen were brought about by variation of pressure Purified air (freed from carbon dioxide, which combines with baryta to form a very stable carbonate) was pumped in under a pressure of about 10 lb per square inch during a period of a few minutes, when oxygen was absorbed by the baryta, whilst the nitrogen escaped by a safety valve Oxygen containing about 4% of nitrogen was then obtained by reversing the pumps to produce a partial vacuum

(*b*) Oxygen is now prepared by the fractional distillation of liquid air (p 480) The product, which contains 99% or more of oxygen, is compressed into steel cylinders for transport. It is used in medicine to enrich the air when respiration is difficult It is also used in the oxy-hydrogen blowpipe for working platinum and silica, and in the oxy-acetylene blowpipe for welding metals and for cutting through steel plates

**Physical properties of oxygen.**—Oxygen is a colourless, odourless gas, which appears slightly bluish in thick layers when under pressure It can

be condensed to a pale blue mobile liquid boiling at $-183°$ The density of the gas is 1 429 grams per litre at 0° and 760 mm pressure It is sparingly soluble in water, which dissolves 4% by volume of oxygen at 8°, as compared with 2% of nitrogen , on account of the greater solubility of oxygen, the air dissolved in water contains 34% of oxygen by volume, instead of the 21% present in the atmosphere

**Chemical properties of oxygen.**—Oxygen is a very active gas, which combines either directly or indirectly with all the elements, except the inert gases of the helium family, and with a large number of compounds Except in the case of the halogens and the noble metals, such as silver, gold and platinum, oxides can be prepared by direct combination of the element with oxygen Thus sodium, magnesium, phosphorus, sulphur, etc burn, when heated, in air or oxygen, according to the equations

$$2Na + O_2 = Na_2O_2 \qquad P_4 + 5O_2 = P_4O_{10}$$
$$2Mg + O_2 = 2MgO \qquad S + O_2 = SO_2$$

Nitric oxide, sulphurous acid, ferrous and stannous salts react *in the cold* with air or oxygen as shown by the equations

$$2NO + O_2 = N_2O_4 \qquad 4FeSO_4 + 2H_2SO_4 + O_2 = 2Fe_2(SO_4)_3 + 2H_2O$$
$$2H_2SO_3 + O_2 = 2H_2SO_4 \qquad 2SnCl_2 + 4HCl + O_2 = 2SnCl_4 + 2H_2O$$

**Oxidation by oxygen in the presence of a catalyst** —Oxygen, like hydrogen, becomes much more active in the presence of finely-divided metals Thus oxygen and hydrogen combine together at low temperatures in the presence of palladium and platinum Finely-divided platinum is also used to promote the combination of sulphur dioxide and oxygen (p 259), and red-hot platinum gauze is used to promote the oxidation of ammonia to steam and nitric oxide (p 196)

**Oxidising agents.**—Although it is not customary to speak of nascent oxygen, there are many oxidising agents which will bring about OXIDATIONS that cannot be effected by means of gaseous oxygen, *e g* ozone (p 235), hydrogen peroxide (p 85), nitric acid, aqua regia (p 282), chromic acid (p 369), potassium permanganate (p 374), chlorine water (p 279), electrolytic oxidation (p 288)

**Classification of oxides.**—The oxides may be classified as follows

(*a*) *Basic oxides* —A BASIC OXIDE is an oxide which interacts with an acid to give a salt and water Basic oxides are generally formed by the union of oxygen with a metal Thus, copper oxide, which is obtained by the direct combination of copper with oxygen, is a basic oxide because it dissolves in acids to give salts and water, *e g*

$$CuO + H_2SO_4 = CuSO_4 + H_2O$$

The basic oxides of the alkali metals and the alkaline earths unite with water to form soluble hydroxides, which are also basic

$$Na_2O + H_2O = 2NaOH \qquad CaO + H_2O = Ca(OH)_2$$
$$2NaOH + H_2SO_4 = Na_2SO_4 + 2H_2O \qquad Ca(OH)_2 + 2HCl = CaCl_2 + 2H_2O$$

(*b*) *Acidic oxides* —ACIDIC OXIDES are those oxides which interact

with a base to give a salt The oxides of the non-metals are usually acidic, and may unite with water to form an acid, *e g*

$$CO_2 + H_2O = H_2CO_3 \text{ (Carbonic acid)},$$
$$SO_2 + H_2O = H_2SO_3 \text{ (Sulphurous acid)}$$

The *higher* oxides of some of the metals are also acidic Thus chromic oxide, $Cr_2O_3$, is basic, whilst chromium trioxide, $CrO_3$, is acidic

*Basic oxide* $\quad Cr_2O_3 + 3H_2SO_4 = Cr_2(SO_4)_3 + 3H_2O$

*Acidic oxide* $\quad CrO_3 + 2NaOH = Na_2CrO_4 + H_2O$

(*c*) *Amphoteric oxides* —Oxides which have both acidic and basic properties are known as AMPHOTERIC OXIDES Thus aluminium oxide, $Al_2O_3$, interacts with acids and with bases to give salts

*Basic action* $\quad Al_2O_3 + 3H_2SO_4 = Al_2(SO_4)_3 + 3H_2O$

*Acidic action* $\quad 2NaOH + Al_2O_3 = 2NaAlO_2 + H_2O$ (Sodium aluminate)

Zinc oxide, ZnO, stannous oxide, SnO, and antimonious oxide, $Sb_4O_6$, are also amphoteric

(*d*) *Peroxides* —This term should only be applied to those oxides which yield hydrogen peroxide on acidification with a dilute acid, *e g*

$$BaO_2 + H_2SO_4 = BaSO_4 + H_2O_2,$$
$$Na_2O_2 + H_2SO_4 = Na_2SO_4 + H_2O_2$$

Lead dioxide, $PbO_2$, and manganese dioxide, $MnO_2$, are not peroxides because they do not give hydrogen peroxide with dilute acids This difference in behaviour is due, no doubt, to the fact that peroxides have an electrovalent structure whilst the above dioxides have a covalent structure, viz

$$\overset{+}{Na}\ \overset{-}{O}—\overset{-}{O}\ \overset{+}{Na} \qquad \overset{++}{Ba}\ \overset{-}{O}—\overset{-}{O}$$
$$O{=}Mn{=}O \qquad O{=}Pb{=}O$$

Oxides similar to lead dioxide may be described as *polyoxides*, like peroxides, they yield oxygen on ignition and give chlorine with hot concentrated hydrochloric acid

(*e*) *Compound oxides* —Some oxides may be regarded as formed by the combination of two oxides Thus, **red lead,** $Pb_3O_4$, may be regarded as a COMPOUND OXIDE formed by the union of **litharge,** PbO, acting as a base, with **lead dioxide,** $PbO_2$, acting as an acid Similarly **trimanganese tetroxide,** $Mn_3O_4$, may be regarded as a " salt " formed by combination of the basic oxide, MnO, with the acidic dioxide, $MnO_2$

(*f*) *Neutral oxides* —Certain oxides do not behave as acids, bases or salts, and are therefore called neutral oxides Water, which is sometimes cited as a neutral oxide, is really amphoteric since it behaves both as an acid and as a base (p 45)

Carbon monoxide unites with sodium hydroxide to form sodium formate (p. 715),

$$NaOH + CO = H\ \ CO\ \ \overset{-}{O}\overset{+}{Na},$$

but this action is not an ordinary neutralisation, since it only takes place

at temperatures above 200°. Carbon monoxide may therefore be regarded as a neutral oxide, like nitrous oxide, $N_2O$, which does not combine under any conditions either with acids or with bases

(*g*) *Suboxides*.—Many metals, and some non-metals, combine with a smaller amount of oxygen than is required by their normal valencies The products, which are described as SUBOXIDES, are usually unstable **Carbon suboxide**, $C_3O_2$, is the best-known suboxide, but the term is a misnomer, since this oxide is the anhydride of malonic acid (p 751), and is therefore an acidic oxide

$$C_3O_2 + 2H_2O = CH_2(CO{\cdot}OH)_2$$

Lead suboxide, $Pb_2O$, and sodium suboxide, $Na_4O$, are examples of metallic suboxides, but the molecular structure of these compounds is usually obscure, and some of them may be merely mixtures

**Oxygen as an acidifying agent.**—The name oxygen was introduced by Lavoisier to express the fact that the oxides of the non-metals possess acid properties The fact that the oxides of the metals are basic was ignored, perhaps because at that time it was not known definitely that the strongest bases, such as lime and the alkalis, contained oxygen The acid-producing power of oxygen is, however, shown by the tendency of the metals, as the proportion of oxygen in their oxides is increased, to give acidic rather than basic oxides Thus, whilst chromic oxide, $Cr_2O_3$, and manganous oxide, MnO, possess basic properties, chromium trioxide, $CrO_3$, and dimanganese heptoxide, $Mn_2O_7$, are acid anhydrides from which important series of salts are derived In the same way, the higher oxides of the non-metals give stronger acids than the lower oxides, *e g* sulphuric acid, $H_2SO_4$, is stronger than sulphurous acid, $H_2SO_3$, and nitric acid, $HNO_3$, is stronger than nitrous acid, $HNO_2$

**Respiration.**—Living creatures derive their energy and warmth of body from the exothermic oxidation of complex organic substances, such as glucose (p. 738)

$$C_6H_{12}O_6 + 6O_2 = 6CO_2 + 6H_2O + 673{,}000 \text{ calories}$$

Thus when air is drawn into the lungs, oxygen enters the blood-vessels by diffusion, and there forms a loose compound, **oxyhaemoglobin**, with the **haemoglobin** in the blood The oxygenated blood is pumped through the arteries to tissues all over the body, where it is required for oxidations of the above type The products of oxidation, carbon dioxide and moisture, are carried back by the deoxidised blood through the veins to the lungs and exhaled Respired air contains roughly Oxygen 15%, carbon dioxide 4% to 5%, nitrogen 76% and water-vapour 5% The foulness of air is often judged by its content of carbon dioxide, amounting to a few parts in 10,000, but this gas itself is harmless at concentrations up to a few parts in 100, and is actually mixed with oxygen to serve as a stimulant for respiration in new-born babes The oppressive atmosphere of an ill-ventilated and crowded room is therefore due to the suppression of evaporation by excessive moisture and by the absence of draughts, and not to a reduction in the proportion of oxygen or an increase in the proportion of carbon dioxide, as is popularly supposed

## Ozone.

**History.**—In 1785 van Marum directed attention to the peculiar smell which was produced when a frictional electrical machine was in action Schonbein (1839) came to the conclusion that the smell was due to a new gas and called it *ozone* (Greek ὄζω, I smell), whilst Soret (1866) proved that it was an allotrope of oxygen of formula $O_3$

**Preparation of ozone.**—Ozone is best prepared by the action of a SILENT DISCHARGE on air or oxygen This discharge differs from the ordinary spark discharge in that one or two layers of an insulating material, such as glass or mica, are inserted between the metallic terminals The formation of large sparks or of an electric arc (which tend to produce oxides of nitrogen) is thereby prevented, and the discharge is restricted to a series of minute sparks oscillating to and fro between the insulating surfaces

The formation of ozone from oxygen is a strongly endothermic action

$$3O_2 = 2O_3 - 2 \times 34{,}000 \text{ calories}$$

It is therefore favoured by rise of temperature, like the endothermic decomposition of water into hydrogen and oxygen At ordinary temperatures, however, ozone tends to decompose completely, and, as it is even less stable than a mixture of hydrogen and oxygen, the " quenching " of the heated molecules must be very rapid and efficient in order to retain the ozone which is produced at high temperatures It is for this reason that the minute sparks of the silent discharge are better agents for producing ozone than a heavier discharge , indeed any discharge which heated the whole current of gas to 200° would be useless for making ozone, since ozone is decomposed very rapidly and completely at this temperature

In the laboratory ozone is generally prepared by using the Siemens' Ozoniser or Brodie's Ozoniser.

(i) **Siemens' ozoniser** —The outside of the outer and the inside of the inner of two coaxial glass tubes (Fig 65) are covered with tinfoil A

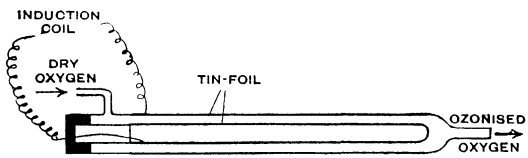



FIG 65 DIAGRAM OF SIEMENS' OZONISER

slow current of dry oxygen is passed through the space between the tubes, and is subjected to a silent discharge by connecting the sheets of tinfoil to the terminals of an induction coil

(ii) **Brodie's ozoniser.**—In Brodie's ozoniser (Fig 66), tinfoil is replaced by dilute sulphuric acid or by a solution of copper sulphate The conducting wires which dip into the acid are made of copper

The concentration of ozone produced by the above methods is less than 10% Higher concentrations may be obtained by collecting the gas

liberated at a small platinum anode, when ice-cold dilute sulphuric acid is electrolysed with a high current density Small quantities of ozone are produced when fluorine acts on water at 0°, and when white phosphorus smoulders in air On the industrial scale ozone is always prepared by an electrical discharge

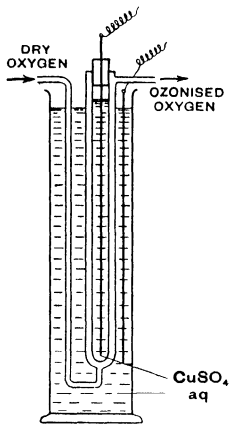


FIG 66 BRODIE'S OZONISER

**Physical properties of ozone.**—When ozonised oxygen is cooled by means of liquid air, the ozone condenses to a deep blue liquid, which is strongly magnetic, like liquid oxygen Pure liquid ozone, prepared by the fractional distillation of this liquid, boils at $-112°$ ($O_2$ boils at $-185°$) It is fairly stable when pure, but explodes violently in the presence of the smallest trace of organic matter

Ozone is more soluble in water than oxygen and imparts to it a disagreeable taste and smell Water which has been sterilised by means of ozone must therefore be exposed to air in order to render it palatable again

**Chemical properties of ozone** —Ozone decomposes slowly at atmospheric temperatures and rapidly at 200° The decomposition is greatly accelerated by platinum black, and by oxides such as silver oxide and manganese dioxide, all of which remain unaltered at the end of the reaction, other finely-divided metals have a similar effect to platinum black but are usually oxidised at the same time Water, on the other hand, acts as a stabilizer or negative catalyst

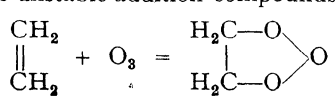
Ozone is a very powerful oxidising agent Thus it oxidises lead sulphide to lead sulphate and ferrous salts to ferric salts, liberates iodine from acidified potassium iodide, rots rubber and bleaches indigo

$$PbS + 4O_3 = PbSO_4 + 4O_2,$$
$$2FeSO_4 + H_2SO_4 + O_3 = Fe_2(SO_4)_3 + O_2 + H_2O,$$
$$2KI + 2HCl + O_3 = 2KCl + I_2 + O_2 + H_2O$$

In these oxidations only one atom of oxygen in the molecule appears to be active , but there are a few reactions in which the whole of the oxygen is used up, *e g* in the oxidation of sulphur dioxide to trioxide and of stannous chloride to stannic chloride

$$3SO_2 + O_3 = 3SO_3 ,$$
$$3SnCl_2 + 6HCl + O_3 = 3SnCl_4 + 3H_2O$$

The whole of the molecule also unites with organic compounds containing a double bond, *e g* ethylene (p 670), turpentine and benzene (p 781), giving rise to unstable addition compounds which are known as OZONIDES



Ethylene Ethylene ozonide

Ozone behaves as a reducing agent towards hydrogen peroxide

$$H_2O_2 + O_3 = H_2O + 2O_2,$$

but it is without action on potassium permanganate

The physiological effects of ozone are disagreeable, except at extreme dilutions, since it attacks the mucous membrane of the throat and produces headache Owing to its disinfectant properties it is used in the purification of air, *e g* in underground railways, and sometimes also in the sterilisation of water The presence of ozone in sea air is probably a myth, founded upon the presence of salt-spray in the air, and perhaps on the odour of decaying sea-weed , but it is an important constituent of the upper atmosphere

**Formula of ozone** —(*a*) The formula of ozone was determined by Soret in 1866 by placing equal volumes of the same specimen of ozonised oxygen in two flasks with long calibrated necks which dipped into water The contraction produced in one flask by the addition of turpentine gave the total volume of ozone, and was found to be double the expansion in the other when the ozone was decomposed into oxygen by heating Therefore 2 volumes of ozone decompose into $2 + 1 = 3$ volumes of oxygen , hence by Avogadro's hypothesis

2 mols ozone = 3 mols oxygen

or $2O_3 = 3O_2$

EXPT 30 **Volumetric composition of ozone**

The apparatus shown in Fig 67 is a modified Brodie Ozoniser It is filled with oxygen and the contraction produced by partial ozonisation is measured on a calibrated scale The small tube of turpentine is then crushed between projecting glass points by rotating the inner tube, and the further contraction in volume, representing the volume of ozone, is measured on the scale This further contraction will be found to be two-thirds of the total contraction thus showing that three volumes of oxygen give two volumes of ozone

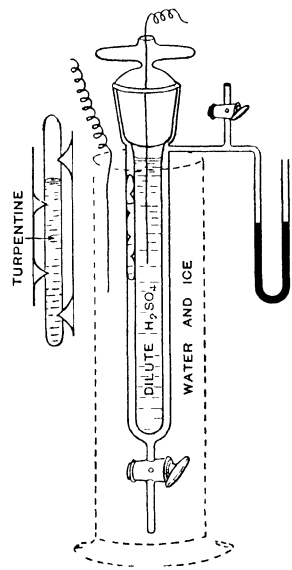



FIG 67 VOLUMETRIC ANALYSIS OF OZONE

(*b*) The formula of ozone was confirmed by Soret in 1868 from its density as determined by comparing its rate of diffusion with that of chlorine

The usual method of allowing the gas to diffuse through a porous partition could not be used, as ozone is rapidly destroyed by contact with porous materials Soret therefore measured in a series of samples of ozonised oxygen the proportion of ozone which passed in the course of 45 minutes through a cylindrical hole (5 mm in diameter) from a cylinder of 250 c c capacity into a similar cylinder containing oxygen only A

series of tests was also made with chlorine The proportions in the two cases were 0 2708 and 0·2270 According to Graham's Law of Diffusion, taking the density of chlorine as 35 46 (oxygen = 16) and that of ozone as $x$,

$$\sqrt{x} \quad \sqrt{35\ 46} = 0{\cdot}2270 \quad 0{\cdot}2708, \quad \text{and} \quad x = 24\ 9$$

The density of ozone is therefore about 25 and its molecular weight is about 50, corresponding with the formula $O_3 = 48$

(*c*) In recent years, direct determinations of the vapour density of pure ozone, corrected for decomposition during the course of the experiment, have confirmed the formula $O_3$

**Detection and estimation of ozone.**—In addition to its smell, one of the most distinctive properties of ozone is its action on mercury, which when ozonised leaves behind a dirty " tail " on glass, possibly owing to the formation of an oxide Like hydrogen peroxide and oxides of nitrogen, ozone liberates iodine from solutions of potassium iodide, but may be distinguished from these gases by the fact that it turns paper soaked in " tetrabase " (tetramethyl-*p*-*p*-diamino-diphenylmethane) a purple colour, whereas oxides of nitrogen turn it yellow and hydrogen peroxide has no effect

Ozone is estimated by passing it through a neutral or alkaline solution of potassium iodide, and afterwards liberating the iodine by the addition of dilute acid

$$2KI + O_3 + H_2O = 2KOH + I_2 + O_2 = KI + KIO + H_2O + O_2\,,$$
$$KI + KIO + 2HCl = 2KCl + I_2 + H_2O$$

The iodine can be estimated in the usual way by standard thiosulphate (p 419) If acidified potassium iodide is used in the first place, more iodine is liberated than is represented by the above equations, owing to the oxidation of hydriodic acid by the molecular oxygen set free from the ozone

## The Atmosphere

**Constituents of air.**—From very early times air was regarded as an element The presence of water vapour was recognised, but it was not considered to be an essential constituent

The first evidence that air was a mixture was found in the fact that its volume was diminished by mice breathing and by substances burning in air over water, and that the residue was unfit for further combustion or for respiration The presence in air of the principal product of combustion or respiration, namely carbon dioxide, was recognised in 1755 by Black, who gave to this gas the name of " fixed air " Finally, the isolation and identification of oxygen and nitrogen by Priestley and Scheele in 1774 led Lavoisier to the idea that air was a mixture of these two gases with moisture and carbon dioxide The existence in the air of the inert gases of the helium family was not suspected until more than a hundred years later, when Rayleigh observed that " atmospheric " nitrogen was about a half per cent heavier than " chemical " nitrogen and proceeded to isolate the heavier impurity (p 64)

**Composition of air.**—(*a*) **Oxygen and nitrogen** —The percentage of oxygen by volume in the air may be estimated by exploding a measured volume of air with a measured excess of hydrogen in a Volta Eudiometer (Fig 68) provided with platinum points for sparking Since two volumes of hydrogen combine with one volume of oxygen to form liquid water of negligible volume, one-third of the contraction after the explosion is due to oxygen The volume of the original air, minus the volume of the oxygen, gives the volume of nitrogen and inert gases

Oxygen can also be estimated volumetrically by placing a given volume of air, freed from carbon dioxide, in a graduated tube over mercury, and removing the oxygen by adding (by means of a bent pipette) a few c c of an alkaline solution of pyrogallol (p 796)

The proportion of oxygen in air can be determined gravimetrically by a method due to Dumas and Boussingault They admitted air, freed from carbon dioxide and moisture, into a vacuous tube filled with red-hot copper to remove the oxygen, whilst the nitrogen passed forward into an empty globe and was weighed directly (Fig 69) In one experiment 3 680 grams of oxygen were absorbed by the copper, leaving a residue of 12 304 grams of nitrogen in the globe and 0 069 gram of nitrogen in the copper oxide tube The ratio of oxygen to nitrogen was therefore 3 680 12 373 or oxygen nitrogen = 22 92 77 08% Allowing for the presence of 0 933% by volume of argon, the composition of normal air, after removing water-vapour and carbon dioxide, is now known to be

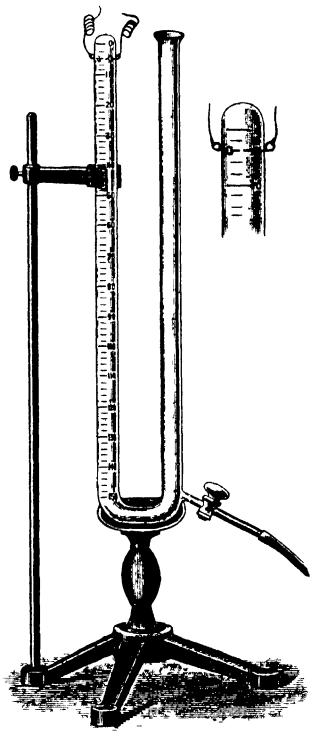


FIG 68 EUDIOMETER FOR EXPLODING A MIXTURE OF HYDROGEN AND OXYGEN

The gases are collected over mercury in the graduated limb of the eudiometer, the volume being measured with the mercury at the same level in both limbs In order to diminish the violence of the explosion, mercury is run out, so that the gases are under reduced pressure when exploded by a spark between the platinum wires of the graduated limb

| | By volume | By weight |
|---|---|---|
| Oxygen - - | - 20 96 | 23 2 |
| Nitrogen - - | - 78 11 | 75 5 |
| Argon - - | - 0 93 | 1 3 |
| | 100 00 | 100 0 |

(*b*) **Carbon dioxide**—The proportion of carbon dioxide in normal air is about 3 parts in 10,000 by volume, in large towns the proportion sometimes rises to 6 parts in 10,000, and in crowded rooms 30 parts in 10,000 may be found

The percentage of carbon dioxide in the atmosphere remains constant, in spite of the fact that millions of tons of it are being put into the air every day by the respiration of all living things, and the combustion of coal and other carbonaceous matter This constancy is due to the simultaneous removal of carbon dioxide by the following agents

(1) *The growth of plants*—Plants, like animals, derive energy from the oxidation of complex organic compounds The necessary oxygen is taken in through tiny pores in the leaves, called *stomata*, and the resulting carbon dioxide is returned to the air by the same means Under the

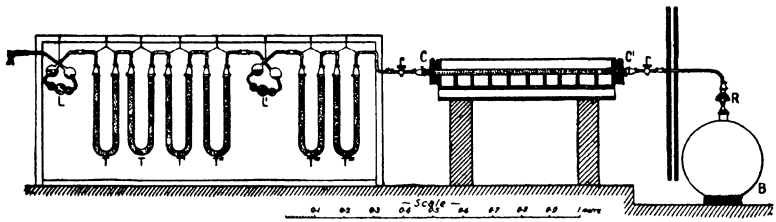



FIG 69 APPARATUS FOR DETERMINING THE GRAVIMETRIC COMPOSITION OF AIR (Dumas and Boussingault)

$X$ = tube for admission of air $L$ = Liebig potash-bulbs $TT$ = pumice moistened with potash $T'$ = potash in fragments $1''$ = ignited potash in fragments $L'$ = sulphuric acid in Liebig bulbs $T'''1'''$ = pumice moistened with strong sulphuric acid $CC'$ = hard glass tube filled with copper reduced from oxide $rr$ = taps for use in evacuating tube $B$ = large globe into which nitrogen flows on opening the tap, $R$

influence of light, however, plants also feed on carbon dioxide and water and give oxygen as a waste product Thus, the green colouring matter in the leaves, known as **chlorophyll**, absorbs energy in the form of sunlight and brings about a reduction which may be represented provisionally by the following equation

$$CO_2 + H_2O + \text{energy} = \underset{\text{Formaldehyde}}{H_2CO} + O_2$$

The formaldehyde shown in this equation is a hypothetical intermediate product in the formation of sugars and starches, *e g*

glucose, $C_6H_{12}O_6$, sucrose, $C_{12}H_{22}O_{11}$, starch, $C_{6x}H_{10x}O_{5x}$,

which can be derived from it by polymerisation and by the removal of water (p 700)

The reduction of carbon dioxide by the plant depends on the absorption of radiant energy, and therefore does not take place in the dark In the day-time the oxygen thus liberated greatly exceeds the amount absorbed by respiration; but at night the reduction ceases, and carbon dioxide only is exhaled Fungi, which possess no chlorophyll, cannot reduce

carbon dioxide, they therefore derive their energy and the materials used for building up their tissues by living parasitically on green plants or on dead organic matter

(ii) *The weathering of rocks*.—It has been estimated that more than 1500 million tons of carbon dioxide are removed annually from the air by the weathering of rocks. Thus igneous rocks such as felspars are attacked by carbonic acid to give sodium and potassium carbonate

$$2NaAlSi_3O_8 + 2H_2O + CO_2 = Na_2CO_3 + H_4Al_2Si_2O_9 + 4SiO_2,$$
$$2KAlSi_3O_8 + 2H_2O + CO_2 = K_2CO_3 + H_4Al_2Si_2O_9 + 4SiO_2$$
(China clay)

Sedimentary rocks such as limestone, $CaCO_3$, and dolomite, $MgCO_3$, $CaCO_3$, also absorb carbon dioxide from the air, giving rise to soluble, but unstable, bicarbonates which are carried into the oceans

$$CaCO_3 + CO_2 + H_2O \rightleftharpoons Ca(HCO_3)_2,$$
$$MgCO_3 + CO_2 + H_2O \rightleftharpoons Mg(HCO_3)_2$$

The reversible decomposition of these bicarbonates in sea water probably acts as a buffer to regulate the proportion of carbon dioxide in air, so that it does not undergo appreciable fluctuations.

The proportions of moisture and of carbon dioxide in the air may be estimated gravimetrically by drawing a known volume of air, say 40 litres, through drying tubes containing calcium chloride and then through a strong solution (20%) of potassium hydroxide in a series of weighed potash bulbs. Calcium chloride is also used to prevent loss of moisture from the last potash bulb. Carbon dioxide can be estimated volumetrically by PETTENKOFER'S METHOD, as described below.

EXPT. 31. **Estimation of carbon dioxide in air (Pettenkofer's method).**

A dry bottle of about 8 litres capacity is fitted with a rubber stopper containing a hole rather larger than the narrow end of a burette. After the addition of 50 c.c. of standard N/100 baryta water (p. 123), this hole is stopped with a glass rod and the bottle shaken at intervals over a period of 40 minutes. In this way all the carbon dioxide in the bottle is absorbed. The excess of baryta is then estimated by removing the glass rod, adding a few drops of phenolphthalein and titrating with standard (N/100) oxalic acid. The capacity of the bottle is determined by adding water from a measuring cylinder, and the volume of the air in the bottle at the time of the experiment is estimated by subtracting the volume (50 c.c.) of the baryta from this volume and reducing to N.T.P. One c.c. of N/100 baryta is equivalent to 0·112 c.c. of carbon dioxide at N.T.P.

**Air a mixture**.—That air is a mixture and not a compound is proved

(i) By small variations in the proportions of nitrogen and oxygen in different localities and at different times.

(ii) By the fact that the composition of air can be altered, and its constituents separated mechanically, by diffusion through a porous membrane, or by solution in water, in which oxygen is more soluble than nitrogen.

(iii) By the fractional distillation of liquid air, which gives no evidence of the presence of chemical compounds

(iv) By the absence of any marked change of volume, or liberation or absorption of heat, when the constituents are mixed to give a product having just the same properties as natural air

(v) By the fact that its composition does not correspond with any definite chemical formula, even when the minor constituents are regarded as impurities Thus, if air were a compound, its percentage composition could not be represented by a simpler molecule than $N_{11}O_3$, whilst its vapour density does not differ much from that of NO.

# CHAPTER XX

## SULPHUR

### 16 SULPHUR S = 32 06

**Classification.**—In the Periodic Classification of the elements, sulphur appears as a member of the oxygen family At first sight this classification appears to be entirely wrong, since oxygen is almost unique in its rôle as a " supporter of combustion "—the only gas except chlorine in which both metals and non-metals burn fiercely Sulphur, on the other hand, is a combustible solid, which is intermediate in this respect between phosphorus and carbon. As in the nitrogen and phosphorus group, however, the classification thus indicated can be justified by referring to the electronic structures of the atoms of the two elements, and then deducing their valencies

The electronic structures of oxygen and sulphur atoms are represented by the following schemes

| | *K* | *L* | *M* |
|---|---|---|---|
| Oxygen $Z$ = | 8 = | 2 + | 6 |
| Sulphur $Z$ = | 16 = | 2 + | 8 + 6 |

Both elements can therefore acquire the electronic structures of the nearest inert gases (namely, Neon $Z = 10$ and Argon $Z = 18$) (i) by sharing two electrons with other atoms and thus forming two covalent bonds, or (ii) by accepting two electrons from other atoms and thus forming bivalent anions

(i) H – O – H
H – S – H

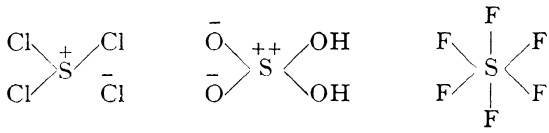
(ii) $Na_2^{++}\ O^{--}$
$Na_2^{++}\ S^{--}$

It must be admitted that water and sulphuretted hydrogen show no marked similarity to one another, but the metallic oxides and sulphides often show a general similarity in their properties and reactions, *e g.*

$$Sb_2O_3 + 6HCl \rightleftharpoons 2SbCl_3 + 3H_2O,$$
$$Sb_2S_3 + 6HCl \rightleftharpoons 2SbCl_3 + 3H_2S,$$
$$Sb_2O_3 + 2NaOH = 2NaSbO_2 + H_2O,$$
$$Sb_2S_3 + 2NaSH = 2NaSbS_2 + H_2S$$

Since the oxygen atom of water still carries two lone pairs of electrons, it can form tervalent and perhaps quadrivalent ions, by sharing them with other atoms, *e g* $H_3O^+$ and $H_4O^{++}$ This capacity to assume a higher valency, which is very restricted in oxygen, is fully developed in sulphur,

which appears to be tercovalent in $SCl_4$, quadricovalent in $H_2SO_4$, and hexacovalent in $SF_6$



Further points of resemblance between oxygen and sulphur may be found in the allotropy of the two elements, and in the wide range of metals and non-metals with which they combine

**Occurrence** —Large quantities of native sulphur are found in the volcanic districts of Sicily, and in Louisiana and Texas in America In combination, sulphur is found as *sulphide*, *e g* IRON PYRITES, $FeS_2$, GALENA, PbS, BLENDE, ZnS, and CINNABAR, HgS, and as *sulphate*, *e g* EPSOM SALTS, $MgSO_4,7H_2O$, GYPSUM, $CaSO_4,2H_2O$, and BARYTES, $BaSO_4$

**Preparation.**—The crude sulphur dug up in Sicily, containing about 20% of the element, is *melted* out from the limestone and other rocks with which it is mixed, either by setting fire to and burning a part of the sulphur, or by using a certain amount of auxiliary fuel In the GILL PROCESS the waste heat of the hot gases from one chamber is utilised to heat up the crude sulphur in another chamber, with a consequent saving of sulphur The product still contains about 5% of rocky impurity, but can be used in this state for a number of purposes, *e g* in horticulture It is purified by *distilling* it from an iron pot (Fig 70) into a brickwork chamber Solid FLOWERS OF SULPHUR are first deposited, but when the chamber heats up liquid sulphur is condensed, which is cast into sticks and sold as ROLL SULPHUR or sent out in massive blocks

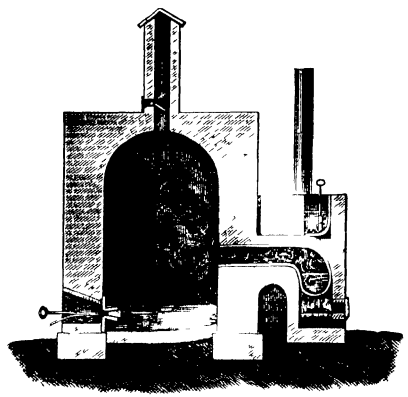


FIG 70 DISTILLATION OF SULPHUR

Molten sulphur is admitted by means of a valve to the retort, *G* The vapour distils into the chamber, *A*, where it condenses to liquid sulphur, *S*

The sulphur deposits in Louisiana and Texas are now the largest source of supply They contain as much as 70% of sulphur, but are several hundred feet below the surface, and covered by layers of limestone, quicksand and clay The ordinary methods of mining cannot be used owing to the quicksand and to the presence of the poisonous gases, hydrogen sulphide and sulphur dioxide In the FRASCH PROCESS (Fig 71) three concentric pipes (protected in part by an outer casing, *B*) are sunk through the quicksand and limestone strata, as far as the

impervious gypsum, which underlies the sulphur-bearing limestone Superheated water (at 165° and under a pressure of 10-18 atmospheres) is forced down the outer 8″ pipe, and out through the apertures, *W*, on to the impervious bed of gypsum, where it collects and melts the sulphur The latter is forced through the apertures, *S*, and up an inner 4″ pipe as shown in the diagram The passage of the sulphur to the surface is assisted by compressed air, under a pressure of 35 atmospheres , this converts the molten sulphur into a light froth which is delivered into steam-heated pans at the surface It is then pumped into large bins, where it solidifies ready for immediate use, since it does not usually contain more than 0 1% of impurities

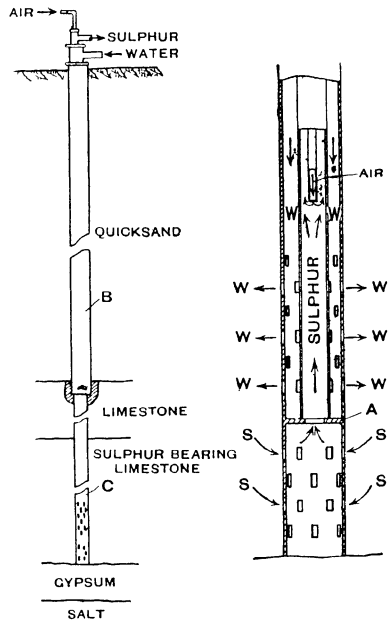



FIG 71 THE FRASCH PROCESS FOR OBTAINING SULPHUR

Sulphur was formerly recovered from the alkali waste (CaS) of the Leblanc carbonate process The alkali waste was mixed with water and treated with limekiln gas ($CO_2$ and $N_2$), and the resulting hydrogen sulphide was burnt to water and sulphur in specially constructed kilns

$$CaS + CO_2 + H_2O = CaCO_3 + H_2S,$$
$$2H_2S + O_2 = 2H_2O + 2S$$

Since the Leblanc process is now obsolete, this recovery process is no longer used

Sulphur is also obtained in the purification of coal gas (p 150), but since it is mixed with ferric oxide it is usually burnt to sulphur dioxide for the preparation of sulphuric acid

**Properties of sulphur** —(*a*) *Physical properties* —Sulphur is a pale yellow brittle solid, which melts at about 113° and boils at 444 6° under 760 mm pressure The melting-point varies considerably with the experimental conditions, but the boiling-point is sufficiently constant to be used as a secondary standard in calibrating thermometers and pyrometers for use at high temperatures Sulphur is insoluble in water, but very soluble in carbon disulphide, from which it may be recrystallised

(*b*) *Chemical properties* —Sulphur unites directly with most of the metals to form SULPHIDES similar to those which are found in the native state as minerals It burns in air or oxygen, forming **sulphur dioxide,** $SO_2$, and a little **sulphur trioxide,** $SO_3$ It also unites directly with phosphorus and the halogens, and less readily with carbon and hydrogen It is not acted upon by ordinary dilute acids, but concentrated

nitric and sulphuric acids oxidise it to sulphuric acid and sulphur dioxide respectively

$$S + 2HNO_3 = H_2SO_4 + 2NO,$$

and

$$S + 6HNO_3 = H_2SO_4 + 6NO_2 + 2H_2O,$$

$$S + 2H_2SO_4 = 3SO_2 + 2H_2O$$

Sulphur is dissolved by alkalis, forming " liver of sulphur " (p 252)

## The Allotropy of Sulphur

**Allotropy.**—The term allotropy was introduced by Berzelius in 1841 to describe all those cases in which an element is known to exist in the same state in more than one form It is thus a very general term covering many different phenomena Thus it can be applied equally to the two solid modifications of carbon, namely, diamond and graphite, or to the two gases, oxygen and ozone In the case of sulphur, the three distinct phenomena of polymerism, isomerism, and polymorphism are all covered by this elastic term

**Polymorphism of soluble sulphur.**—The ordinary soluble form of sulphur (p 247) is capable of crystallising in four different ways and thus affords an excellent example of POLYMORPHISM This term was introduced by Mitscherlich, in 1823, to describe those cases in which a " substance, whether simple or compound, may affect two crystalline forms " In most cases the molecules are probably identical, but are marshalled in different ways in the various crystalline forms , the differences between these forms therefore disappear when the crystalline structure is destroyed by fusion or by dissolution The four polymorphic forms of sulphur are known as

| | |
|---|---|
| $S_I$, Rhombic Sulphur | $S_{II}$, Prismatic Sulphur |
| $S_{III}$, Nacreous or Pearly Sulphur | $S_{IV}$, Tabular Sulphur |

**$S_I$, Rhombic sulphur.**—The stable form of sulphur separates in orthorhombic crystals on evaporating a solution of sulphur in carbon disulphide It has a density of 2 06 and is soluble in carbon disulphide to the extent of 27 grams in 100 grams of solution at 15° It melts at 112 8° if heated quickly , but if heated slowly it changes at 96° into prismatic sulphur, which melts at 119 25°

**$S_{II}$, Prismatic sulphur.**—When molten sulphur is allowed to solidify in a small crucible or basin, it crystallises in long needles or prisms which are too slender to show the crystalline faces clearly , but when larger quantities are used, crystallisation takes place more slowly, and transparent crystals up to half an inch in diameter may be obtained

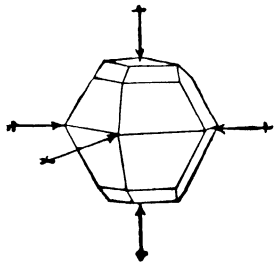
EXPT 32 **Preparation of prismatic sulphur.**

Roll sulphur is melted in a crucible and allowed to cool When the surface has solidified, two holes are made in it and the molten sulphur remaining in the interior is poured out A mass of small prisms is revealed when the surface is cut away

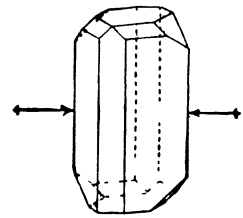
Prismatic sulphur has a density of 1 98 at 0°, *i e* about 4% less than the rhombic form , and it dissolves equally readily in carbon disulphide

When heated quickly it melts at 119 25°, but when the liquid is kept for a short time it undergoes partial conversion into "insoluble sulphur" (p 247) and the freezing-point falls to 114 5° Below 96° prismatic sulphur changes back to rhombic sulphur The temperature at which one allotrope changes into another allotrope is known as the TRANSITION POINT (p 536)

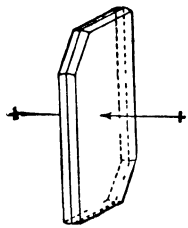
**$S_{III}$, Nacreous sulphur and $S_{IV}$, Tabular sulphur** crystallise in the same (monoclinic or monosymmetric) system of symmetry as prismatic sulphur, but are unstable under all conditions, reverting to prismatic or rhombic sulphur according to whether the temperature is above or below 96°



(*a*) $S_I$, ORTHORHOMBIC SULPHUR.



(*b*) $S_{II}$, PRISMATIC SULPHUR (MONOSYMMETRIC)



(*c*) $S_{III}$, NACREOUS SULPHUR (MONOSYMMETRIC).



(*d*) $S_{IV}$, TABULAR SULPHUR (MONOSYMMETRIC)

FIG 72 THE CRYSTALLINE FORMS OF SULPHUR
(The arrows represent axes of two-fold symmetry)

**Allotropy of liquid sulphur.**—When sulphur is heated above the melting-point, the clear yellow mobile liquid, which is first formed, darkens in colour and suddenly becomes very viscous at about 160° On further heating the liquid turns almost black in colour and gradually becomes more mobile as the boiling-point is approached These changes in viscosity are due to the fact that liquid sulphur is an equilibrium-mixture of two allotropes, $S_\lambda$ and $S_\mu$, which are called SOLUBLE SULPHUR and INSOLUBLE SULPHUR respectively, because of their behaviour to carbon disulphide

$$S_\lambda \rightleftharpoons S_\mu$$

At the melting-point of prismatic sulphur, 119 2°, the proportion of $S_\mu$ is 3 6%, but it increases as the temperature rises If molten sulphur near its boiling-point, in the presence of sulphur dioxide, is quenched

quickly by pouring into cold water, a stringy mass of PLASTIC SULPHUR is produced, half of which consists of insoluble sulphur, *i e* $S_\mu$ Sulphur dioxide checks the reversion of insoluble to soluble sulphur and is regarded as an anti-catalyst , hydrogen sulphide and ammonia, on the other hand, accelerate the change so much as to make it impossible to preserve the insoluble sulphur by quenching

The crystalline varieties of sulphur which have been considered above are composed of soluble sulphur, $S_\lambda$, and the reason why the melting-point of prismatic sulphur falls from 119 2° to 114 5° on standing is because 3 6% of insoluble sulphur, $S_\mu$, are formed at 119 2° and thereby lower the melting-point The non-crystalline form of sulphur, known as FLOWERS OF SULPHUR, differs from ordinary ROLL SULPHUR in that it contains about 30% of insoluble sulphur, due to the fact that the equilibrium between $S_\lambda$ and $S_\mu$ is " frozen " by the direct solidification of sulphur vapour

Determinations of molecular weight, by lowering of freezing-point, etc , show that $S_\lambda$ and $S_\mu$ have the same molecular weight and are therefore represented by the same molecular formula, namely $S_8$, although they differ widely in their properties and especially in their behaviour towards carbon disulphide They are therefore said to be ISOMERIC, a term that is used to describe substances of which the molecules are built up from the same number and kinds of atoms, but arranged in different ways in the molecule The existence of isomerism, in this and in many other cases, affords clear evidence that the atoms are not merely jumbled together in the molecule, but are built up into some definite structure

**Sulphur vapour** —Sulphur boils at 444 6° Its vapour-density, measured at 200° under reduced pressure, agrees with that required by the formula $S_8$, but falls progressively as the temperature is raised, until at 1000° it corresponds with the formula $S_2$ Sulphur vapour therefore affords an example of ASSOCIATION or POLYMERISATION, in the grouping together of the molecules of $S_2$ into molecules of $S_8$ on cooling from 1000° downwards, and of the converse process of DISSOCIATION, or reversible decomposition of these larger molecules, when the vapour is heated again to 1000° When heated still further to 2000°, the vapour consists mainly of monatomic molecules, $S_1$

**Allotropy, polymerism, isomerism, and polymorphism.**—From the preceding paragraphs it appears that the term allotropy as applied to sulphur covers three distinct phenomena

(*a*) *Association and dissociation* —The vapour affords an illustration of reversible polymeric change, the two components of gaseous sulphur differing in the *number of atoms in the molecule*

(*b*) *Isomerism* —In liquid sulphur there is an equilibrium between two isomeric forms of the element which, when solid, are known as soluble and insoluble sulphur The molecules of soluble and insoluble sulphur differ in the *arrangement of the atoms in the molecule* , thus soluble sulphur contains rings of 8 atoms, whilst in insoluble sulphur these atoms are arranged in chains, the length of which may be increased still further by polymerisation

(*c*) *Polymorphism* —In the solid state the four crystalline forms of soluble sulphur afford an example of polymorphism, since all the crystals appear to be built up from identical molecules, but differ in the *arrange-*

*ment of the molecules in the crystal* Of the four crystalline varieties, two, the rhombic and prismatic forms, being readily convertible into one another, are described as ENANTIOTROPIC (Greek, ἐναντίος, opposite, τρέπω, I turn), the other two, the nacreous and tabular forms, which can only change in one direction, namely, into a more stable form, are described as MONOTROPIC (p 536).

Finely-divided sulphur can be obtained quite readily as a "colloidal suspension" (p 641) in water Thus **colloidal sulphur** may be prepared by atmospheric oxidation of ammonium sulphide, in the presence of gelatine, or by pouring an alcoholic solution of sulphur into water

**Uses of sulphur.**—Sulphur is used in the manufacture of sulphuric acid (p. 256), calcium bisulphite (p 259), carbon disulphide (p 148), sulphur chloride (p 265), matches, gunpowder, etc Sulphur is also used in the free state as a fungicide for vines and hops, probably because the element readily yields traces of sulphur dioxide and sulphuretted hydrogen by oxidation and reduction

## SULPHUR AND HYDROGEN

**Hydrogen sulphide or sulphuretted hydrogen**, $H_2S$ —Sulphuretted hydrogen, the most important compound of sulphur with hydrogen, has been known for a long period as a constituent of "sulphur waters," such as those of Harrogate, and as a malodorous product of the decomposition of organic compounds containing sulphur, such as albumen

**Preparation of hydrogen sulphide.**—Hydrogen sulphide is produced when sulphur is boiled in an atmosphere of hydrogen, if the resulting vapours are passed over finely-divided nickel at 450°, almost complete combination takes place and very pure hydrogen sulphide can be condensed out by cooling with solid carbon dioxide

$$S(\text{solid}) + H_2(\text{gas}) \rightleftharpoons SH_2(\text{gas}) + 2730 \text{ cals}$$

When the temperature is raised above 500°, the reverse reaction, indicated by the lower arrow, becomes more and more important, because the combination is exothermic. Thus the dissociation increases from 2 5% at 700° to 75% at 1700°.

Hydrogen sulphide is usually prepared, *e g* in Kipp's apparatus (p 70), by the action of dilute sulphuric or hydrochloric acid on ferrous sulphide

$$FeS + H_2SO_4 = H_2S + FeSO_4$$

The gas may be collected over water already saturated with hydrogen sulphide, or it may be dried by means of fused calcium chloride or phosphoric oxide and collected over mercury, or by displacement of the air from the vessel to be filled with the gas

In addition to acid spray, the gas prepared in this way always contains hydrogen, owing to the presence of free iron in the ferrous sulphide, which is prepared by melting together iron and sulphur It may be purified from acid spray by passing the gas through a saturated solution of sodium hydrogen sulphide,

$$NaHS + HCl = NaCl + H_2S,$$

and from moisture by calcium chloride or phosphoric oxide If the product is then liquefied by means of a mixture of carbon dioxide snow and methylated spirit, the hydrogen passes on and pure liquid hydrogen sulphide is left

The pure gas can also be obtained by the action of water on aluminium sulphide,

$$Al_2S_3 + 6H_2O = 2Al(OH)_3 + 3H_2S,$$

but, when more than small quantities are required, it is prepared by direct synthesis from its elements, as indicated above

**Physical properties.**—Hydrogen sulphide is a colourless gas with an odour of rotten eggs It condenses to a colourless liquid which boils at $-60\ 75^\circ$ It is moderately soluble in water, 4 7 and 2 6 volumes dissolving in 1 volume of water at $0^\circ$ and $20^\circ$ respectively It is not generally known that hydrogen sulphide is very poisonous at concentrations above 0 1%, when it is at least as dangerous as prussic acid vapour The danger from the gas is enhanced by the fact that at concentrations above the fatal limit it paralyses the olfactory nerves, and therefore cannot be smelt

**Chemical properties.**—In excess of air, hydrogen sulphide burns with a blue flame to water and sulphur dioxide,

$$2H_2S + 3O_2 = 2H_2O + 2SO_2,$$

but in a restricted supply of air sulphur is deposited, because hydrogen has the greater affinity for oxygen

$$2H_2S + O_2 = 2H_2O + 2S$$

Since its heat of formation from its elements is only small, namely 2730 calories for the dry gas and 7300 calories for the aqueous solution, hydrogen sulphide is very ready to part with its hydrogen and to act as a reducing reagent. Thus sulphur may be liberated from it by any of the ordinary oxidising agents, such as air, chlorine, aqueous bromine or iodine, nitric acid, chromic acid, ferric chloride, etc

$$Cl_2 + H_2S = S + 2HCl,$$

$$2HNO_3 + H_2S = S + 2NO_2 + 2H_2O,$$

$$2CrO_3 + 6HCl + 3H_2S = 3S + 2CrCl_3 + 6H_2O,$$

$$2FeCl_3 + H_2S = S + 2FeCl_2 + 2HCl$$

Hydrogen sulphide reduces sulphuric acid, which cannot therefore be used for drying the gas

$$H_2SO_4 + H_2S = 2H_2O + SO_2 + S.$$

It also reduces sulphur dioxide to sulphur.

$$SO_2 + 2H_2S = 2H_2O + 3S.$$

In this action sulphur dioxide, which usually acts as a reducing agent, is compelled by the sulphuretted hydrogen to part with its oxygen and thus to play the part of an oxidising agent

In the presence of bases, hydrogen sulphide acts as a reducing agent by absorbing oxygen instead of by liberating hydrogen Thus, calcium sulphide in aqueous solutions is oxidised to calcium sulphite and sulphate on exposure to air,

$$2CaS + 3O_2 = \underset{\text{Calcium sulphite}}{2CaSO_3} \quad \text{or} \quad CaS + 2O_2 = \underset{\text{Calcium sulphate}}{CaSO_4},$$

and moist ferrous sulphide is oxidised to ferrous sulphate,

$$FeS + 2O_2 = \underset{\text{Ferrous sulphate}}{FeSO_4}$$

Hydrogen sulphide imparts an acid reaction to water and in many of its chemical properties behaves as a weak dibasic acid from which a series of SULPHIDES are derived Thus, it is absorbed by caustic potash with the production of **potassium sulphide,** $K_2S$, and **potassium hydrogen sulphide,** KSH

$$2KOH + H_2S = K_2S + 2H_2O ,$$
$$KOH + H_2S = KSH + H_2O$$

In qualitative analysis (p 379), use is made of the fact that hydrogen sulphide will precipitate the sulphides of some metals from acid solutions of their salts, *e g* copper and lead, whereas the sulphides of other metals are only precipitated from neutral or alkaline solutions of their salts, *e g* zinc and manganese

$$Pb(NO_3)_2 + H_2S = PbS + 2HNO_3,$$
$$ZnSO_4 + (NH_4)_2S = ZnS + (NH_4)_2SO_4$$

Paper soaked in lead acetate solution is turned brown and then black by hydrogen sulphide, and is used as a sensitive test for the gas

**Formula of hydrogen sulphide.**—The vapour density of hydrogen sulphide is 17 and indicates therefore a molecular weight of 34, which would be satisfied by the molecular formula $H_2S$ If dry hydrogen sulphide is sparked in a graduated tube over mercury, it is slowly decomposed into hydrogen and solid sulphur without any alteration in volume, and hence contains its own volume of hydrogen

$$\underset{1 \text{ vol}}{\text{Hydrogen sulphide}} = \underset{1 \text{ vol}}{\text{Hydrogen}} + \underset{\text{(Negligible volume)}}{\text{Sulphur}}$$

$$\text{by Avogadro's hypothesis,} \quad \underset{(1 \text{ molecule})}{H_xS} = \underset{(1 \text{ molecule})}{H_2} + S \text{ and } x = 2$$

EXPT 33 **Volumetric composition of hydrogen sulphide.**

Hydrogen sulphide may be shown to contain its own volume of hydrogen by heating it with metallic copper

Copper foil is placed in a wide glass tube (Fig 73), the ends of which are drawn out and fitted with rubber tubes and clips The apparatus is filled with hydrogen sulphide at room temperature and pressure, and then clipped up On heating gently in a Bunsen flame, the copper interacts

with the hydrogen sulphide to form cuprous sulphide, $Cu_2S$, and hydrogen The tube is allowed to cool, and the volume of hydrogen shown to be equal to the original volume of hydrogen sulphide by opening one end under mercury

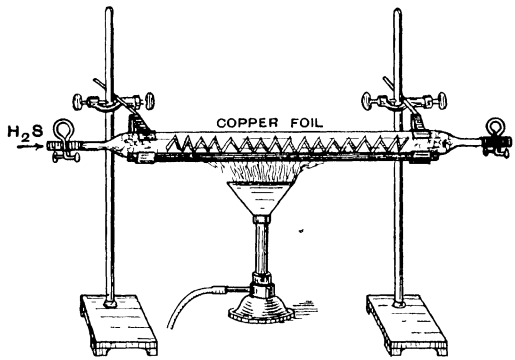



FIG 73 VOLUMETRIC COMPOSITION OF HYDROGEN SULPHIDE

**Estimation of hydrogen sulphide.**—Hydrogen sulphide can be estimated in aqueous solutions by adding an excess of standard iodine and titrating the residual iodine with sodium thiosulphate

$$H_2S + I_2 = 2HI + S$$

More accurate results are obtained when hydrogen sulphide is estimated by standard acidified arsenious oxide solution (p 420)

$$3H_2S + As_2O_3 = As_2S_3 + 3H_2O$$

**Liver of sulphur** —Hydrogen sulphide and sulphur dioxide interact to form sulphur and water, according to the equation

$$2H_2S + SO_2 = 2H_2O + 3S\ ,$$

but, as the hydride and oxide are both acids, this action can be reversed by the addition of alkalis These dissolve sulphur, forming, for instance, potassium sulphide and potassium sulphite as shown in the equation

$$\underset{}{3S} + \underset{}{6KOH} = \underset{\text{Potassium sulphide}}{2K_2S} + \underset{\text{Potassium sulphite}}{K_2SO_3} + \underset{}{3H_2O}$$

On the addition of acids the sulphur is reprecipitated

$$2K_2S + K_2SO_3 + 6HCl = 6KCl + 3H_2O + 3S.$$

The sulphide formed in this action may combine with a further quantity of sulphur to form POLYSULPHIDES, such as $K_2S_2$ and $K_2S_4$, whilst the sulphite may combine with sulphur to form a THIOSULPHATE, *e g* $K_2S_2O_3$ The formation of these compounds increases the amount of sulphur which is dissolved by the alkali and reprecipitated by the addition of acids A

mixture of polysulphides and thiosulphate, obtained as a liver-brown mass by fusing potassium carbonate with sulphur, *e g*

$$3K_2CO_3 + 6S = \underset{\text{Potassium disulphide}}{2K_2S_2} + \underset{\text{Potassium thiosulphate}}{K_2S_2O_3} + 3CO_2,$$

is used in medicine under the name of LIVER OF SULPHUR, and the sulphur which is reprecipitated by acids is known as MILK OF SULPHUR

**Hydrogen persulphides**, corresponding with the alkali polysulphides, are known but are not important

## SULPHUR AND OXYGEN

**Oxides and acids of sulphur** —Sulphur forms a large number of oxides and oxy-acids The most important oxides are

**Sulphur dioxide** $SO_2$ (or sulphurous anhydride) — **Sulphur trioxide**, $SO_3$ (or sulphuric anhydride)

The corresponding acids are

**Sulphurous acid**, $H_2SO_3$, forming a series of SULPHITES — **Sulphuric acid**, $H_2SO_4$, forming a series of SULPHATES

Sulphurous and sulphuric acids, being dibasic, can form two series of salts, *e g*

**Sodium sulphite**, $Na_2SO_3$
**Sodium hydrogen sulphite,** or **sodium bisulphite**, $NaHSO_3$

**Sodium sulphate**, $Na_2SO_4$
**Sodium hydrogen sulphate,** or **sodium bisulphate**, $NaHSO_4$

**Sulphur dioxide**, $SO_2$ —(*a*) *Preparation* — Sulphur dioxide is usually prepared in the laboratory by heating concentrated sulphuric acid with copper turnings (Fig 74)

$$Cu + 2H_2SO_4 = CuSO_4 + 2H_2O + SO_2$$

The action is more complex than is indicated by the above equation, since appreciable quantities of cuprous and cupric sulphides are also formed (p 314) The gas prepared in this way contains sulphur trioxide and traces of hydrogen sulphide, which may be removed by washing with lead acetate solution

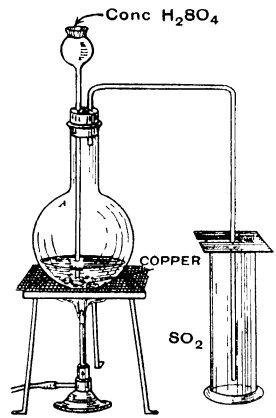



FIG 74 PREPARATION OF SULPHUR DIOXIDE

The gas is collected by the upward displacement of air or over mercury, since it is very soluble in water

Sulphur dioxide is prepared commercially (*e g* in the manufacture of sulphuric acid) by burning iron pyrites

$$4FeS_2 + 11O_2 = 2Fe_2O_3 + 8SO_2$$

The crude gas contains arsenious oxide, $As_4O_6$, sulphur trioxide, $SO_3$, and

dust as impurities. It may be purified by passing it through settling chambers, coke filters, and coke towers with sulphuric acid flowing down them

Crude sulphur dioxide is also prepared by roasting other mineral sulphides, *e g* ZnS, or by burning sulphur, or " spent iron oxide " from the gas works (p 150), which contains ferrous sulphide, FeS, and free sulphur

Liquid commercial sulphur dioxide is prepared by dissolving the crude gas in cold water, driving it out again by heat, drying with sulphuric acid, and then compressing to a liquid The gas delivered from a siphon of liquid sulphur dioxide is substantially pure

**Physical properties.**—Sulphur dioxide is a colourless gas with a pungent odour, and is very soluble in water, 80 volumes of the gas dissolving in 1 volume of water at 0° It can be liquefied at 18° by a pressure of three atmospheres to a colourless liquid which boils at − 10° under atmospheric pressure The liquid is of interest because it dissolves a number of metallic salts, *e g* potassium iodide, to give solutions which are ionised and conduct the electric current

**Chemical properties.**—(*a*) *Acid properties* —Sulphur dioxide in aqueous solutions has all the properties of a weak dibasic acid It combines with alkalis and with basic oxides to form neutral SULPHITES and acid BISULPHITES, in addition to METABISULPHITES derived from the hypothetical acid, $H_2S_2O_5$

$$2NaOH + SO_2 = \underset{\text{Sodium sulphite}}{Na_2SO_3} + H_2O ,$$

$$2NaOH + 2SO_2 = \underset{\text{Sodium bisulphite}}{2NaHSO_3} = \underset{\text{Sodium metabisulphite}}{Na_2S_2O_5} + H_2O$$

**Sodium metabisulphite,** $Na_2S_2O_5$, prepared by evaporating a solution of the bisulphite, is used in photography as a developer (p 326), whilst **calcium bisulphite,** $Ca(HSO_3)_2$, prepared by the action of sulphur dioxide on milk of lime, is used to disintegrate wood fibre in the manufacture of paper pulp

(*b*) *Sulphur dioxide as a reducing agent* —Although gaseous sulphur dioxide has very little tendency to combine directly with oxygen, it is slowly oxidised by air in the presence of water or alkalis, and very rapidly by hydrogen peroxide, chlorine water, ferric chloride, acidified dichromate and potassium permanganate

$$H_2O_2 + H_2SO_3 = H_2O + H_2SO_4 ,$$

$$Cl_2 + H_2O + H_2SO_3 = 2HCl + H_2SO_4 ,$$

$$\underset{\text{Ferric chloride}}{2FeCl_3} + H_2O + H_2SO_3 = \underset{\text{Ferrous chloride}}{2FeCl_2} + 2HCl + H_2SO_4 ,$$

$$\underset{\text{Potassium dichromate}}{K_2Cr_2O_7} + H_2SO_4 + 3H_2SO_3 = \underset{\text{Potassium sulphate}}{K_2SO_4} + \underset{\text{Chromium sulphate}}{Cr_2(SO_4)_3} + 4H_2O ,$$

$$\underset{\text{Potassium permanganate}}{2KMnO_4} + 5H_2SO_3 = \underset{\text{Potassium sulphate}}{K_2SO_4} + \underset{\text{Manganese sulphate}}{2MnSO_4} + 2H_2SO_4 + 3H_2O$$

(*c*) *Bleaching action of sulphur dioxide*.—Sulphur dioxide reduces many coloured compounds to colourless derivatives and is frequently used as a bleaching agent for substances, such as straw and sponge, which are injured by bleaching powder, the oxidising action of air and light restores the original yellow colour to straw, but it may be rendered white again by washing it with a solution of sulphur dioxide. Sulphur dioxide is also used as a disinfectant.

(*d*) *Oxidising action of sulphur dioxide*.—Although sulphur dioxide usually acts as a reducing agent, it can sometimes be made to part with its oxygen and thus to assume the rôle of an oxidising agent. Thus it reacts with hydrogen sulphide according to the equation,

$$SO_2 + 2H_2S = 2H_2O + 3S,$$

and oxidises coke to carbon dioxide

$$SO_2 + C = S + CO_2$$

The last reaction is exothermic and takes place rapidly and almost completely at 1100°. It is becoming of considerable industrial importance for the manufacture of sulphur, now that methods have been devised for isolating the small percentages (3-7%) of sulphur dioxide in the waste gases of certain metallurgical processes.

(*e*) *Additive compounds of sulphur dioxide*.—Although most of the combining power of sulphur is satisfied by combination with two atoms of oxygen, a certain amount of affinity remains available for the direct combination of sulphur dioxide with other substances. Thus it combines with *water* to form sulphurous acid, $H_2SO_3$, with *metallic oxides* to form sulphites and with certain *metals* to form HYDROSULPHITES, *e g*

$$Zn + 2SO_2 = ZnS_2O_4, \quad \text{(Zinc hydrosulphite)}$$

It combines with some solid metallic peroxides with incandescence to form sulphates

$$PbO_2 + SO_2 = PbSO_4,$$
$$Na_2O_2 + SO_2 = Na_2SO_4$$

Sulphur dioxide also combines with oxygen in the presence of platinum black to form **sulphur trioxide**, $SO_3$, and with chlorine in bright sunlight, or in the presence of activated charcoal, to form **sulphuryl chloride**, $SO_2Cl_2$.

**Sulphur trioxide**, $SO_3$, is manufactured on a large scale by the oxidation of sulphur dioxide by air in the presence of a catalyst, usually platinum (see p. 260). It can also be prepared by distilling pyrosulphuric acid, or ferric sulphate

$$H_2S_2O_7 = H_2SO_4 + SO_3,$$
$$Fe_2(SO_4)_3 \rightleftharpoons Fe_2O_3 + 3SO_3$$

Sulphur trioxide exists in two solid forms. The $\alpha$-form consists of colourless needles, melting at 17°, but in contact with moist air it changes into the $\beta$-form, an asbestos-like solid which volatilises without melting at 50°.

Sulphur trioxide reacts violently with water, forming a number of hydrates, the most important of which are **sulphuric acid**, $SO_3,H_2O$ or $H_2SO_4$, and **pyrosulphuric acid**, $2SO_3,H_2O$ or $H_2S_2O_7$. It combines directly with basic oxides to form sulphates, and with hydrochloric acid to form **chlorosulphonic acid**, Cl $SO_2$ OH. Under special conditions it

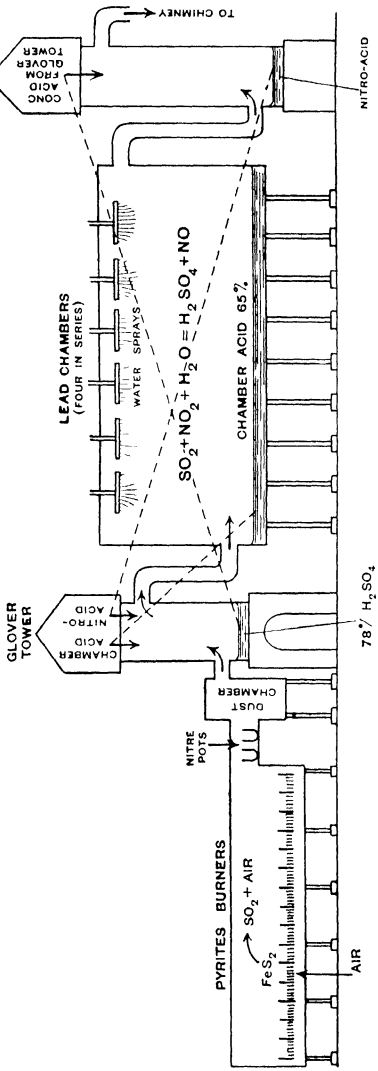



FIG 75 DIAGRAM OF LEAD CHAMBER PROCESS

will also unite with oxygen to form **sulphur heptoxide**, $S_2O_7$, and with sulphur to form **sulphur sesquioxide**, $S_2O_3$

**Sulphuric acid**, $H_2SO_4$ — Sulphuric acid is manufactured on the large scale by

(*a*) The Lead Chamber Process,

(*b*) The Contact Process

**The lead chamber process** —In this process (Fig 75) sulphur dioxide, usually prepared by burning iron pyrites, $FeS_2$, is oxidised in large lead chambers to sulphuric acid by the action of air, oxides of nitrogen and water The changes which take place may be represented by the following equations

(i) $4FeS_2 + 11O_2 = 2Fe_2O_3 + 8SO_2$ ,

(ii) $SO_2 + H_2O + NO_2 = H_2SO_4 + NO$ ,

(iii) $2NO + O_2 = 2NO_2$

The precise mechanism of the catalytic action of the oxides of nitrogen is in dispute, but it is probable that nitrogen peroxide gives up part of its oxygen to sulphur dioxide and that the resulting nitric oxide is reoxidised by the air to nitrogen peroxide Theoretically, therefore, a small quantity of nitrogen peroxide should be capable of oxidising an unlimited amount of sulphur dioxide, but in practice this is not so because some escapes with the waste gases or is decomposed into nitrogen or nitrous oxide

The hot gases, prepared by roasting pyrites (50% S), " spent iron oxide " from the gas works (40% S), or zinc blende (28% S), are passed into a long flue, in which dust is deposited and into which oxides of nitrogen are distilled from nitre pots standing in the flue (Oxides of nitrogen are now often prepared by the catalytic oxidation of ammonia ) The gases are

then led into the base of the GLOVER TOWER, a square shaft packed with earthenware rings, over which trickles a mixture of dilute chamber acid with the nitrosulphonic acid, $NO_2SO_3H$, from the Gay-Lussac tower described below Dilution with weak chamber acid liberates the oxides of nitrogen in the nitrated acid,

$$(iv)\quad 2NO_2SO_3H + H_2O = 2H_2SO_4 + NO_2 + NO,$$

and these are carried by the hot gases into the first of three or four large wooden chambers lined with lead Water is sprayed from the top of the chambers and dilute (65%) sulphuric acid, produced by reaction (ii) above, collects on the floors of the chambers The gases leaving the last chamber contain oxides of nitrogen together with much atmospheric nitrogen from the pyrites burners In order to save the valuable oxides of nitrogen, the gases are sent up the GAY-LUSSAC TOWER and washed by means of concentrated acid (from the Glover tower) flowing down over layers of coke The oxides of nitrogen are thereby absorbed, probably in the form of **nitrosulphonic acid,** $NO_2SO_3H$, which is returned to the Glover tower and decomposed by dilute chamber acid as described above The function of the Gay-Lussac tower is therefore to prevent the loss of oxides of nitrogen, whilst the Glover tower serves (i) to return the oxides of nitrogen to the chamber, (ii) to cool the hot gases from the burners, (iii) to deprive the chamber acid of water, and (iv) to remove from the chamber acid any oxides of nitrogen which it may contain The final product of the process is the partially concentrated acid collected at the base of the Glover tower

**Concentration of chamber acid** —Chamber acid contains about 65% of sulphuric acid, and is suitable for use in the manufacture of ammonium sulphate (p 186) and of superphosphate (p 215) When a more concentrated acid is required the " contact " acid (p 259) is generally used, but

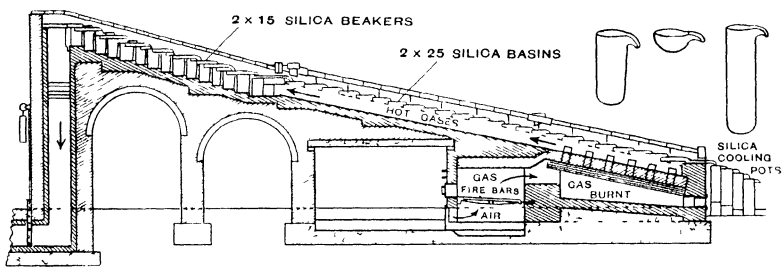



FIG 76 CASCADE FOR CONCENTRATION OF SULPHURIC ACID
The acid flows down a series of silica beakers and silica basins, which are heated by hot air from a furnace

" chamber " acid may be concentrated by evaporation in lead pans until it contains 77% of $H_2SO_4$, after which lead dissolves rapidly in the hot acid Further concentration is effected

(i) by evaporation in cascades of basins of silica, or of acid-resisting cast-iron, heated by a coke fire or by oil fuel (Fig 76) ,
(ii) by passing hot gases from a coke generator over the surface of the dilute acid, as in the Kessler plant ,

(iii) by spraying it down a Gaillard tower (Fig 77) up which hot gases from the combustion of producer gas are passed

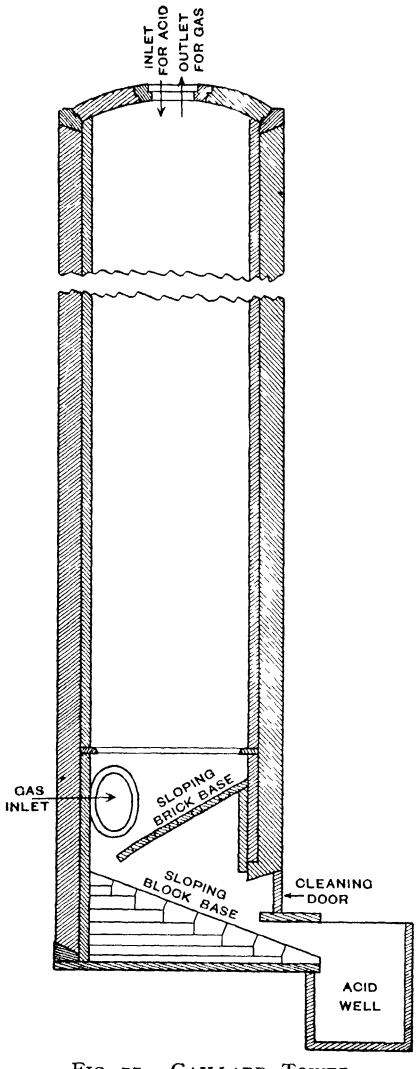



FIG 77 GAILLARD TOWER.

In each case much acid is liable to be lost as "acid mist," but most of this can be condensed and recovered by coke filters, whilst the residual fog is condensed by exposure to an electrical potential of some 80,000 volts

**Purification of chamber acid.**—The acid prepared by the lead chamber process is liable to contain traces of lead sulphate, oxides of nitrogen and arsenic The first two impurities may be removed by distilling with a little ammonium sulphate, when the lead sulphate is left behind and the oxides of nitrogen are reduced to nitrogen gas

$$(NH_4)_2SO_4 + N_2O_3 = 2N_2 + H_2SO_4 + 3H_2O$$

The arsenic may be precipitated as sulphide by the action of sulphuretted hydrogen on the dilute acid

EXPT 34 **To illustrate the lead chamber process**

Nitric oxide, prepared by the action of dilute nitric acid on copper, is passed in a slow stream, through a water bubbler, *A* (Fig 78), into a large flask, *C* At the same time steam from a flask, *E*, air from hand bellows, *D*, and sulphur dioxide from a syphon are also passed into the flask The rate of the flow of sulphur dioxide is indicated by the sulphuric acid bubbler, *B*, and should be three or four times as rapid as that of the nitric oxide , the supply of air must also be plentiful Reactions similar to those in the lead chambers take place and dilute sulphuric acid collects in the bottom of the flask

**The contact process.**—Under ordinary conditions sulphur dioxide does not unite directly with oxygen, since the two gases can exist together in

dry air for an indefinite period Rapid combination can be brought about, however, by making use of a solid catalyst, and this method of making sulphur trioxide for the production of sulphuric acid is now used on a large scale under the name of the CONTACT PROCESS The most effective catalyst is finely-divided platinum (" platinum black "), but this is generally used in the form of platinised asbestos (" Badische process "), or deposited on anhydrous magnesium sulphate (" Grillo process ") Vanadium oxide, usually supported on some inactive material, is also used

The first attempts to use this method failed, because the platinum soon lost its catalytic power The loss of activity was traced to " poisoning "

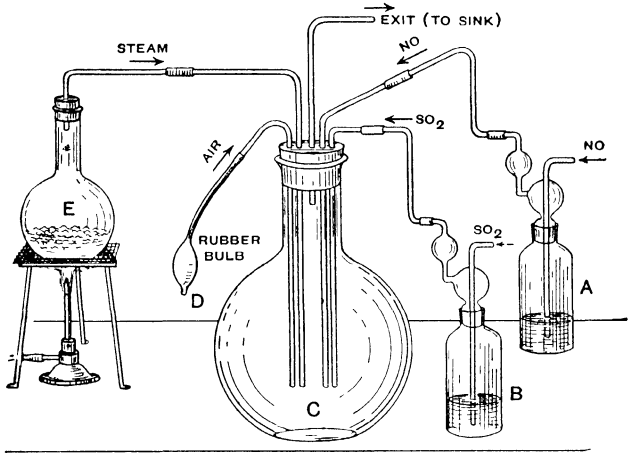



FIG 78 LABORATORY ILLUSTRATION OF THE LEAD CHAMBER PROCESS

of the catalyst, in part by " acid mist " from the pyrites burners, but more especially by arsenious oxide, $As_4O_6$ The gas (Fig 79) is therefore passed through a dust chamber and cooler to a series of filter boxes , it is then washed with a weak solution of sodium carbonate, and dried by passing through towers containing coke drenched with concentrated sulphuric acid It is then perfectly clear and free from fog, with the result that the activity of the catalyst can be maintained over a period of some years

The combination of sulphur dioxide and oxygen is a balanced exothermic action, as shown by the equation

$$2SO_2 + O_2 \rightleftharpoons 2SO_3 + 64{,}320 \text{ cals.}$$

The percentage of sulphur dioxide converted into sulphur trioxide therefore increases with the quantity of oxygen present (see Chapter XLI) In the commercial process three times as much oxygen is present as would be required to convert the whole of the sulphur dioxide to sulphur trioxide

Since the reaction is exothermic, the reverse change, leading to the

decomposition of the trioxide, becomes more and more important as the temperature rises Thus, for the composition, 7% $SO_2$, 10% $O_2$, 83% $N_2$, the maximum conversion at different temperatures is as follows

at 434°, 99% $SO_3$, at 550°, 85% $SO_3$, at 640°, 60% $SO_3$

Platinum, which will bring about a rapid oxidation at 440°, is therefore much more effective as a catalyst than ferric oxide, which becomes an active catalyst only at 600°, since at the latter temperature oxidation stops when two-thirds of the dioxide has been converted into trioxide

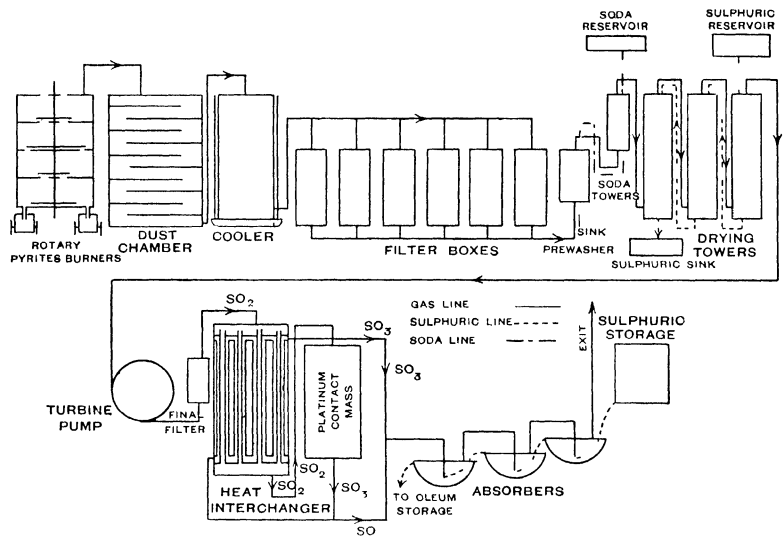



FIG 79 DIAGRAM OF CONTACT PROCESS FOR MANUFACTURE OF SULPHUR TRIOXIDE

Even with platinum as the catalyst, however, it is usual to effect a preliminary oxidation at 600° – 700°, because, although the equilibrium is unfavourable at this temperature, the reaction is very rapid, the oxidation is then completed at the optimum temperature of 440° The waste heat from the hot impure gases and from the converter is utilised to heat the cold pure gases before they are passed into the contact chambers In the MANNHEIM PROCESS, the sulphur dioxide and air from the pyrites burners are passed direct to a tower containing ferric oxide (in the form of burnt pyrites) at a temperature of 600° to 700° This brings about a preliminary oxidation of about one-half of the sulphur dioxide, and in addition removes the impurities The gases which remain after absorbing the sulphur trioxide can therefore be passed over a platinum catalyst *without further purification*, whilst the cheap ferric oxide catalyst, which absorbs the " poison," can be replaced as soon as it becomes inactive The sulphur trioxide produced by the contact process is mixed with large

quantities of nitrogen and, in spite of its hygroscopic nature, is not easily absorbed by water In practice, therefore, it is absorbed by oil of vitriol containing 97-99% of sulphuric acid, and if the product is too strong it is diluted by the addition of water or dilute acid

The sulphuric acid produced by the above process has the advantage of being specially pure, and in particular is practically free from arsenic, it is therefore suitable for use in the manufacture of edible products, where freedom from arsenic is essential, and for filling accumulators The main value of this process is, however, in the production of a highly concentrated acid, known commercially as FUMING SULPHURIC ACID or OLEUM, which may contain as much as 70% of sulphur trioxide dissolved in the pure acid Very large quantities of oleum are used for oxidation and sulphonation (p 777) in the synthetic dye and drug industries

**Physical properties of sulphuric acid** —Sulphuric acid containing more than 98 33% $H_2SO_4$ cannot be obtained by distillation, since an acid of this composition has a constant maximum boiling-point (330°) Thus, if the dilute acid is distilled, water is lost until an acid of this composition is obtained, whilst more concentrated specimens lose sulphur trioxide until the concentration falls to 98 33% $H_2SO_4$ The anhydrous acid of the composition, $H_2SO_4$, known commercially as "monohydrate," was formerly prepared by freezing the strongest acid obtained by distillation, and draining the crystals on a centrifugal machine, at the present time such an acid would be prepared by mixing the commercial acid with fuming acid, containing enough sulphur trioxide to convert all the water into sulphuric acid

Anhydrous sulphuric acid crystallises readily and melts at 10 4°, at 15° it has a density of 1 848 Pure sulphuric acid, as represented by the formula $H_2SO_4$, is a very poor electrical conductor, and would perhaps be an insulator if no dissociation took place when the crystals are melted, an aqueous solution containing 30% $H_2SO_4$ is, however, one of the best electrolytic conductors, the specific resistance being only 1 4 ohms per centimetre cube

**Chemical properties of sulphuric acid.**—(*a*) *Affinity for water* —Sulphuric acid has a great affinity for water When the concentrated acid is added to water, great heat is evolved, and hydrates, such as $H_2SO_4,H_2O$, $H_2SO_4,2H_2O$ and $H_2SO_4,4H_2O$, can be frozen out from the product The avidity of sulphuric acid for water is also shown by its dehydrating action on organic compounds, such as sugar and formic acid, which contain the elements of water

$$C_{12}H_{22}O_{11} - 11H_2O = 12C,$$
$$H\,CO\,OH - H_2O = CO$$

(*b*) *Acid properties* —Dilute sulphuric acid reddens litmus, liberates carbon dioxide from carbonates and reacts with basic oxides to give normal and acid SULPHATES (see below) In decinormal solution the acid is ionised to the extent of about 60%, it is therefore a "strong" acid, although not so strong as nitric and hydrochloric acids, which are almost completely ionised at this dilution The acid is dibasic and its

ionisation may therefore be regarded as taking place in two stages, the second of which only takes place to a small extent

$$H_2SO_4 + H_2O \rightleftharpoons H_3O^+ + HSO_4^-,$$

$$HSO_4^- + H_2O \rightleftharpoons H_3O^+ + SO_4^{--}.$$

The liberation of hydrochloric acid from common salt by concentrated sulphuric acid is due to the much higher boiling-point of the latter and not, as might be supposed, to a superiority in strength For the same reason silica, which has only feeble acid properties, can displace sulphuric acid from its salts at high temperatures

(*c*) *Sulphuric acid as an oxidising agent* —Concentrated sulphuric acid, unlike the dilute acid, has oxidising properties, which increase in power as the concentration of sulphur trioxide increases Thus the hot concentrated acid oxidises charcoal to carbon dioxide and sulphur to sulphur dioxide,

$$C + 2H_2SO_4 = CO_2 + 2SO_2 + 2H_2O,$$
$$S + 2H_2SO_4 = 3SO_2 + 2H_2O\ ,$$

it also liberates bromine and iodine from their hydrides,

$$2HBr + H_2SO_4 = Br_2 + SO_2 + 2H_2O,$$
$$2HI + H_2SO_4 = I_2 + SO_2 + 2H_2O$$

(*d*) *Action of sulphuric acid on the metals* —Dilute sulphuric acid interacts with the more electropositive metals, such as magnesium, zinc and iron, to give hydrogen and a sulphate

$$Fe + H_2SO_4 = FeSO_4 + H_2$$

The hot concentrated acid, owing to its oxidising powers, will also dissolve lead, copper, mercury and silver, but sulphur dioxide is liberated in place of hydrogen, *e g*

$$Cu + 2H_2SO_4 = CuSO_4 + SO_2 + 2H_2O$$

(*e*) *Decomposition* —When the vapour of sulphuric acid is passed through a red-hot silica tube, it is decomposed as shown in the equation

$$2H_2SO_4 = 2H_2O + 2SO_2 + O_2$$

Some of its salts break down in the same way when heated, *e g*

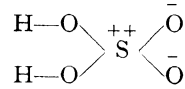
$$2Al_2(SO_4)_3 = 2Al_2O_3 + 6SO_2 + 3O_2\ ,$$

but some yield sulphur trioxide, as, for instance, ferrous sulphate, which was formerly heated in clay retorts to produce fuming or NORDHAUSEN OIL OF VITRIOL,

$$2FeSO_4 = Fe_2O_3 + SO_2 + SO_3\ ,$$

others, however, are strongly resistant to heat, as, for instance, $Na_2SO_4$, $K_2SO_4$, $MgSO_4$, and $CaSO_4$

(*f*) *Formula of sulphuric acid* —Sulphuric acid is represented by the structural formula



Two oxygen atoms are held to the sulphur atom by semi-polar bonds, the local charges of which may account for the relatively high boiling-point of the acid (p 261)

**The sulphates.**—Since sulphuric acid is a dibasic acid it forms two series of salts, viz ACID SULPHATES and NORMAL SULPHATES **Potassium bisulphate,** $KHSO_4$, and **sodium bisulphate,** $NaHSO_4$, are the only important acid sulphates They are colourless solids which are converted into the PYROSULPHATE, $K_2S_2O_7$ or $Na_2S_2O_7$, and eventually into the normal sulphate, $K_2SO_4$ or $Na_2SO_4$, by strong ignition

$$2NaHSO_4 \rightarrow Na_2S_2O_7 + H_2O$$
$$Na_2S_2O_7 \rightarrow Na_2SO_4 + SO_3$$

Sulphates are colourless unless the metallic ion is coloured Barium, strontium, lead and mercurous sulphates are insoluble in water , but the other sulphates are soluble, and usually crystallise as hydrates from their aqueous solutions Thus the bivalent sulphates of the transition metals form

(i) *heptahydrates*, isomorphous with Epsom salts, $MgSO_4, 7H_2O$, and
(ii) *double sulphates* of the Schonite type, $K_2SO_4, MgSO_4, 6H_2O$, *e g* ferrous ammonium sulphate, $(NH_4)_2SO_4, FeSO_4, 6H_2O$

The tervalent sulphates of the transition metals form a similar isomorphous series of ALUMS These are double sulphates of the formula M M$^{\cdots}$, $(SO_4)_2, 12H_2O$, where M$^{\cdot}$ is a univalent and M a tervalent metal, *e g* **potash alum,** $KAl(SO_4)_2, 12H_2O$, **ferric alum,** $(NH_4)$ Fe $(SO_4)_2, 12H_2O$, and **chrome alum,** $KCr(SO_4)_2, 12H_2O$

The sulphates are of considerable importance in everyday life, *e.g.* **sodium sulphate** (p 104) is used in the manufacture of glass, **ammonium sulphate** (p 186) as a fertiliser, **barium sulphate** (p 124) as a paint, **calcium sulphate** (p 122) as plaster of Paris, **magnesium sulphate** in the form of Epsom salts (p 116) as a purgative, **copper sulphate** (p 318) as a fungicide, **potash alum** (p 134) as a mordant, **chrome alum** (p 367) for tanning, etc

**Perdisulphuric anhydride,** $S_2O_7$, can be prepared in the form of white needles by sparking a cold dry mixture of sulphur dioxide and oxygen for some hours

$$4SO_2 + 3O_2 = 2S_2O_7$$

It sublimes at 10° and decomposes slowly into sulphur trioxide and oxygen It unites with water to form an unstable solution of perdisulphuric acid .

$$S_2O_7 + H_2O = H_2S_2O_8$$

**Perdisulphuric acid,** $H_2S_2O_8$, is most conveniently prepared by electrolysing an ice-cold 60% solution of sulphuric acid, since at room temperatures oxygen and hydrogen are the main products of electrolysis The

cathode consists of a sheet of platinum-foil enclosed in a porous pot, whilst the anode is a single turn of platinum wire wound round the porous pot

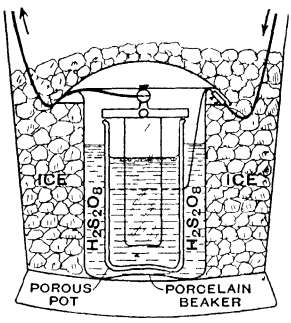



FIG 80 APPARATUS FOR THE PREPARATION OF PERDISULPHURIC ACID

The whole apparatus is kept cold by placing it in a bucket filled with ice, the porcelain beaker containing the acid being covered with an inverted basin to keep out ice and ice-water

The primary decomposition by the current is probably

$$H_2SO_4 = H + HSO_4 ;$$
compare $HCl = H + Cl$,

the $HSO_4$ groups liberated at the anode then unite in pairs exactly the same way as chlorine atoms

$$2HSO_4 = H_2S_2O_8 , \text{ compare } 2Cl = Cl_2$$

The solutions prepared in this way are not stable and soon decompose with formation of **permonosulphuric acid**, $H_2SO_5$, hydrogen peroxide and finally gaseous oxygen

$$H_2S_2O_8 + H_2O = H_2SO_4 + H_2SO_5,$$
$$H_2SO_5 + H_2O = H_2SO_4 + H_2O_2,$$
$$2H_2O_2 = 2H_2O + O_2$$

If a strong solution of potassium hydrogen sulphate is similarly electrolysed, the sparingly soluble **potassium perdisulphate**, $K_2S_2O_8$, crystallises out This salt, like the parent acid, slowly liberates iodine from potassium iodide,

$$K_2S_2O_8 + 2KI = 2K_2SO_4 + I_2,$$

oxidises ferrous salts to ferric salts,

$$2FeSO_4 + K_2S_2O_8 = Fe_2(SO_4)_3 + K_2SO_4,$$

and dissolves zinc without liberation of hydrogen

$$Zn + K_2S_2O_8 = ZnSO_4 + K_2SO_4$$

**Thiosulphuric acid**, $H_2S_2O_3$, is formed in small quantities by the direct combination of sulphurous acid and sulphur, but is very unstable, and when liberated from its salts decomposes as shown by the lower arrow in the equation:

$$H_2O + SO_2 + S \rightleftharpoons H_2S_2O_3$$

**Sodium thiosulphate**, $Na_2S_2O_3,5H_2O$, commonly but incorrectly called "hyposulphite of soda" or "hypo," crystallises out when a solution of sodium sulphite is boiled with flowers of sulphur and evaporated ·

$$Na_2SO_3 + S = Na_2S_2O_3.$$

It is very soluble in water, dissolving in less than its own weight of water even at 0°, when heated it melts in its own water of crystallisation.

Sodium thiosulphate is decomposed by dilute acids with liberation of sulphur dioxide and deposition of sulphur

$$Na_2S_2O_3 + 2HCl = 2NaCl + SO_2 + S + H_2O$$

It is oxidised quantitatively by iodine to **sodium tetrathionate** :

$$2Na_2S_2O_3 + I_2 = 2NaI + Na_2S_4O_6$$

Chlorine and bromine oxidise it mainly to sulphate,

$$Na_2S_2O_3 + 4Br_2 + 5H_2O = 2NaHSO_4 + 8HBr,$$

although small amounts of tetrathionate are also formed (p 423)

Sodium thiosulphate is used in photography for "fixing" (p 326), on account of its property of dissolving silver chloride and bromide

$$Na_2S_2O_3 + AgCl = NaAgS_2O_3 + NaCl$$

**Halogen compounds of sulphur** —The affinity of sulphur for the halogens diminishes steadily in the series, fluorine, chlorine, bromine and iodine **Sulphur hexafluoride,** $SF_6$, prepared by the direct union of the elements, is a very stable, colourless and odourless gas Its great stability is attributed to the fact that the maximum covalency of sulphur, which is six, is completely satisfied **Disulphur dichloride,** $S_2Cl_2$, commonly called "sulphur monochloride," is used in the vulcanisation of rubber It can be prepared as a yellow liquid by passing chlorine over sulphur in an apparatus similar to that used in the preparation of phosphorus trichloride It is the most stable chloride of sulphur, but, unlike the hexafluoride, it is hydrolysed by water according to the equation

$$2S_2Cl_2 + 3H_2O = 4HCl + H_2SO_3 + 3S$$

**Oxyhalogen compounds of sulphur** —**Thionyl chloride,** $SOCl_2$, is prepared by passing sulphur dioxide over phosphorus pentachloride

$$PCl_5 + SO_2 = POCl_3 + SOCl_2$$

The thionyl chloride (boiling-point 78°) is separated from the phosphorus oxychloride (boiling-point 107°) by fractional distillation It is a colourless liquid, which fumes in moist air, and is decomposed by water into sulphurous acid and hydrochloric acid (see also p 789)

$$SOCl_2 + 2H_2O = H_2SO_3 + 2HCl$$

**Chlorosulphonic acid,** $HO\,SO_2\,Cl$, is prepared by the direct addition of hydrogen chloride to sulphur trioxide, or by distilling a mixture of fuming sulphuric acid which has been saturated with hydrogen chloride

$$SO_3 + HCl = HO\,SO_2{\cdot}Cl.$$

It is a colourless fuming liquid which boils at 155° It is decomposed by water, yielding sulphuric and hydrochloric acids

$$HO{\cdot}SO_2\,Cl + H_2O = H_2SO_4 + HCl$$

**Sulphuryl chloride,** $SO_2Cl_2$, can be prepared by the direct union of sulphur dioxide with chlorine in bright sunlight, or in the presence of a catalyst such as charcoal, $SO_2 + Cl_2 = SO_2Cl_2$ It is also formed by the prolonged action of phosphorus pentachloride on concentrated sulphuric acid

$$2PCl_5 + H_2SO_4 = SO_2Cl_2 + 2POCl_3 + 2HCl$$

Sulphuryl chloride is a colourless liquid which boils at 69° It is readily decomposed by water, with the formation of sulphuric and hydrochloric acids

$$SO_2Cl_2 + 2H_2O = H_2SO_4 + 2HCl$$

**Estimation of sulphur.**—Sulphur is estimated by converting it to sulphuric acid and weighing as barium sulphate, $BaSO_4$, or as lead sulphate, $PbSO_4$ (p 442)

# CHAPTER XXI

## THE HALOGENS

| | | | | | |
|---|---|---|---|---|---|
| 9 | FLUORINE, | F = 19 00 | 35 | BROMINE, | Br = 79 916 |
| 17 | CHLORINE, | Cl = 35 457 | 53 | IODINE, | I = 126 92 |

**Classification and valency.**—(*a*) *Negative valence of the halogens*.—In the periodic classification of the elements the inert gases are preceded by the halogens and are followed by the alkali metals, thus

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 9 | Fluorine | 17 | Chlorine | 35 | Bromine | 53 | Iodine |
| 10 | Neon | 18 | Argon | 36 | Krypton | 54 | Xenon |
| 11 | Sodium | 19 | Potassium | 37 | Rubidium | 55 | Caesium |

The halogens are therefore the best examples of NEGATIVE ELEMENTS, since they are very ready to *accept* an electron in order to acquire the electronic configuration of an inert gas, just as the alkali metals are the best examples of POSITIVE ELEMENTS, in view of the readiness with which they *lose* an electron. In this process the halogens form univalent *anions*, whilst the alkali metals form univalent *cations*, *e g*

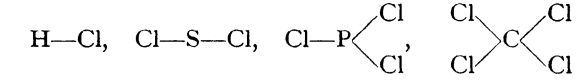
$$Cl + e = \overset{-}{Cl}, \qquad K - e = \overset{+}{K}$$

When, therefore, a halogen and an alkali metal are brought together in equivalent proportions, a HALIDE SALT is formed by the transfer of an electron from each atom of metal to each atom of halogen, $K + Cl = K^+ Cl^-$. The product is an IONIC AGGREGATE, since these ions are more stable than neutral atoms of potassium and chlorine.

(*b*) *Covalence*.—On account of their tendency to acquire the electronic structure of an inert gas, the halogens exist in the free state in the form of diatomic molecules, the atoms of which are bound together by a pair of shared electrons, *e g*

$$Cl \quad + \quad Cl \quad \rightarrow \quad Cl \;\; Cl$$

The same tendency accounts for the formation of a large number of covalent compounds, in which the halogen is bound by a single covalent bond to another non-metal as in



In each of these compounds the halogen is united to the non-metal by a

pair of shared electrons, whereas in the typical halogen salts it forms a univalent anion as in

$$\overset{+}{\text{Na}}\overset{-}{\text{Cl}}, \quad \overset{-}{\text{Cl}}\ \overset{++}{\text{Ba}}\ \overset{-}{\text{Cl}}, \text{ etc}$$

The less electropositive metals also form covalent compounds with the halogens, so that bonds must be broken when the salt is "ionised," *e g* in aqueous solutions

$$\text{Cl} - \text{Hg} - \text{Cl} \rightleftharpoons \overset{-}{\text{Cl}} + \overset{++}{\text{Hg}} + \overset{-}{\text{Cl}}$$

The salts formed in this way are weak electrolytes and resemble the weaker acids in exhibiting REVERSIBLE IONISATION in solution, compare

$$\text{HCN} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\overset{+}{\text{O}} + \overset{-}{\text{CN}}$$

(*c*) *Coordination with oxygen*.—The halogens can develop a higher valency than one by acting as donors of electrons Thus the chloride ion with a complete octet of valency electrons, can combine with *four* atoms of oxygen by sharing each of its four duplets with an atom of oxygen

$$\cdot\underset{\cdot\cdot}{\text{Cl}} + 4\ \text{O} \rightarrow \begin{matrix} & & \text{O} & & \\ \text{O} & & \text{Cl} & & \text{O} \\ & & \text{O} & & \end{matrix}$$

or

$$\text{Cl}^- + 4\text{O} \rightarrow [\text{ClO}_4]^-$$

The dative bonds between chlorine and oxygen, which are used to convert the chlorine ion into a perchlorate ion, impart a negative charge to the oxygen atom (which gains a half-share in a pair of electrons by acting as an acceptor) and a positive charge to the chlorine (which loses a half-share in a pair of electrons when it acts as donor) The perchlorate ion may therefore be represented by the formula

$$\begin{matrix} \overset{-}{\text{O}} & & \overset{-}{\text{O}} \\ & \overset{+++}{\text{Cl}} & \\ \overset{-}{\text{O}} & & \overset{-}{\text{O}} \end{matrix}$$

Similarly the iodide ion, $\text{I}^-$, can combine with four oxygen atoms to form a periodate ion, $\text{IO}_4^-$, but neither a perfluorate ion, $\text{FO}_4^-$, nor a perbromate ion, $\text{BrO}_4^-$, have yet been identified Indeed, fluorine is so reluctant to develop a higher valency by coordination that it is only recently that evidence has been obtained of the existence of fluorates *e g* $\text{AgFO}_3$, and of the fluorate ion, $\text{FO}_3^-$.

(*d*) *Coordination with hydrogen*.—Fluorine differs from the other halogens in being able to form a coordination compound with hydrogen Thus two fluoride ions can combine with a hydrogen ion to form an acid-fluoride ion

$$\overset{-}{\text{F}} + \overset{+}{\text{H}} + \overset{-}{\text{F}} = \text{HF}_2^-$$

This ion is probably formed by the attraction of a proton for two duplets, thus

$$F + H + F \rightarrow F\ H\ F$$

The abnormal behaviour of fluorine towards oxygen and hydrogen may perhaps be associated with the smallness of the ion, which would make it easier for two fluoride ions to associate with a single proton, but would make it more difficult for three or four oxygen atoms to cluster round one fluoride ion

**Physical properties of the halogens.**—The halogens show a regular gradation in most of their physical properties, as is shown in Table 19

TABLE 19.—PHYSICAL PROPERTIES OF THE HALOGENS

| | Atomic weight | Melting-point | Boiling-point | Density | Solubility in water at 15° |
|---|---|---|---|---|---|
| Fluorine, pale yellow gas | 19 00 | −223° | −187° | 1 14 at −200° | Attacks water |
| Chlorine, greenish-yellow gas | 35 46 | −102° | − 34° | 1 42 at 18° | 260 c c /100 c c |
| Bromine, reddish-brown liquid | 79 92 | − 7° | + 59° | 3 14 at 18° | 3 5 g /100 c c |
| Iodine, violet-brown solid | 126 92 | +113° | +184° | 4 94 at 17° | 0 025g /100c c |

**Chemical properties of the halogens**.—(*a*) *Dissociation*.—The stability of the molecules decreases progressively from fluorine to iodine, as shown by the heats of dissociation

$$F_2 = 2F \quad -76{,}000 \text{ cal},$$
$$Cl_2 = 2Cl \quad -56{,}800 \text{ cal},$$
$$Br_2 = 2Br \quad -45{,}200 \text{ cal},$$
$$I_2 = 2I \quad -35{,}600 \text{ cal}$$

Iodine, which is the least stable of the halogens, is completely dissociated into atoms at 1700°, whilst chlorine is dissociated only to the extent of about 1%

(*b*) *Combination with metals*.—The name HALOGEN, or "salt-producer," which was introduced by Berzelius in 1825 to describe those non-metals which form salts by direct combination with metals, is now applied exclusively to the four elements, fluorine, chlorine, bromine and iodine, even though sulphur also unites directly with metals to form salts The electronegative character of the halogens, as measured by their affinity for electrons, decreases progressively from fluorine to iodine (see p 53) Fluorine will therefore displace chlorine from its salts, chlorine will displace bromine, and bromine will displace iodine, *e g*

$$F_2 + 2KCl = Cl_2 + 2KF, \quad \text{or} \quad F_2 + 2Cl^- = Cl_2 + 2F^-,$$
$$Cl_2 + 2KBr = Br_2 + 2KCl, \quad \text{or} \quad Cl_2 + 2Br^- = Br_2 + 2Cl^-,$$
$$Br_2 + 2KI = I_2 + 2KBr, \quad \text{or} \quad Br_2 + 2I^- = I_2 + 2Br^-$$

These actions can be represented as a competition for electrons, viz

$$F_2 + 2\bar{C}l = Cl_2 + 2\bar{F}, \quad Cl_2 + 2\bar{B}r = Br_2 + 2\bar{C}l, \quad Br_2 + 2\bar{I} = I_2 + 2\bar{B}r$$

Even iodine, however, is sufficiently electronegative to accept electron from nearly all the metals and thus to unite directly with them, *e g* two iodides of mercury can be prepared by merely rubbing the two element together, namely, a red **mercuric iodide**, $HgI_2$, when iodine is in excess and a green **mercurous iodide**, $Hg_2I_2$, when mercury is in excess

(*c*) *Combination with hydrogen* —The four halogens combine directly with hydrogen, but their affinity for this element decreases progressively from fluorine to iodine, as would be expected from their position in the electrochemical series, p 53 Thus

(i) Solid fluorine explodes violently with liquid hydrogen at $-253°$

(ii) Hydrogen and chlorine explode only when heated or exposed to sunlight , but the product is so stable that only slight dissociation (about 1%) occurs even at 2000°

(iii) Bromine vapour will not explode with hydrogen , and the hydrogen bromide formed by their combination is dissociated to the same degree at 1200° as hydrogen chloride is at 2000°

(iv) Hydrogen and iodine unite only partially, one-fourth of the material remaining uncombined at 500° Moreover, the product is so unstable that hydrogen iodide is an effective reducing agent, like hydrogen sulphide (p 250) The heats of formation (Table 20) show in a more precise way this progressive diminution in affinity for hydrogen

Table 20 shows that, with the exception of hydrogen fluoride, there is a general gradation in the physical properties of these hydrides

TABLE 20 —PHYSICAL PROPERTIES OF THE HALOGEN HYDRIDES

| | Melting-point | Boiling-point | Heat of formation of gas | Solubility in water at 0° | Composition of acid at maximum boiling-point |
|---|---|---|---|---|---|
| HF | −92° | +19 5° | +38,500 cals | Miscible | 37% HF at 120° |
| HCl | −111° | −83° | +22,000 cals | 45% | 20% HCl at 110° |
| HBr | −80° | −69° | + 8,600 cals | 68% | 48% HBr at 125° |
| HI | −51° | −36° | − 6,400 cals | 70% | 58% HI at 127° |

The four hydrides are known as **hydrofluoric, hydrochloric, hydrobromic** and **hydriodic acids,** since they dissolve in water with evolution of heat giving rise to strongly acid solutions These acids contain hydrogen but not oxygen, and were therefore described by Gay-Lussac in 1814 a HYDRO-ACIDS, in order to distinguish them from OXY-ACIDS, such as sulphuric acid and chloric acid, in which oxygen is the acidifying element

(*d*) *Combination with oxygen* —Whilst the affinity of the halogens for hydrogen diminishes progressively from fluorine to iodine, the affinity of fluorine and bromine for oxygen is less than that of chlorine and iodine

(i) *Fluorine* forms only two oxides, viz , $F_2O$ and $F_2O_2$

(ii) *Chlorine* forms five oxides ($Cl_2O$, $ClO_2$, $ClO_3$, $Cl_2O_7$, $ClO_4$), but

these can only be prepared by indirect methods, and with the exception of the heptoxide, $Cl_2O_7$, are so unstable that they are liable to explode

(iii) *Bromine*, instead of being intermediate between chlorine and iodine, resembles fluorine in forming only very unstable oxides, $Br_2O$, etc , and no perbromates The reality of this anomaly is seen in the following thermochemical data

| Compound | Formula | Heat of formation |
|---|---|---|
| Chloric acid | $HClO_3$ aq | +23,000 calories |
| Bromic acid | $HBrO_3$ aq | +12,500 calories |
| Iodic acid | $HIO_3$ aq | +56,000 calories |

(iv) *Iodine* is the only halogen which can be oxidised directly by hot concentrated nitric acid and yields a stable pentoxide, $I_2O_5$, which is the anhydride of iodic acid, $HIO_3$ The sesquioxide, $I_2O_3$, is of particular interest because it has basic properties, *e g* it forms a basic sulphate $(IO)_2SO_4,\frac{1}{2}H_2O$ Finally, both iodic acid, $HIO_3$, and periodic acid, $HIO_4,2H_2O$, form a series of complex iodates and periodates, the chlorine or bromine analogues of which have never been isolated

The contrast between the affinity of the halogens for hydrogen and the metals on the one hand, and for oxygen and the non-metals on the other, is illustrated by the fact that, whilst chlorine will displace iodine from potassium iodide to form potassium chloride, iodine, when heated with potassium chlorate, will displace chlorine and form the iodate

$$2KI + Cl_2 = 2KCl + I_2 , \quad 2KClO_3 + I_2 = 2KIO_3 + Cl_2$$

In the last equation the two salts may be formulated, in accordance with Lavoisier's theory, as $K_2O,Cl_2O_5$ and $K_2O,I_2O_5$, and the displacement of chlorine by iodine may be represented by the equation

$$Cl_2O_5 + I_2 = I_2O_5 + Cl_2$$

**Abnormal properties of fluorine.**—The properties of fluorine and its compounds often differ abruptly from those of the other halogens Thus

(i) Calcium fluoride is insoluble whilst the chloride, bromide, and iodide are soluble deliquescent salts On the other hand, silver fluoride is soluble in water, whilst the chloride, bromide, and iodide are insoluble

(ii) Hydrogen fluoride is a much weaker acid than the chloride, bromide, and iodide Its abnormally high boiling-point of 19 5° (see Table 20) may be traced, like that of water (p 77), to polymerisation, since the vapour contains molecules greater than $H_2F_2$ in the neighbourhood of the temperature of liquefaction The polymerisation may be attributed to the sharing by a hydrogen atom of a lone pair of electrons belonging to the fluorine atom of another molecule, as represented by the equation

$$H\cdot F + H\ F = H\ F\ H\ F \quad \text{or} \quad H-\overset{+}{F}-\overset{-}{H}-F$$

The polarity of the resultant molecule, like that of the water molecule, accounts, not only for the abnormal boiling-point, but also for the fact that the anhydrous acid is an excellent ionising solvent. Hydrogen fluoride also forms addition compounds with neutral fluorides, *e g* $K^+[FHF]^-$, in

which two fluoride ions are united to a single proton, just as the hydrogen atoms in a crystal of ice are each linked to two oxygen atoms The similarity of fluorine to oxygen is also indicated by a curious resemblance between the physical properties of silicon tetrafluoride, $SiF_4$, and of carbon dioxide, and by the fact that fluorine unites directly with carbon, whereas the other halogens are without action

(iii) Fluorine differs from the other halogens in that it does not react with alkalis to form oxy-salts, instead a fluoride and difluorine monoxide $OF_2$, or oxygen, are produced according to the equations

*Cold dilute alkali*, $2NaOH + 2F_2 = F_2O + 2NaF + H_2O$ ,

contrast $2NaOH + Cl_2 = NaCl + NaClO + H_2O$

*Hot concentrated alkali*, $4NaOH + 2F_2 = 4NaF + O_2 + 2H_2O$ ,

contrast $6NaOH + 3Cl_2 = NaClO_3 + 5NaCl + 3H_2O$

## 9 FLUORINE F = 19 00

**Occurrence.**—The most important minerals containing fluorine are FLUORSPAR (Latin, *fluere*, to flow , Old English, *spaer*, chalk), or **calcium fluoride**, $CaF_2$, and CRYOLITE (Greek, κρύος, ice , λίθος, stone), or **sodium aluminofluoride**, $Na_3AlF_6$, two minerals which bear in their names the record of their low melting-points Fluorspar is a common constituent of mineral veins Cryolite, of which important deposits are found in Greenland, is used as a solvent for bauxite in the manufacture of aluminium (p 129)

**Isolation of fluorine.**—Hydrogen fluoride has been known, under the name of "fluor acid," as an agent for etching glass since 1670, but the element fluorine was not isolated until 1886, since it interacts with nearly all the materials from which chemical apparatus can be constructed Attempts to prepare fluorine by the electrolysis of aqueous hydrogen fluoride failed owing to the presence of water, which is attacked vigorously by it , and, when the anhydrous acid was eventually prepared it was found that it no longer conducted the electric current Moissan, however, prepared a conducting solution by adding potassium fluoride to the anhydrous acid, and isolated the element by electrolysis of this mixture

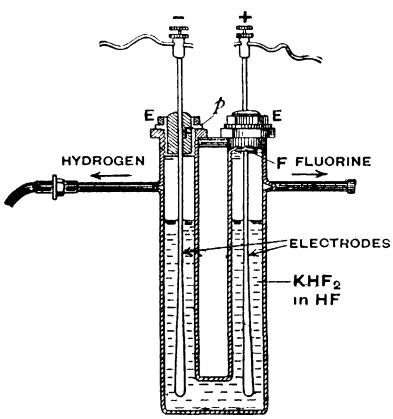



FIG 81 MOISSAN'S APPARATUS FOR THE PREPARATION OF FLUORINE

The electrolysis was carried out in a U-tube, Fig 81, made of a platinum iridium alloy, and cooled to −23° by the evaporation of methyl chloride The electrodes, of the same alloy, were insulated from the U-tube by stoppers, *FF*, of fluorspar, the joints being made air-tight by leaden washers, *p*, screwed down by brass caps, *E* Hydrogen was liberated at the negative and fluorine at the positive electrode

Fluorine can now be made as a laboratory product, by the electrolysis of fused potassium hydrogen fluoride, $KHF_2$, in a copper vessel which acts as the cathode, whilst a graphite rod is used for the anode The copper is attacked by fluorine but becomes protected by a coating of copper fluoride

**Physical properties of fluorine.**—Fluorine is a light yellow, pungent gas, it condenses to a liquid at $-188°$, and crystallises to a pale yellow solid melting at $-233°$

**Chemical properties of fluorine** —Fluorine is the most active of the elements It unites explosively with hydrogen even at $-253°$ It also decomposes water, forming hydrofluoric acid and liberating oxygen in the form of ozone or (in the presence of alkali) as an oxide of fluorine It ignites charcoal, combines vigorously with phosphorus, liberates chlorine from potassium chloride, and unites directly with nearly all the metals, but it has no marked action on dry glass, and does not combine directly with oxygen, nitrogen or chlorine

**Hydrogen fluoride.**—(*a*) *Preparation* —Hydrogen fluoride is liberated from fluorspar, just as hydrogen chloride is liberated from common salt, by the action of concentrated sulphuric acid

$$CaF_2 + H_2SO_4 = CaSO_4 + 2HF,$$

compare $$2NaCl + H_2SO_4 = Na_2SO_4 + 2HCl$$

Since hydrofluoric acid attacks glass, it is distilled in retorts of silver or lead, collected in receivers of the same metal, and stored in rubber or wax (ceresin) flasks with stoppers of the same material

The anhydrous acid is prepared from the acid salt, $KHF_2$ This is melted to remove all traces of water and decomposed by heating to redness in a platinum retort, with a platinum condenser and receiver, the latter being cooled with a freezing mixture to condense the acid The last traces of moisture may be removed by electrolysing with platinum electrodes, hydrogen and ozone are liberated until all the water is removed, when the acid becomes non-conducting

The anhydrous acid is dangerous to handle, since the liquid blisters the skin, and inhalation of the vapour may have a fatal effect Unlike the aqueous acid it destroys rubber bottles, but is without action on glass

(*b*) *Physical properties* —Anhydrous hydrogen fluoride has a density of 0 987 at 13° and is therefore slightly lighter than water, it boils at 19 5° and freezes at $-92°$ It is completely miscible with water and, like hydrogen chloride, forms a mixture of constant boiling-point ♦ this contains 37% of hydrogen fluoride and boils at 120°

The vapour density of hydrogen fluoride at temperatures above 70° corresponds with that required by the formula HF, but at 27° the density is about 2 5 times greater, so that the liquid probably contains molecules not less complex than $H_3F_3$ Anhydrous hydrogen fluoride is not an electrolyte but is an excellent ionising solvent In aqueous solution it behaves as a weak acid, since it is dissociated only to the extent of 15% in decinormal solution

(*c*) *Metallic fluorides* —Hydrogen fluoride forms a series of FLUORIDES by acting on metals or their oxides The fluorides are analogous to the chlorides , but they differ from the chlorides in that many of them combine with a further quantity of hydrogen fluoride to form acid fluorides

$$KF + HF = KHF_2,$$

compare $$K_2O + H_2O = 2KHO$$

(*d*) *Action on silica and etching of glass* —Hydrogen fluoride attacks silica, with the formation of silicon tetrafluoride and water

$$SiO_2 + 4HF = SiF_4 + 2H_2O$$

The use of hydrofluoric acid in etching glass depends upon this action of the acid on the silica in the glass , the glass is coated with wax, the lines which are to be etched are scratched with a metal point to remove the wax, and the plate is then exposed to the action of the vapour during a period of several hours

(*e*) *Double fluorides* —The action shown above is a balanced one, which is reversed by the addition of water The fluorine is, however, set free from the silicon, not as hydrofluoric acid, but in the form of a **silicifluoric acid**, $H_2SiF_6$ (p 159)

$$\underset{\text{Silicon tetrafluoride}}{3SiF_4} + 4H_2O = \underset{\text{Silicifluoric acid}}{2H_2SiF_6} + \underset{\text{Silicic acid}}{Si(OH)_4}$$

From this acid a series of SILICIFLUORIDES * is derived, *e g*

Potassium silicifluoride, $K_2SiF_6$
Lead silicifluoride, $PbSiF_6$

These compounds are typical of a series of DOUBLE FLUORIDES, in which fluorine resembles oxygen in combining both with a metal and with a non-metal, forming a pair of fluorides which unite to form a salt, just as oxy-salts are formed by the union of a basic oxide with an acid oxide, *e g*

$$KF + BF_3 = KBF_4 \text{ (Potassium borofluoride)}$$
$$K_2O + B_2O_3 = 2KBO_2 \text{ (Potassium metaborate)}$$

**Difluorine monoxide**, $F_2O$, is prepared as a colourless gas by passing fluorine in a fine stream through 2% aqueous sodium hydroxide

$$2F_2 + 2NaOH = 2NaF + F_2O + H_2O$$

**Estimation of fluorine.**—Fluorine may be estimated gravimetrically by bringing it into solution as an alkali fluoride, precipitating it as calcium fluoride by adding an excess of calcium chloride, and igniting the precipitate at a low red heat

## 17 CHLORINE Cl = 35 457

**Discovery of chlorine.**—Chlorine was discovered in 1774 by Scheele, who prepared the gas by heating hydrochloric acid (muriatic acid) with manganese dioxide It was at first thought to be an oxide of the acid, and

* Sometimes called silicofluorides

was therefore called "oxymuriatic gas", but Davy, who was not able to extract oxygen from it, even by the action of an electric arc between carbon poles, came to the conclusion that it was an element, and called it CHLORINE

**Occurrence of chlorine.**—Chlorine is a minor constituent of igneous rocks, from which soluble chlorides are produced by weathering These are washed out and are carried down by rivers to the sea, where they have accumulated to such an extent that the chlorine alone forms 2% by weight of the ocean This chlorine is present mainly in the form of **sodium chloride** or COMMON SALT, which if crystallised out would form a layer more than 100 feet in thickness over the surface of the earth Salt beds, formed by the evaporation of salt water, are found all over the world **Potassium chloride** and **magnesium chloride** are also found in the upper layers of the salt beds at Stassfurt and elsewhere, *e g* as CARNALLITE, $KCl, MgCl_2,6H_2O$, whilst insoluble **silver chloride** is found as the mineral HORN-SILVER, $AgCl$

**Laboratory preparation of chlorine** —Chlorine is usually prepared in the laboratory by oxidising hydrochloric acid with manganese dioxide, potassium permanganate or bleaching powder Thus

(*a*) Chlorine can be prepared in large quantity by Scheele's method of heating concentrated hydrochloric acid with manganese dioxide (apparatus like Fig 74, p 253)

$$MnO_2 + 4HCl = MnCl_2 + Cl_2 + 2H_2O$$

Manganese tetrachloride is probably formed first and then decomposed by heat,

$$MnO_2 + 4HCl = MnCl_4 + 2H_2O, \quad MnCl_4 = MnCl_2 + Cl_2,$$

since with cold concentrated hydrochloric acid only a little chlorine is evolved and a dark brown liquid is formed, which contains manganese tetrachloride and trichloride, $MnCl_4$ and $MnCl_3$ The gas can be purified and collected as in (*b*)

(*b*) An easily regulated supply of chlorine can be obtained by dropping cold concentrated hydrochloric acid on to crystals of potassium permanganate in a flask as in Fig 82

$$2KMnO_4 + 16HCl = 2KCl + 2MnCl_2 + 5Cl_2 + 8H_2O$$

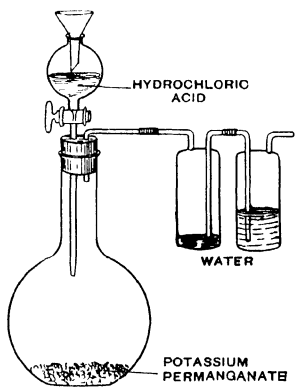



FIG 82 APPARATUS FOR PREPARING CHLORINE

Since the reaction takes place rapidly in the cold, the evolution of chlorine can be regulated by adjusting the rate of flow of hydrochloric acid, the method is therefore particularly suitable for experiments which require a steady flow of chlorine (see $PCl_3$, p 216) If necessary, the chlorine can be freed from (1) hydrogen chloride by passing it through water in a pair of wash-bottles, arranged

back-to-back so as to prevent sucking back, and (ii) from moisture by means of concentrated sulphuric acid Since chlorine is soluble in water and attacks mercury, the gas must be collected over hot water or brine, in which it is much less soluble, or by "upward" displacement of air, in virtue of its high density

(*c*) Chlorine can also be prepared by the action of any acid on bleaching powder

$$Ca(OCl)_2 + 4HCl = CaCl_2 + 2Cl_2 + 2H_2O$$

Compressed blocks of bleaching powder can be obtained for use in Kipp's apparatus (Fig 12, p 70)

(*d*) Very pure chlorine is prepared by the electrolysis of fused silver chloride in a glass U-tube fitted with carbon electrodes (Fig 83)

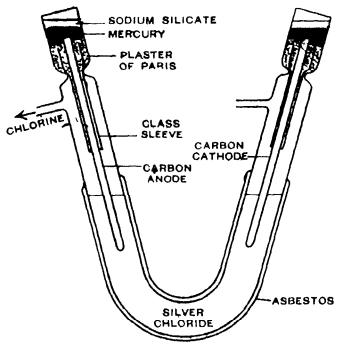



FIG 83 PREPARATION OF PURE CHLORINE BY ELECTROLYSIS OF FUSED SILVER CHLORIDE

$$2AgCl = 2Ag + Cl_2$$

**The manufacture of chlorine.**—(*a*) *Weldon's process* —Concentrated hydrochloric acid and manganese dioxide were heated by steam in stoneware stills and the chlorine led off through stoneware pipes The commercial success of the process depended on regenerating manganese dioxide in the form of **calcium manganite**, CaO, $MnO_2$, or $CaMnO_3$ The spent liquor, consisting largely of manganous chloride together with a little hydrochloric acid, was neutralised with limestone and treated with 30%-40% excess of milk of lime in a tall iron cylinder The resulting suspension of manganous hydroxide was heated to 60° with steam, and then oxidised by blowing air through it for about five hours

$$MnCl_2 + Ca(OH)_2 = Mn(OH)_2 + CaCl_2,$$
$$2Mn(OH)_2 + 2Ca(OH)_2 + O_2 = 2CaMnO_3 + 4H_2O$$

The excess of lime was required to avoid incomplete oxidation through the formation of a **manganous manganite**, $2MnO, MnO_2$, or $Mn_3O_4$, which is not oxidised any further by air The so-called WELDON MUD was separated from waste liquor by allowing it to settle out in a tank, and was then returned to the chlorine-generator together with a little fresh manganese dioxide to make good unavoidable losses

$$CaMnO_3 + 6HCl = CaCl_2 + MnCl_2 + Cl_2 + 3H_2O$$

(*b*) *Deacon's process* —The great disadvantage of Weldon's process was that at least two-thirds of the hydrochloric acid was wasted as calcium chloride. It was therefore largely superseded by the DEACON PROCESS, in which a copper salt was used as a catalyst to promote the oxidation of hydrogen chloride by air at 450°

$$4HCl + O_2 \rightleftharpoons 2Cl_2 + 2H_2O + 28{,}000 \text{ cal}$$

Hydrogen chloride, mixed with four volumes of air, was preheated to 450°, and passed over broken bricks impregnated with copper chloride About 60% of the gas was oxidised , the remainder was absorbed in water, leaving a gas containing about 10% of chlorine, which (after drying with sulphuric acid) was used for making bleaching powder

Since the oxidation is exothermic, a larger proportion of chlorine would be obtained if equilibrium could be established at lower temperatures , but in practice 450° was the lowest temperature at which catalysis was sufficiently rapid

The main disadvantages of this process were that (i) the gas was too dilute for compression into iron cylinders for transport, and (ii) the catalyst had to be renewed from time to time

(*c*) *By electrolysis* —Very large quantities of chlorine are obtained as a by-product in the manufacture of caustic soda and sodium, by the electrolysis of, respectively, brine (p 97) and fused sodium chloride (p 94) The gas is either used on the spot to prepare hydrogen chloride, bleaching powder, etc , or is dried by the action of strong sulphuric acid, liquefied by pressure, and stored for transport in large iron cylinders or drums, which are not attacked by the dry halogen The manufacture of caustic soda by electrolysis is actually limited by the demand for chlorine and its derivatives, so that chlorine is now never manufactured on a large scale by the much less efficient Deacon or Weldon processes

**Uses of chlorine.**—Very large quantities of chlorine are used for the bleaching of cotton and linen goods, paper pulp, etc For this purpose chlorine may be used directly with water, or it may be first converted into bleaching powder (p 286) or sodium hypochlorite It is also extensively used in the manufacture of dyes and non-inflammable solvents, such as trichlorethylene (p 676), and in the production of hydrogen chloride It is a powerful germicide, and is therefore widely employed in the sterilisation of water for industrial and domestic use

**Physical properties of chlorine.**—Chlorine is a greenish-yellow gas with a pungent odour and very corrosive properties It can be condensed to a yellow liquid which freezes at $-102°$ and boils at $-34°$ It has a normal vapour density up to 1200°, but above this temperature dissociation takes place, the calculated proportions of the diatomic and monatomic molecules being 99% and 1% at 1667°, and 90% and 10% at 1997°

Water dissolves 4 6 volumes of chlorine at 0° and half this amount at 20° The solution, which is known as CHLORINE WATER, can be prepared by bubbling the gas through water in two bottles arranged as in Fig 82 When the saturated solution is cooled, **chlorine hydrate,** $Cl_2,8H_2O$, crystallises out in the form of regular octahedra



FIG 84 BENT TUBE FOR LIQUEFACTION OF CHLORINE

Chlorine hydrate was used by Faraday in the preparation of liquid chlorine The hydrate was placed in one limb of a bent tube (Fig 84), and the other limb cooled by a freezing mixture, on warming the hydrate, chlorine was set free and condensed as a liquid in the cold limb

**Combination of chlorine with hydrogen.**—(*a*) Hydrogen and chlorine combine slowly when exposed to diffused daylight, but (unless especially dry) explode violently in direct sunlight

The combination of hydrogen with chlorine in daylight is of particular interest because interaction does not take place immediately on exposure to light The time lag between exposure and reaction is known as a PERIOD OF INDUCTION, and has been shown to be due to the presence of impurities, in particular to **nitrogen trichloride,** $NCl_3$, formed by the action of chlorine on ammonia in the water over which the gases are confined Substances which hinder a reaction are known as NEGATIVE CATALYSTS or INHIBITORS Certain reactions, including this combination, are extraordinarily sensitive to inhibitors, a very small quantity of inhibitor (*e g* 1%) being sufficient almost to stop the reaction for a considerable period Such reactions are now known to be CHAIN REACTIONS, *i e* reactions in which an active molecule or a free atom, produced by the absorption of energy from light or by other means, may be responsible for the combination of several thousands of molecules Thus it has been shown that the decomposition of a chlorine molecule into two chlorine atoms can be responsible for the production of 100,000 molecules of hydrogen chloride

It has been suggested that a chlorine molecule, $Cl_2$, activated by receiving energy from light, splits up into atoms, which then react as indicated below

$$Cl_2 = Cl + Cl,$$
$$Cl + H_2 = HCl + H,$$
$$H + Cl_2 = HCl + Cl, \text{ etc}$$

The combination of chlorine with hydrogen is strongly exothermic

$$H_2(\text{gas}) + Cl_2(\text{gas}) = 2HCl(\text{gas}) + 44{,}000 \text{ cals}$$

Chlorine molecules therefore become activated by the heat of the reaction, and give rise to so many chains that the reaction becomes explosive in character

(*b*) The great affinity of chlorine for hydrogen may be illustrated by the following experiments

(i) A burning jet of hydrogen will continue to burn when thrust into a jar of chlorine, with the production of hydrogen chloride
(ii) A lighted candle will burn in chlorine with the liberation of soot and the formation of hydrogen chloride
(iii) A piece of paper moistened with warm turpentine, $C_{10}H_{16}$, will ignite spontaneously in chlorine and continue to burn with a smoky flame

In (ii) and (iii) the smokiness of the flame is due to the fact that the chlorine unites only with the hydrogen and not with the carbon, which is therefore deposited in the form of soot

**Combination of chlorine with other non-metals.**—Chlorine combines directly with sulphur, boron and phosphorus, of which the white variety ignites spontaneously

$$2S + Cl_2 = S_2Cl_2,$$
$$2B + 3Cl_2 = 2BCl_3,$$
$$P_4 + 6Cl_2 = 4PCl_3$$

It is without action on carbon, nitrogen and oxygen, but chlorides of these elements can be prepared indirectly (p 279)

**Combination of chlorine with metals.**—Chlorine unites directly with metals to form metallic chlorides, *e g*

*Zinc chloride*, $Zn + Cl_2 = ZnCl_2$
*Ferric chloride*, $2Fe + 3Cl_2 = 2FeCl_3$
*Stannic chloride*, $Sn + 2Cl_2 = SnCl_4$
*Silver chloride*, $2Ag + Cl_2 = 2AgCl$

The action usually takes place in the cold, but is easily stopped by the formation of a protecting layer of chloride, this may be got rid of by vaporisation, as in the case of ferric chloride, or by fusion, as in the case of silver chloride Some finely-divided metals take fire and burn in chlorine, thus, when powdered antimony is shaken into a jar of chlorine, it immediately catches fire, producing a shower of sparks

**Addition and substitution of chlorine.**—(*a*) Chlorine combines directly with many UNSATURATED COMPOUNDS (p 668) in which the combining power of the constituent elements is not yet fully satisfied, and thus gives rise to ADDITION PRODUCTS, *e g*

$$CO + Cl_2 = COCl_2 \text{ (Phosgene)},$$
$$C_2H_4 + Cl_2 = C_2H_4Cl_2 \text{ (Ethylene dichloride)}$$

The combination of chlorine with $PCl_3$, $SnCl_2$, $FeCl_2$, etc, may be cited as other examples of the *addition* of chlorine

(*b*) On the other hand, SATURATED COMPOUNDS, in which the combining power of the elements is already fully satisfied, often give rise to chlorides by a process of SUBSTITUTION, *e g*

(i) *Replacement of hydrogen*

$$CH_4 + 4Cl_2 = 4HCl + CCl_4 \text{ (Carbon tetrachloride)}$$
$$NH_3 + 3Cl_2 = 3HCl + NCl_3 \text{ (Nitrogen trichloride)}$$

(ii) *Replacement of oxygen*

$$2H_2O + 2Cl_2 = O_2 + 4HCl \text{ (Hydrogen chloride)}$$

(iii) *Replacement of sulphur*

$$CS_2 + 3Cl_2 = S_2Cl_2 + CCl_4 \text{ (Carbon tetrachloride)}$$

**Action of chlorine on water.**—When chlorine is dissolved in water, small quantities of hypochlorous and hydrochloric acids are formed by the reversible reaction

$$H_2O + Cl_2 \rightleftharpoons HClO + HCl$$

Evidence of this reaction is provided by the following facts

(i) Chlorine water is a much better conductor of electricity than pure water, since hydrochloric acid is a strong electrolyte

(ii) The more volatile hypochlorous acid can be separated by distillation, leaving behind a solution of hydrochloric acid Since one of the constituents is thus removed from the equilibrium, the reaction proceeds almost to completion

(iii) The bleaching properties of moist chlorine are attributed to the presence of hypochlorous acid, because dry chlorine will not bleach Thus, dry chlorine is without action on dry blue litmus, whereas chlorine water

first reddens it and then bleaches it, by the successive action of hydrochloric and hypochlorous acids For the same reason ordinary writing ink and red flannel are unaffected by dry chlorine, but are bleached rapidly on the introduction of moisture, printers' ink, however, is not bleached by chlorine under any conditions, because it is composed of carbon

(iv) On exposure to bright sunlight chlorine water evolves oxygen, owing to the decomposition of hypochlorous acid by light (p 285), and to the action of activated chlorine on water

$$2HClO = 2HCl + O_2, \qquad \therefore 2Cl_2 + 2H_2O = 4HCl + O_2$$

In diffused sunlight chloric acid is formed, and the yield of oxygen is much smaller

$$3HClO \rightleftharpoons 2HCl + HClO_3$$

(v) Finally, the reaction of chlorine with an excess of dilute alkali (see below) provides further evidence for the above reaction

**Action of chlorine on alkalis.**—Chlorine reacts with cold dilute alkalis to give a mixture of chloride and hypochlorite, provided that the alkali is in *excess*, *e g* with an excess of sodium hydroxide

$$2NaOH + Cl_2 = NaCl + NaClO + H_2O$$

With an *excess* of chlorine, especially if the alkali is hot and concentrated, a chloride and chlorate are obtained

$$6NaOH + 3Cl_2 = 5NaCl + NaClO_3 + 3H_2O$$

**Oxidation by chlorine.**—Chlorine is a very powerful oxidising agent in terms of the definition given on p 49 Thus it will convert stannous salts to stannic salts, ferrous salts to ferric salts, and will liberate sulphur and iodine from their hydrides

$$SnCl_2 + Cl_2 = SnCl_4, \qquad H_2S + Cl_2 = 2HCl + S,$$
$$2FeCl_2 + Cl_2 = 2FeCl_3, \qquad 2HI + Cl_2 = 2HCl + I_2$$

In the presence of water, it can also bring about an addition of *oxygen* instead of *chlorine* to a reducing agent Thus sulphurous acid is oxidised to sulphuric acid, and potassium sulphide to potassium sulphate

$$H_2SO_3 + H_2O + Cl_2 = H_2SO_4 + 2HCl,$$
$$K_2S + 4H_2O + 4Cl_2 = K_2SO_4 + 8HCl$$

## Chlorine and Hydrogen

**Hydrogen chloride.**—(*a*) *Laboratory preparation* —Hydrogen chloride can be prepared in the laboratory by dropping concentrated sulphuric acid on to rock salt in an apparatus similar to that used for the preparation of sulphur dioxide (Fig 74, p 253) The action,

$$NaCl + H_2SO_4 = HCl + NaHSO_4,$$

takes place in the cold, although gentle heating is sometimes necessary to secure a sufficiently rapid flow of gas The further action,

$$NaHSO_4 + NaCl = Na_2SO_4 + HCl,$$

does not take place until the temperature is raised to about 500°, and is

therefore not carried out owing to the danger of cracking the flask If the gas is to be dissolved in water, two wash bottles, arranged as in Fig 82, must be used to prevent sucking back

An easily regulated supply of the gas can be obtained by dropping concentrated sulphuric acid from a tap funnel into a solution of commercial hydrochloric acid

(*b*) *Industrial preparation* —Hydrogen chloride was formerly manufactured on a large scale by the action of sulphuric acid on salt, as part of the Leblanc soda process, and is still produced in the same way on a limited scale (Fig 85), owing to the demand for sodium sulphate The calculated quantity of "chamber acid" (p 257) is added to salt in a shallow cast-iron pan, *A*, heated to a modest temperature by flue gases when the valves $f_1$, $f_2$ are opened

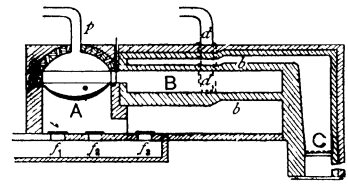



FIG 85 SALTCAKE MUFFLE FURNACE

A copious stream of hydrogen chloride is led off through the pipe *p* In order to bring about the second stage of the interaction, the paste of salt and acid sodium sulphate is raked on to the hearth of a fireclay muffle furnace, *B*, where it is heated *externally* to a high temperature by producer gas from the furnace, *C* The gas thus produced is led off through *d*

The hydrogen chloride is dissolved in water by the countercurrent system (p 198) It usually contains arsenious oxide, iron chlorides, and sulphuric acid Contamination by arsenic can be avoided by using sulphuric acid free from arsenic The other impurities can be removed by distillation after treatment with (i) copper to reduce ferric chloride to non-volatile ferrous chloride, and (ii) barium chloride to convert sulphuric acid into barium sulphate

Hydrochloric acid is also made by the combustion of hydrogen and chlorine, formed as by-products in the manufacture of caustic soda by the electrolytic process

$$H_2 + Cl_2 = 2HCl$$

The acid thus produced is very pure, but may contain traces of chlorine , these can be removed by treatment with copper, followed by distillation, when the chlorine remains behind as copper chloride The commercial product has a density of 1 14 and contains 28% of acid , a stronger acid of density 1 18, containing about 36% of hydrogen chloride, is sold as " fuming hydrochloric acid "

**Physical properties of hydrogen chloride.**—Hydrogen chloride is a colourless gas, which fumes strongly in air and has a pungent suffocating odour It can be condensed to a colourless liquid (b -pt $-83°$), which does not conduct electricity and is chemically inactive in the absence of water

**Hydrogen chloride and water.**—Hydrogen chloride dissolves in water with liberation of much heat

$$HCl + Aq = HCl, aq + 17{,}500 \text{ calories.}$$

Thus at 0° water dissolves 500 volumes of the gas, as compared with 1300 volumes of ammonia, and a solution saturated at 18° contains 42% HCl. Since only 3600 calories are liberated, as latent heat of vaporisation, when the gas is liquefied, about 14,000 calories must be due to the combination of the gas with water. Hydrates with 1, 2, and 3 $H_2O$ can be frozen out below $-15°$, and a MIXTURE OF MAXIMUM BOILING-POINT (prepared by distilling off *gas* from a strong acid, or *water* from a weak acid, until the temperature rises to 110°), which distils without change of composition under a pressure of 760 mm., contains 20.24% HCl and has the composition (calc. 20.19%) of an octahydrate, $HCl,8H_2O$. Since the composition of this mixture varies with the pressure, from 23.2% HCl at 50 mm. to 18% HCl at 2500 mm., it cannot represent a pure chemical compound, but it is possible that the constant-boiling liquid is a compound of hydrogen chloride and water mixed with the products of dissociation,

$$HCl,nH_2O \rightleftharpoons HCl + nH_2O,$$

in proportions which vary with the pressure under which the distillation is carried out.

**Chemical properties of hydrogen chloride.**—(*a*) *Action on metals*.—Liquid hydrogen chloride does not act on metals (except aluminium), but when mixed with water it behaves as a strong acid, and acts readily on base metals with liberation of hydrogen, *e.g.*

$$Zn + 2HCl = H_2 + ZnCl_2 \text{ (Zinc chloride)},$$
$$Fe + 2HCl = H_2 + FeCl_2 \text{ (Ferrous chloride)},$$
$$Sn + 2HCl = H_2 + SnCl_2 \text{ (Stannous chloride)}$$

(Notice that free chlorine converts iron into ferric chloride, $FeCl_3$, and tin into stannic chloride, $SnCl_4$.) Copper, which is attacked by dilute sulphuric acid only in presence of oxygen, dissolves slowly in concentrated hydrochloric acid, forming cuprous chloride and hydrogen, and silver is slowly attacked in presence of air, since silver chloride, which is insoluble in water, is readily soluble in the strong acid

$$2Cu + 4HCl = H_2 + 2HCuCl_2 \text{ (p. 316)},$$
$$4Ag + 4HCl + O_2 = 4AgCl + 2H_2O$$

The precious metals, platinum and gold, do not dissolve in hydrochloric acid, but are attacked by AQUA REGIA, a mixture of one part nitric and three parts hydrochloric acid, which readily liberates free chlorine and nitrosyl chloride

$$3HCl + HNO_3 = Cl_2 + 2H_2O + NOCl \text{ (Nitrosyl chloride)},$$
$$Au + 4HCl + HNO_3 = NO + 2H_2O + HAuCl_4 \text{ (Aurichloric acid)}$$

(*b*) *Action on bases*.—Hydrogen chloride combines directly with *ammonia*, in presence of traces of moisture, to form ammonium chloride

$$NH_3 + HCl = NH_4Cl$$

It also forms salts with metallic *oxides*, water being eliminated in the process

$$CuO + 2HCl = CuCl_2 + H_2O$$

With *carbonates*, water and carbon dioxide are set free

$$Na_2CO_3 + 2HCl = 2NaCl + H_2O + CO_2,$$
$$CaCO_3 + 2HCl = CaCl_2 + H_2O + CO_2$$

**Composition of hydrogen chloride.**—One volume of hydrogen unites with one volume of chlorine to give two volumes of hydrogen chloride

$$\underset{1\text{ vol}}{H_2} + \underset{1\text{ vol}}{Cl_2} = \underset{2\text{ vols}}{2HCl}$$

EXPT. 35 **Volumetric composition of hydrogen chloride.**

(*a*) The limb, *A*, of the apparatus (Fig 86) is filled with hydrogen, and the limb, *B*, which is half the size of *A*, is filled with chlorine The gases are allowed to mix by opening the central tap, $T_2$, and the apparatus is left exposed to diffuse daylight for two days On opening the tap, $T_1$, under

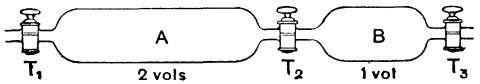



FIG 86 VOLUMETRIC COMPOSITION OF HYDROGEN CHLORIDE

*mercury*, no change of volume takes place, but when opened under *water* the level of the water rises inside the apparatus up to $\frac{1}{2}$, showing that two-thirds of the mixture has been converted into hydrogen chloride, but *without change of volume* The residual gas cannot be chlorine, since it is colourless and insoluble in water, and may be shown to be hydrogen by opening the tap, $T_3$, and applying a lighted taper

(*b*) Hydrogen chloride can be shown to contain half its own volume of hydrogen by adding pellets of sodium amalgam to a measured volume of the gas in a graduated tube over mercury

$$2NaHg_x + 2HCl = 2NaCl + 2xHg + H_2$$

## CHLORINE AND OXYGEN

**Oxides and oxy-acids**—Chlorine does not unite directly with oxygen, but several oxides have been prepared by indirect methods and three of them are tabulated below, together with the corresponding oxy-acids and oxy-salts

| | | | |
|---|---|---|---|
| Dichlorine monoxide, | $Cl_2O$ | Hypochlorous acid, | $HClO$, |
| | | Sodium hypochlorite, | $NaClO$. |
| Chlorine dioxide, | $ClO_2$ | Chlorous acid, | $HClO_2$, |
| | | Sodium chlorite, | $NaClO_2$ |
| | | Chloric acid, | $HClO_3$, |
| | | Sodium chlorate, | $NaClO_3$. |
| Dichlorine heptoxide, | $Cl_2O_7$ | Perchloric acid, | $HClO_4$, |
| | | Sodium perchlorate, | $NaClO_4$ |

**Dichlorine monoxide**, $Cl_2O$, is prepared as a brownish-yellow gas by passing chlorine over dried precipitated yellow mercuric oxide in a tube cooled by a jacket of cold water

$$2HgO + 2Cl_2 = Cl_2O + HgO,HgCl_2 \text{ (Basic mercuric chloride)}$$

The gaseous monoxide is freed from surplus chlorine by passing into a tube immersed in ice, when it condenses to a dark brown liquid, boiling at 20° It is a strongly endothermic compound, and explodes in the presence of organic matter, or when heated It dissolves in water, forming hypochlorous acid, and reacts with alkalis to form hypochlorites .

$$H_2O + Cl_2O = 2HClO\ , \quad Cl_2O + 2KOH = 2KClO + H_2O$$

**Chlorine dioxide**, $ClO_2$, can be prepared by adding dry powdered potassium chlorate to well-cooled concentrated sulphuric acid, and then warming the mixture very cautiously

$$3KClO_3 + 3H_2SO_4 = 3KHSO_4 + HClO_4 + 2ClO_2 + H_2O$$

A less explosive gas (diluted with carbon dioxide) is obtained by heating dilute sulphuric acid, potassium chlorate, and oxalic acid to a temperature of 70°

$$2KClO_3 + H_2C_2O_4 + H_2SO_4 = K_2SO_4 + 2ClO_2 + 2CO_2 + 2H_2O$$

Chlorine dioxide is a brownish-yellow gas with a peculiar smell It condenses to a reddish-brown liquid boiling at +11° The gas and liquid explode violently when heated or in the presence of organic matter This explains the " crackling " produced when strong sulphuric acid acts on potassium chlorate, an action which distinguishes the chlorates from the more stable perchlorates It is a powerful oxidising agent, and phosphorus ignites spontaneously in the gas It dissolves in alkalis with the formation of a chlorite and chlorate and is therefore a mixed acid anhydride

$$2KOH + 2ClO_2 = KClO_2 + KClO_3 + H_2O$$

**Chlorine trioxide**, $ClO_3$, has been prepared as a liquid product of the action of ozone on the dioxide It decomposes, even at atmospheric temperatures, into chlorine, oxygen, and chlorine dioxide

**Dichlorine heptoxide**, $Cl_2O_7$, the most stable of the oxides of chlorine, is obtained by adding perchloric acid slowly to phosphoric oxide cooled below −10°

$$P_2O_5 + 2HClO_4 = 2HPO_3 + Cl_2O_7$$

The mixture is kept at −10° for a day and is then slowly warmed on a water-bath until the heptoxide distils over It is a colourless oil, boiling at 82°, which explodes violently on percussion, but is without action on wood or paper It dissolves in water and is converted slowly into perchloric acid

$$Cl_2O_7 + H_2O = 2HClO_4$$

**Hypochlorous acid**, HClO, is formed when dichlorine monoxide is dissolved in water,

$$Cl_2O + H_2O = 2HClO,$$

and (with hydrochloric acid) by the action of chlorine on water

$$Cl_2 + H_2O \rightleftharpoons HCl + HClO.$$

Small quantities can be prepared by the action of chlorine on freshly-precipitated yellow mercuric oxide suspended in water,

$$2HgO + 2Cl_2 + H_2O = HgO,HgCl_2 + 2HClO,$$

the insoluble basic mercuric chloride being removed by filtration This action is analogous to that of chlorine on caustic potash,

$$2KOH + Cl_2 = KCl + KClO + H_2O,$$

but differs from it in that the mercuric oxide is too weak a base to hold the weak hypochlorous acid, which is therefore obtained as a free acid

Hypochlorous acid is prepared on a large scale by the action of carbon dioxide on bleaching powder suspended in ice-cold water

$$Ca(OCl)_2 + CO_2 + H_2O = CaCO_3 + 2HClO$$

Hypochlorous acid is very volatile and its odour can easily be detected Solutions of hypochlorous acid in water are golden yellow in colour, they cannot be concentrated beyond 5% by distillation, as decomposition then takes place according to the equations

$$2HClO = 2HCl + O_2, \quad 3HClO = 2HCl + HClO_3$$

This decomposition also occurs on exposure to light When mixed with hydrochloric acid, chlorine is set free according to the equation

$$HClO + HCl \rightleftharpoons Cl_2 + H_2O$$

A solution of hypochlorous acid may be distinguished from chlorine water by shaking with mercury, when hypochlorous acid produces a brownish-yellow precipitate of basic mercuric chloride, whilst chlorine water produces a white precipitate of calomel

$$Hg + HClO = Hg(OH)Cl, \quad 2Hg + Cl_2 = Hg_2Cl_2$$

Hypochlorous acid is a powerful oxidising and bleaching agent and is perhaps the active agent in bleaching by means of hypochlorites or of bleaching powder

**Sodium hypochlorite.**—A solution of sodium hypochlorite is a valuable disinfectant and bleaching agent It is manufactured on a large scale by electrolysing brine in such a way that the liberated chlorine comes in contact with the caustic soda

$$2NaOH + Cl_2 = NaCl + NaClO + H_2O$$

Solid sodium hypochlorite cannot be obtained from the solution, since on evaporation it decomposes into chloride and chlorate

$$3NaClO = 2NaCl + NaClO_3$$

**Bleaching powder.**—(*a*) *Preparation* —In one process, slaked lime is gradually raked over and down the eight floors of a cylindrical tower, which is made of reinforced concrete and protected with a coating of Stockholm tar and fireclay Chlorine is passed up the tower from the bottom but one floor, and is brought into intimate contact with the slaked lime by means of mechanical rakes The formation of calcium chlorate

is largely prevented by keeping the temperature down by circulating cold water through pipes inside the lower floors The bleaching powder is freed from uncombined chlorine by a blast of hot air in the bottom chamber, and is then mechanically discharged into wooden tubs, it contains from 36-40% of available chlorine

(*b*) *Constitution* —Bleaching powder appears to be a mixture, the chief constituents of which are *basic calcium chloride*, $CaCl_2,Ca(OH)_2,H_2O$, and *calcium hypochlorite*, $Ca(OCl)_2,aH_2O$ In the following paragraphs, however, bleaching powder is represented as a hypochlorite because many of its reactions are undoubtedly due to the presence of this radical

(*c*) *Properties and uses* —Bleaching powder is a white powder which absorbs moisture from the air but is not deliquescent Its characteristic odour is due to the action of atmospheric carbon dioxide, which liberates hypochlorous acid according to the equation

$$Ca(OCl)_2 + CO_2 + H_2O = CaCO_3 + 2HClO$$

It reacts with dilute acids to give chlorine, *e g*

$$Ca(OCl)_2 + 4HCl = CaCl_2 + 2Cl_2 + 2H_2O,$$
$$Ca(OCl)_2 + CaCl_2 + 2H_2SO_4 = 2CaSO_4 + 2Cl_2 + 2H_2O$$

The last reaction takes place in two stages, in the first of which sulphuric acid liberates hydrochloric acid from the (basic) calcium chloride

When bleaching powder is heated oxygen is evolved

$$Ca(OCl)_2 = CaCl_2 + O_2$$

The same decomposition can be brought about in aqueous solution by the catalytic action of a cobalt salt

$$Ca(OCl)_2 = CaCl_2 + O_2$$

In this process, the cobalt is precipitated as hydroxide by the free lime in the solution, and then oxidised by the hypochlorite to a peroxide

$$CoCl_2 + Ca(OH)_2 = Co(OH)_2 + CaCl_2,$$
$$2Co(OH)_2 + Ca(OCl)_2 = 2CoO_2 + CaCl_2 + 2H_2O$$

The cobalt peroxide then acts as a catalyst for the liberation of oxygen as indicated by the equations

$$2CoO_2 + Ca(OCl)_2 = 2CoO + CaCl_2 + 2O_2,$$
$$2CoO + Ca(OCl)_2 = 2CoO_2 + CaCl_2$$

The ease with which bleaching powder gives oxygen or chlorine accounts for the fact that it is a powerful oxidising and chlorinating agent Thus a suspension of it in water is used to oxidise litharge to lead dioxide,

$$2PbO + Ca(OCl)_2 = 2PbO_2 + CaCl_2,$$

and chlorinate acetone, $CH_3COCH_3$, to chloroform, $CHCl_3$, (p 702)

Bleaching powder is used as a disinfectant, but its principal use is for bleaching cotton, linen and paper pulp The fabric to be bleached is boiled with dilute sodium hydroxide to remove greasy impurities, immersed in a very dilute solution of bleaching powder, and left exposed to the air for several hours, when bleaching is effected probably through

the agency of atmospheric carbon dioxide which liberates hypochlorous acid as shown above The fabric is then placed in a bath of very dilute sulphuric acid, in order to destroy any traces of bleaching powder which still remain , it may also be freed from the last traces of chlorine by the action of sulphurous acid or a sulphite

**Chlorous acid**, $HClO_2$, can be prepared by adding sulphuric acid to a solution of **barium chlorite** and filtering off the precipitated barium sulphate

$$Ba(ClO_2)_2 + H_2SO_4 = BaSO_4 + 2HClO_2.$$

The solution is colourless, and decomposes at atmospheric temperatures into hypochlorous and chloric acids CHLORITES are produced, together with chlorates, by the action of chlorine dioxide on aqueous alkalis, but in the presence of hydrogen peroxide only chlorites are formed

$$2ClO_2 + 2NaOH = NaClO_2 + NaClO_3 + H_2O ,$$
$$H_2O_2 + 2ClO_2 + 2NaOH = 2NaClO_2 + O_2 + 2H_2O$$

Chlorites are powerful oxidising and bleaching agents They may be distinguished from hypochlorites by their power to bleach after treatment with sodium arsenite solution

**Chloric acid**, $HClO_3$, is formed when an aqueous solution of barium chlorate is mixed with dilute sulphuric acid

$$Ba(ClO_3)_2 + H_2SO_4 = BaSO_4 + 2HClO_3$$

After filtering off the barium sulphate, the solution can be concentrated over sulphuric acid in a vacuum until it contains 40% of the acid On further concentration, or on heating the solution, the acid is decomposed, perchloric acid being formed and chlorine dioxide set free

$$3HClO_3 = HClO_4 + 2ClO_2 + H_2O$$

Chloric acid is a powerful oxidising agent It oxidises hydrochloric acid to chlorine, hydriodic acid to iodine, and sulphurous acid to sulphuric acid

$$8HClO_3 + 16HCl = 9Cl_2 + 6ClO_2 + 12H_2O ,$$
$$HClO_3 + 6HI = 3I_2 + HCl + 3H_2O ,$$
$$3H_2SO_3 + HClO_3 = 3H_2SO_4 + HCl$$

If the reducing agent is not present in excess, the reduction of the chloric acid may not be complete Thus insufficient sulphurous acid reduces chloric acid only to hypochlorous acid,

$$HClO_3 + 2H_2SO_3 = HClO + 2H_2SO_4$$

The solution thus produced will bleach indigo (in addition to oxidising a further supply of sulphurous acid), whereas chloric acid oxidises sulphurous acid but does not bleach indigo, and the more stable perchloric acid is inert towards both

**Potassium chlorate.**—*Preparation* —(1) Chlorates are formed, together with chlorides, when chlorine is passed into hot concentrated solutions of alkalis

$$6KOH + 3Cl_2 = KClO_3 + 5KCl + 3H_2O$$

EXPT 36 **Preparation of potassium chlorate**

Chlorine is passed through an inverted funnel into 100 c c of a hot 30% solution of potassium hydroxide When the solution is saturated with chlorine it is allowed to cool and the crystals which separate are washed with a little cold water and recrystallised from 20 c c of boiling water

The wastefulness of a process in which five-sixths of the caustic potash is converted into potassium chloride was avoided commercially by bubbling chlorine through milk of lime and precipitating potassium chlorate by addition of potassium chloride

$$6Ca(OH)_2 + 6Cl_2 = 5CaCl_2 + Ca(ClO_3)_2 + 6H_2O ,$$
$$Ca(ClO_3)_2 + 2KCl = CaCl_2 + 2KClO_3$$

(11) Potassium chlorate is now manufactured by electrolysing an aqueous solution of potassium chloride at a temperature of 60° to 70°, under conditions which do not keep the anode and cathode products separate, but allow them to mix freely At the *anode*, potassium chloride undergoes ELECTROLYTIC OXIDATION to potassium chlorate, whilst hydrogen is evolved at the *cathode* The final result is expressed by the equation

$$KCl + 3H_2O = KClO_3 + 3H_2$$

Potassium chlorate (unlike sodium chlorate) is only sparingly soluble in cold water (5 7% at 15°), and so crystallises out of solution before the unchanged chloride It melts at 370° and is slowly converted into a mixture of chloride and perchlorate (Expt 37) , at higher temperatures it decomposes with effervescence into potassium chloride and oxygen

$$2KClO_3 = 2KCl + 3O_2$$

In the presence of manganese dioxide this decomposition takes place below the melting-point and no perchlorate is formed (p 230)

Potassium chlorate must be evaporated in lead-lined vessels, since the solution oxidises iron It is reduced quantitatively to the chloride by the action of a hot solution of sulphurous acid

$$KClO_3 + 3SO_2 + 3H_2O = KCl + 3H_2SO_4$$

It is also reduced to potassium chloride when heated with concentrated hydrochloric acid, chlorine and chlorine dioxide being liberated as shown in the equation

$$8KClO_3 + 24HCl = 8KCl + 9Cl_2 + 6ClO_2 + 12H_2O$$

When acted upon by strong sulphuric acid, the unstable and explosive gas, chlorine dioxide, $ClO_2$, is again produced

$$3KClO_3 + 3H_2SO_4 = 3KHSO_4 + HClO_4 + 2ClO_2 + H_2O$$

On account of its powerful oxidising action, potassium chlorate forms dangerous mixtures with phosphorus, charcoal, and sugar When mixed with carbon and sulphur, it forms a gunpowder resembling that obtained by using nitre, but unsuitable for general use on account of its excessive sensitiveness.

Potassium chlorate is used in the manufacture of fireworks, photographic flash-powders (mixed with magnesium and a little red phosphorus), and matches (p 208)

**Perchloric acid,** $HClO_4$, the most stable acid of this series, is prepared by distilling under reduced pressure a mixture of potassium perchlorate and strong sulphuric acid

$$KClO_4 + H_2SO_4 = KHSO_4 + HClO_4$$

The liquid in the receiver solidifies to a crystalline mass of the **hydrate,** $HClO_4,H_2O$, which on redistillation first gives the anhydrous acid and then a mixture of constant boiling-point containing 71 6% of acid

Perchloric acid is an oily fuming liquid which resembles sulphuric acid in uniting violently with water to form a series of hydrates It is a powerful oxidising agent, which inflames paper and wood, produces burns on the skin, and is liable to decompose violently The aqueous solution is quite stable and, like dilute sulphuric acid, possesses no oxidising properties, *e g* it attacks zinc to give a chlorate and hydrogen

**Potassium perchlorate,** $KClO_4$, is formed (together with potassium chloride) by cautiously fusing potassium chlorate

$$4KClO_3 = 3KClO_4 + KCl$$

EXPT 37 **Preparation of potassium perchlorate.**

Potassium chlorate (50 grams) is melted in a porcelain crucible and stirred thoroughly with a glass rod to equalise the temperature, which is maintained just above the initial melting-point of 370° The heating is stopped (usually after about ten minutes) when the product has largely solidified owing to the higher melting-points of potassium chloride and perchlorate The perchlorate is separated from the much more soluble chloride by grinding the mixture with 50 c c of cold water, filtering, and recrystallising from 200 c c of boiling water

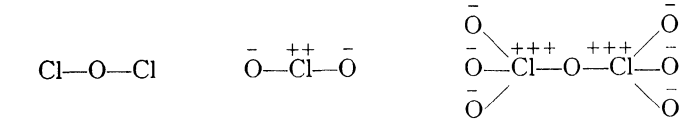
Potassium perchlorate is prepared commercially by electrolysing a solution of sodium chloride so as to form sodium chlorate, which is converted by further electrolytic oxidation into sodium perchlorate , to this solution potassium chloride is added so as to precipitate the less soluble potassium perchlorate

$$NaClO_4 + KCl = KClO_4 + NaCl$$

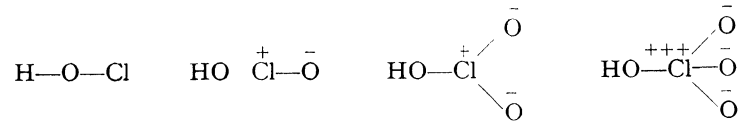
Potassium perchlorate is isomorphous with potassium permanganate, $KMnO_4$ It is one of the least soluble salts of potassium (0 7% at 0°), and is practically insoluble in 95% alcohol containing 0 2% of perchloric acid, a fact which is made use of in the estimation of potassium. It melts at about 600°, but loses oxygen at a much lower temperature when manganese dioxide is present

Although containing a higher proportion of oxygen than potassium chlorate, it is a less powerful oxidising agent, *e g* it does not oxidise solutions of sulphurous acid or hydrochloric acid With concentrated sulphuric acid, it yields perchloric acid, which can be distilled off (as above), whilst potassium chlorate gives chlorine dioxide (see opposite)

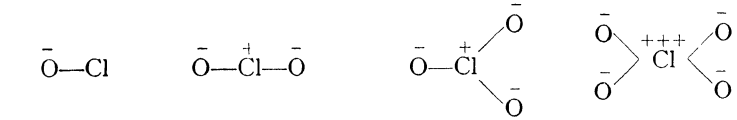
**Structure of the oxy-acids of chlorine.**—The following formulae represent the commonly accepted structures of the oxides and oxy-acids of chlorine, and of the ions which are derived from these acids



Dichlorine monoxide Chlorine dioxide Dichlorine heptoxide



Hypochlorous acid Chlorous acid Chloric acid Perchloric acid



Hypochlorous ion Chlorous ion Chloric ion Perchloric ion

These formulae show that the chlorine atom, which only requires one more electron to complete its octet, can form compounds of higher valency by sharing one or more of its lone pairs of electrons with oxygen atoms Thus, the chlorine atom in hypochlorous acid contains three pairs of lone electrons and can share these with three oxygen atoms to form perchloric acid The stability of perchloric acid and the perchlorates is attributed to the saturation of *all* the lone pairs of electrons of the chlorine atom, giving a high degree of symmetry in the perchlorate ion

**Estimation of chlorine.**—The estimation of chlorine, free and combined, is described on pages 422, 431, 438 and 450

## 35 BROMINE Br=79 916

**Preparation of bromine.**—Bromine was discovered in 1826 by Balard, who obtained the element in the form of a dark red liquid by chlorinating, and then distilling, the mother liquors of sea-water It is prepared commercially by the action of chlorine on the bromides in the mother liquors obtained in the preparation of potassium and magnesium salts from the Stassfurt salt-beds and waters of the Dead Sea

$$2Br^- + Cl_2 = Br_2 + 2Cl^-$$

Chlorine is passed into the bottom of a tower (packed with earthenware balls) down which the bromide liquors are allowed to flow The bromine vapour which escapes from the top of the tower is condensed, and the last traces of bromine and chlorine vapour are absorbed by wet iron filings

The chlorine and bromine in the waste liquor are recovered by treatment with steam and passed back again into the tower

In recent years the demand for bromine has increased enormously on account of the use of ethylene dibromide, $C_2H_4Br_2$, in anti-knock petrols (see p 295) To meet this demand, bromine is now extracted on the Atlantic coast of America from sea-water, which actually contains only 0 007% of the element as bromide The bromine is liberated by the action of chlorine, as in the above process, but the extraction is complicated by the fact that owing to its high dilution a considerable proportion of the element is hydrolysed to bromide and hypobromite,

$$Br_2 + H_2O \rightleftharpoons Br^- + BrO^- + 2H^+,$$

and cannot be set free by further chlorination The previous addition of about 0 27 lb of 96% sulphuric acid to each ton of sea-water, however, reduces the proportion of bromine hydrolysed to under 1% by providing sufficient hydrogen ions to displace the above equilibrium to the left The element is then expelled from solution by a current of air and absorbed in active charcoal, from which it can be recovered from time to time by a current of steam

In the laboratory, bromine may be prepared by distilling a mixture of potassium bromide and manganese dioxide with moderately concentrated sulphuric acid (cf chlorine)

$$2KBr + MnO_2 + 3H_2SO_4 = 2KHSO_4 + MnSO_4 + Br_2 + 2H_2O$$

EXPT 38 **Preparation of bromine from potassium bromide.**

Moderately concentrated sulphuric acid (100 c c of 40% strength) is carefully added to a powdered mixture of potassium bromide (5 grams) and manganese dioxide (15 grams) in a small retort The mixture is heated cautiously, when bromine distils over and is collected in a large test tube cooled by running water

**Purification.**—Commercial bromine is freed from chlorine by distilling it with a metallic bromide, *e g*

$$FeBr_2 + Cl_2 = FeCl_2 + Br_2$$

Final purification from traces of chlorine and iodine can be effected by shaking the bromine with a little aqueous sodium hydroxide, when chlorine and iodine are preferentially attacked, since they are oxidised more easily than bromine

$$2NaOH + Cl_2 = NaCl + NaClO + H_2O$$

The bromine is then dried with anhydrous calcium bromide and redistilled

**Physical properties.**—Bromine is a heavy reddish-black liquid of density 3 12, which boils at 58 8° It has a pungent odour (Greek, *βρῶμος*, a smell) and a highly corrosive action on the skin Like iodine, it is freely soluble in organic solvents, such as carbon disulphide, but only dissolves to the extent of 3 5% in water at 15°

**Chemical properties.**—Bromine is less active than chlorine, but resembles this element very closely in most of its chemical properties

Thus it combines with hydrogen, sulphur and phosphorus (explosively with the white variety), but not with carbon, oxygen or nitrogen It unites with metals to form BROMIDES, and interacts with alkalis in much the same way as chlorine It also forms ADDITION PRODUCTS with "unsaturated compounds," *e g*

$$C_2H_4 + Br_2 = C_2H_4Br_2 \text{ (Ethylene dibromide),}$$

and SUBSTITUTION PRODUCTS by displacing elements such as hydrogen, sulphur and iodine from their saturated compounds, *e g*

$$H_2S + Br_2 = 2HBr + S\ , \quad 2KI + Br_2 = 2KBr + I_2$$

Bromine probably interacts with water to give traces of hydrobromic and hypobromous acid, since its aqueous solution has a greater conductivity than pure water and has bleaching and oxidising properties

$$Br_2 + H_2O \rightleftharpoons HBrO + HBr\ ,$$
$$H_2SO_3 + H_2O + Br_2 = H_2SO_4 + 2HBr$$

Thus, blue litmus is first reddened and then bleached by bromine and water, and sulphurous acid is oxidised to sulphuric acid, but bromine water is not unstable like chlorine water, and in the absence of alkali is hydrolysed only to a very small extent

**Preparation of hydrogen bromide.**—(i) Hydrogen bromide may be synthesised from its elements by passing a mixture of hydrogen and bromine vapour through a tube containing a red-hot spiral of platinum wire A suitable gaseous mixture is obtained by bubbling hydrogen through bromine in a wash-bottle heated to 50° by a bath of hot water

$$H_2 + Br_2 \rightleftharpoons 2HBr$$

The action is reversible, but is practically complete when a slight excess of hydrogen is used, since dissociation of hydrogen bromide only takes place to the extent of about 1% even at 1200°

(ii) Hydrogen bromide cannot be prepared by the action of concentrated sulphuric acid on potassium bromide, because the hydride (unlike HF and HCl) is oxidised by sulphuric acid, so that bromine and sulphur dioxide are also produced

$$2KBr + 2H_2SO_4 = K_2SO_4 + Br_2 + SO_2 + 2H_2O$$

This action is reversible, since bromine oxidises sulphurous acid to sulphuric acid in dilute aqueous solutions, in which sulphuric acid is no longer an oxidising agent

$$H_2SO_3 + H_2O + Br_2 = H_2SO_4 + 2HBr$$

(iii) Small quantities of hydrogen bromide may be prepared in the laboratory by the action of bromine on red phosphorus in the presence of water Phosphorus tribromide is first formed and is then hydrolysed by the water to hydrogen bromide and phosphorous acid

$$P_4 + 6Br_2 = 4PBr_3\ ,$$
$$PBr_3 + 3H_2O = 3HBr + H_3PO_3$$

**Expt 39 Preparation of hydrogen bromide (first method)**

Red phosphorus (15 grams) and clean sand (15 grams) are made into a thick paste with water (15 c c ) and placed in a flask (Fig 87) fitted with a delivery tube and a tap funnel When bromine (20 c c ) is added cautiously from the tap funnel, a vigorous action takes place and hydrogen bromide is liberated as a gas This is freed from (i) bromine vapour by passing it through a U-tube, *A*, packed loosely with pieces of glass smeared with red phosphorus, and (ii) moisture by passing through a U-tube, *B*, containing calcium bromide

(iv) Larger quantities of hydrogen bromide (for the preparation of a solution of the acid, etc ) are more conveniently made by the action of

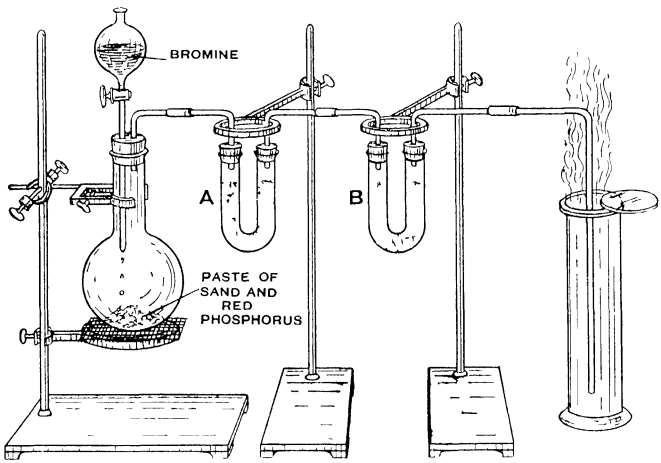



Fig 87 Preparation of Hydrogen Bromide (First Method )

bromine on benzene in the presence of dry aluminium powder, which acts as a catalyst $C_6H_6 + Br_2 = HBr + C_6H_5Br$ (Bromo-benzene)

**Expt 40 Preparation of hydrogen bromide (second method)**

Benzene (50 c c ) and dry aluminium powder (3 grams) are placed in a 500 c c flask (Fig 88) fitted with a tap funnel and delivery tube Bromine (50 c c ) is placed in the funnel and a few c c are added to the benzene The mixture in the flask is heated to start the reaction, which may become so vigorous that the flask has to be immersed in cold water The hydrogen bromide which is evolved is freed from bromine vapour by passing it through a U-tube which contains pieces of glass coated with red phosphorus, and from benzene vapour in a second U-tube which contains lumps of anthracene The gas is very soluble in water and is therefore dissolved by using two wash-bottles, as in the preparation of chlorine water

**Properties of hydrogen bromide.**—Hydrogen bromide, like hydrogen chloride, is a colourless pungent gas which fumes in moist air Water at 0° dissolves 600 volumes of the gas and gives a solution containing over 68% HBr On distillation a mixture of constant boiling-point is obtained, which contains 48% HBr and boils at 125° **Hydrobromic acid** is a strong acid like hydrochloric acid and reacts with metals and bases in exactly the same way (p 282), it is, however, more readily oxidised by air in the presence of sunlight

$$4HBr + O_2 = 2Br_2 + 2H_2O$$

Bromides, like chlorides, are generally soluble in water, but silver, lead and mercurous bromides are insoluble **Potassium bromide,** KBr, is

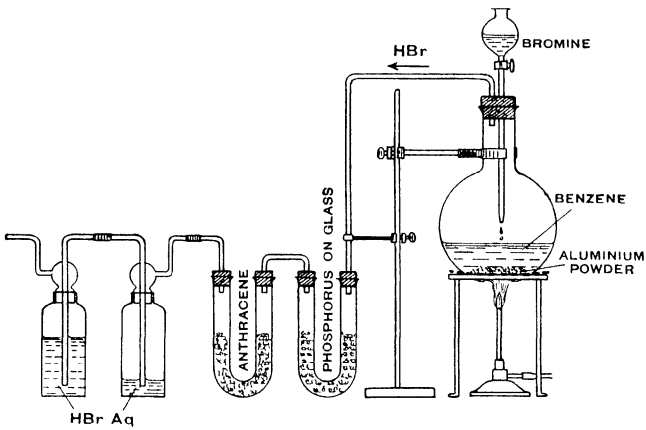



FIG 88 PREPARATION OF HYDROGEN BROMIDE (Second Method)

important as a drug, whilst **silver bromide,** AgBr, is used extensively in photography (p 325)

**Oxy-derivatives of bromine**—A very dilute solution of **hypobromous acid** can be prepared by shaking bromine water with mercuric oxide

$$2Br_2 + HgO + H_2O = HgBr_2 + 2HBrO$$

The acid forms a yellow solution and resembles hypochlorous acid in its oxidising and bleaching properties, but is even more unstable **Sodium hypobromite,** NaBrO, is obtained together with the bromide by the action of bromine on dilute sodium hydroxide

$$2NaOH + Br_2 = NaBr + NaBrO + H_2O,$$

compare $$2NaOH + Cl_2 = NaCl + NaClO + H_2O$$

The solution has bleaching and oxidising properties, but is converted into a mixture of **sodium bromide,** NaBr, and **sodium bromate,** $NaBrO_3$, even more readily than the hypochlorite is converted into chloride and chlorate

$$3NaBrO = 2NaBr + NaBrO_3,$$

compare $$3NaClO = 2NaCl + NaClO_3$$

When hot concentrated alkali is used the bromate is formed immediately:

$$6NaOH + 3Br_2 = 5NaBr + NaBrO_3 + 3H_2O\ ;$$

compare $$6NaOH + 3Cl_2 = 5NaCl + NaClO_3 + 3H_2O$$

**Potassium bromate**, prepared by this method from potassium hydroxide and bromine, resembles potassium chlorate in its small solubility and in liberating oxygen when heated, but does *not* form a perbromate

$$2KBrO_3 = 2KBr + 3O_2\ ,\quad \text{but}\quad 4KClO_3 = 3KClO_4 + KCl$$

Free **bromic acid**, $HBrO_3$, can be prepared by precipitating **silver bromate**, $AgBrO_3$, and digesting it with bromine water

$$5AgBrO_3 + 3Br_2 + 3H_2O = 5AgBr + 6HBrO_3.$$

The aqueous solution can be concentrated *in vacuo*, but decomposes to free bromine and oxygen when heated, since the oxides of bromine are unstable and perbromic acid does not exist

$$4HBrO_3 = 2Br_2 + 5O_2 + 2H_2O\ ,$$

contrast $$3HClO_3 = HClO_4 + 2ClO_2 + H_2O$$

**Uses of bromine and its compounds.**—The principal use of bromine is in the manufacture of ethylene dibromide, $C_2H_4Br_2$ (p 670), for "ethyl" petrol The latter contains lead tetraethyl, $Pb(C_2H_5)_4$, as an anti-knock, and the presence of ethylene dibromide ensures that on the combustion of the petrol vapour in the cylinders, the lead is carried away in the hot exhaust gases in the form of lead bromide vapour, in absence, however, of the dibromide, lead oxide is deposited on the sparking plugs and cylinder walls with very deleterious effects

Bromine is also required for the manufacture of dyes and metallic bromides, such as potassium bromide for medicine, and silver bromide for photography

**Estimation of Bromine.**—See pages 423, 431, 438

## 53 IODINE I=126 92

**Occurrence.**—Sea-water contains traces of iodine, this is absorbed by marine plants and can be manufactured from the ash of burnt seaweed, to which the name of KELP is given The principal source of iodine, however, is the nitrate beds of Chile, which contain iodine in the form of **sodium iodate**, $NaIO_3$ The element was discovered in 1811 by Courtois, who heated with sulphuric acid the mother liquors of kelp from which sodium carbonate had crystallised, and obtained a beautiful violet vapour which condensed to black, lustrous crystals The name of iodine was given to it on account of the violet colour of its vapour (Greek, ἰώδης, violet)

**Preparation of iodine.**—(*a*) *From kelp* —The ash from burnt seaweed is extracted with water After crystallising out potassium sulphate, potassium chloride and common salt, the mother liquor is mixed with sulphuric acid, separated from sulphur (derived from sulphides formed in

burning the ash), and distilled with manganese dioxide from iron pots into a series of earthenware condensers

$$2NaI + 3H_2SO_4 + MnO_2 = I_2 + 2NaHSO_4 + MnSO_4 + 2H_2O$$

As an alternative, the iodine can be precipitated by the action of chlorine

$$2NaI + Cl_2 = I_2 + 2NaCl$$

(*b*) *From caliche or crude sodium nitrate* —The mother liquors from the purification of the crude Chilean sodium nitrate are mixed with the calculated quantity of crude sodium bisulphite to reduce five-sixths of the iodate to iodide

$$NaIO_3 + 3NaHSO_3 = 3NaHSO_4 + NaI$$

The acidity of the sodium bisulphate liberates hydriodic and iodic acids, which give iodine according to the equation

$$HIO_3 + 5HI = 3I_2 + 3H_2O$$

The iodine settles to the bottom and is washed with water, pressed to remove moisture, and sublimed

(*c*) *Purification* —Crude iodine generally contains **iodine chloride,** ICl, **iodine bromide,** IBr, and sometimes **iodine cyanide,** ICN, which cannot be separated by sublimation, since they are also volatile It is therefore purified by subliming with potassium iodide, when the chlorine, bromine and cyanogen are retained by the potassium as chloride, bromide and cyanide, *e g*

$$KI + ICl = KCl + I_2$$

EXPT 41 **Sublimation of iodine**

Iodine (10 grams) and potassium iodide (3 grams) are intimately ground in a mortar and heated cautiously in an evaporating dish on a sand bath A larger evaporating dish, filled with cold water, is placed on the top of the first dish and the heating continued After a few minutes the bottom of the water-cooled dish becomes covered with a glittering mass of crystals, which may be scraped off More iodine is then sublimed and condensed

**Physical properties of iodine** —Iodine forms brilliant black crystals with a lustre that is almost metallic The density of the solid is 4 94 It melts at 113° and boils at 184° , but its vapour-pressure at the melting-point is so high that it sublimes readily without melting

The vapour-density of iodine at low temperatures corresponds with the formula $I_2$, but dissociation takes place when the temperature is raised, the calculated proportions of the two constituents being as follows

TABLE 22 —DISSOCIATION OF IODINE

| | $I_2$ | $\rightleftharpoons$ | $2I$ | | | |
|---|---|---|---|---|---|---|
| At 400° | 99 94% | | 0 06% | | | |
| At 600° | 95 3% | | 4 7% | or | 20 | 1 |
| At 800° | 89 5% | | 10 5% | or | 9 | 1 |
| At 1000° | 62% | | 38% | or | 5 | 3 |
| At 1200° | 26% | | 74% | or | 1 | 3 |

Iodine is only slightly soluble in water (1 part in 5000), but it is freely soluble in aqueous potassium iodide, owing to the formation of **potassium tri-iodide**, $KI_3$

$$KI + I_2 \rightleftharpoons KI_3$$

It is also soluble in alcohol, carbon disulphide and chloroform

**Chemical properties of iodine.**—In its chemical properties iodine shows a general resemblance to the other halogens, although it is much less active

(*a*) *Iodine and the non-metals*—Iodine unites with hydrogen very slowly, even in the presence of sunlight, whereas chlorine and hydrogen explode under these conditions It forms compounds with the other halogens, *e g* $IF_5$, $IF_7$, ICl, $ICl_3$, IBr It combines with phosphorus to form the iodides, $PI_3$ and $P_2I_4$, but it does not combine with sulphur Unlike the other halogens, it can be oxidised by nitric acid to the stable oxide, $I_2O_5$

(*b*) *Iodine and the metals*—Iodine unites directly with metals to form IODIDES These resemble the chlorides in their general properties, but are frequently coloured, even when the corresponding chlorides and bromides are colourless Thus, when mercury and iodine are rubbed together, a green **mercurous iodide**, $Hg_2I_2$, is formed when the mercury is in excess, and a red **mercuric iodide**, $HgI_2$, when the iodine is in excess Unlike chlorine, iodine forms a series of PERIODIDES, the best-known example being **potassium tri-iodide**, $KI_3$

(*c*) *Iodine and the alkalis*—When iodine is dissolved in cold dilute potash, **potassium iodide**, KI, and **potassium hypoiodite**, KIO, are formed

$$I_2 + 2KOH \rightleftharpoons KI + KIO + H_2O$$

This action differs from the corresponding action in the case of chlorine in that (i) it is reversible, the iodine being only partly combined, (ii) the further conversion to iodate, as indicated in the equation

$$3I_2 + 6KOH = 5KI + KIO_3 + 3H_2O,$$

takes place gradually even in cold solutions With hot concentrated potash the iodate is formed directly

(*d*) *Iodine as an oxidising agent*—Iodine is a less powerful oxidising agent than bromine or chlorine, but it oxidises hydrogen sulphide to sulphur, sulphites to sulphates (p 420), arsenites to arsenates (p 421) and sodium thiosulphate to sodium tetrathionate, $Na_2S_4O_6$ (p 419)

$$2Na_2S_2O_3 + I_2 = 2NaI + Na_2S_4O_6$$

**Uses of iodine.**—Iodine is used in the manufacture of certain dyes It is also used in the manufacture of **iodoform**, $CHI_3$, and as a disinfectant for wounds in the form of TINCTURE OF IODINE, which is a solution of iodine in alcohol In the laboratory, iodine is used in volumetric analysis and in organic syntheses

**Hydrogen iodide**, HI—(*a*) *Preparation*—(1) Iodine unites directly with hydrogen when the gas and vapour are passed through a red-hot tube

The action, which is exothermic in the vapour state, is incomplete, the equilibrium being roughly as follows

TABLE 23.—DISSOCIATION OF HYDROGEN IODIDE

| | $2HI \rightleftharpoons$ | $H_2 + I_2$ (vapour) $-2200$ cals |
|---|---|---|
| At 300° - - | 82% | 18% |
| At 400° - - | 80% | 20% |
| At 500° - - | 76% | 24% |

(ii) Hydrogen iodide cannot be prepared by the action of sulphuric acid on potassium iodide, since oxidation takes place to an even larger extent than in the case of the bromide

$$KI + H_2SO_4 = KHSO_4 + HI,$$
$$2HI + H_2SO_4 \rightleftharpoons I_2 + SO_2 + 2H_2O$$

This oxidation (like that of hydrogen bromide) is a balanced action, since dilute solutions of sulphurous acid are completely oxidised by excess of iodine Sulphuretted hydrogen is also produced by the action of strong sulphuric acid on potassium iodide

$$8KI + 9H_2SO_4 = 8KHSO_4 + 4I_2 + H_2S + 4H_2O$$

A dilute solution of hydrogen iodide can be prepared by passing hydrogen sulphide through a suspension of iodine in water, and filtering off the precipitated sulphur

$$H_2S + I_2 = 2HI + S$$

The action tends to reverse at high concentrations, but the dilute solution can be easily concentrated by distillation

(iii) Gaseous hydrogen iodide is usually prepared by the action of water on a mixture of red phosphorus and iodine

$$P_4 + 10I_2 + 16H_2O = 20HI + 4H_3PO_4$$

EXPT 42 **Preparation of hydrogen iodide**

Red phosphorus (5 grams) and iodine (70 grams) are mixed in a dry flask (apparatus like Fig 87), and water (15 c c ) is added gradually from a tap funnel Hydrogen iodide is evolved and is freed from iodine by passing through a U-tube which contains moist red phosphorus If the reaction becomes too vigorous, the flask should be immersed in cold water The gas is collected by the upward displacement of air, since it is very soluble in water and attacks mercury , it can be dried by means of calcium iodide A solution of the gas in water is obtained by the usual device of two wash-bottles (compare Fig 88)

(*a*) *Physical properties* —Hydrogen iodide is a pungent gas, which fumes in moist air It condenses to a heavy liquid of density 2 8 (b -pt $-36°$), and dissolves freely in water, forming an acid solution which is known as **hydriodic acid** An acid of maximum boiling-point boils at 127° and contains 58% HI

(*b*) *Chemical properties* —Hydrogen iodide is a strong acid , but it is also a reducing agent, since the hydrogen which it contains is held very

loosely All the common oxidising agents therefore liberate iodine from hydrogen iodide, and fresh solutions of the acid, which are colourless, rapidly become brown on exposure to the air

$$4HI + O_2 = 2I_2 + 2H_2O$$

The interaction of hydrogen iodide with ferric salts, however, is reversible

$$2FeCl_3 + 2HI \rightleftharpoons 2FeCl_2 + I_2 + 2HCl$$

Concentrated solutions of hydrogen iodide, heated in a sealed tube to prevent escape of gas, are used as reducing agents in organic chemistry, *e g* to replace a hydroxyl group by hydrogen The hydrogen iodide probably acts first as an acid to convert the hydroxide into an iodide, and then as a reducing agent in replacing the iodine by hydrogen

$$ROH + HI = RI + H_2O, \quad RI + HI = RH + I_2$$

This action can be carried out more efficiently when red phosphorus is added to combine with the iodine as it is formed

**Oxy-compounds of iodine**—Iodine forms the following oxides and oxy-acids

| Oxides | Oxy-acids |
|---|---|
| Iodine sesquioxide, $I_2O_3$ | Hypoiodous acid, HIO |
| Di-iodine tetroxide, $I_2O_4$ | Iodic acid, $HIO_3$ |
| Di-iodine pentoxide, $I_2O_5$ | Periodic acids, $HIO_4$, $H_5IO_6$, etc |

**Iodine sesquioxide**, $I_2O_3$, has been prepared by heating di-iodine pentoxide with fuming sulphuric acid

$$I_2O_5 = I_2O_3 + O_2$$

It is chiefly of note because it exhibits basic properties, *e g* it forms a basic iodate, OI $IO_3$, or $I_2O_4$, which was formerly, but erroneously, described as a product of the action of cold concentrated nitric acid on iodine

**Di-iodine pentoxide**, $I_2O_5$, the most stable halogen oxide, is prepared as a white powder by heating iodic acid to 200° It dissolves in water and is reconverted into iodic acid

$$I_2O_5 + H_2O \rightleftharpoons 2HIO_3$$

**Hypoiodous acid**, HIO, is formed by the action of mercuric oxide on a suspension of iodine in water

$$2I_2 + HgO + H_2O = HgI_2 + 2HIO$$

It is a very weak acid and, like hypochlorous acid, has oxidising and bleaching properties

**Iodic acid**, $HIO_3$, is prepared by heating iodine with concentrated nitric acid

$$3I_2 + 10HNO_3 = 6HIO_3 + 10NO + 2H_2O$$

Iodic acid is also formed by the action of chlorine on a suspension of iodine in water

$$I_2 + 5Cl_2 + 6H_2O = 10HCl + 2HIO_3$$

It is a heavy crystalline solid, which dissolves in water to give an acid solution This solution also has oxidising properties, *e g* hydriodic acid is oxidised to iodine and sulphurous acid to sulphuric acid

$$HIO_3 + 5HI = 3H_2O + 3I_2,$$
$$HIO_3 + 3H_2SO_3 = 3H_2SO_4 + HI \text{ (p 296)}$$

EXPT 43 **Preparation of iodic acid**

Iodine (12 grams) and fuming nitric acid (100 c c ) are placed in a round-bottomed flask with a long neck, and heated gently in a fume chamber until the iodine has disappeared The liquor is then evaporated to dryness in an evaporating dish, and the solid is heated until fumes of nitric acid are no longer evolved The residue, which consists of di-iodine pentoxide, is dissolved in the minimum quantity of hot water, evaporated a little, and left to crystallise in a desiccator

**Potassium iodate** can be prepared from potassium chlorate by heating a concentrated solution of the latter with iodine and a few drops of nitric acid

$$2KClO_3 + I_2 = 2KIO_3 + Cl_2$$

This reaction serves to show the superior affinity which iodine has for oxygen

Potassium iodate is a white crystalline solid, which is sparingly soluble in water It resembles the chlorate and bromate, but requires a higher temperature for decomposition by heat

$$2KIO_3 = 2KI + 3O_2$$

It is used in the laboratory for the standardisation of sodium thiosulphate solutions (p 419), since it can be obtained readily in a high state of purity, and reacts quantitatively with potassium iodide in acid solution according to the equation

$$KIO_3 + 5KI + 6HCl = 6KCl + 3I_2 + 3H_2O.$$

**Periodic acid**, $HIO_4,2H_2O$, and **potassium periodate**, $KIO_4$, have been prepared by the electrolytic oxidation of iodic acid and potassium iodate respectively

**Estimation of iodine.**—*Free iodine* is usually estimated by titration with sodium thiosulphate, which it oxidises quantitatively to sodium tetrathionate (p 419)

$$2Na_2S_2O_3 + I_2 = 2NaI + Na_2S_4O_6$$

The end-point is indicated by means of starch, which gives a perceptible blue coloration even when the concentration of iodine has fallen below one part in a million It is not yet known whether the colour reaction between starch and iodine is due to the formation of a compound, or to mere adsorption of elementary iodine on the surface of the grains of starch *Iodides* may be estimated both volumetrically and gravimetrically by the same methods as are used for chlorides (p 290)

# *PART III*

# TRANSITIONAL ELEMENTS

## CHAPTER XXII

### THE TRANSITIONAL ELEMENTS

| I | II | III | IV | V | VI | VII |
|---|---|---|---|---|---|---|
| 19 *K* | 20 *Ca* | 21 Sc | 22 Ti | 23 V | 24 Cr | 25 Mn |
| 37 *Rb* | 38 *Sr* | 39 Y | 40 Zr | 41 Nb | 42 Mo | 43 Ma |
| 55 *Cs* | 56 *Ba* | 57 La* | 72 Hf | 73 Ta | 74 W | 75 Re |
| — | 88 *Ra* | 89 Ac | 90 Th | 91 Pa | 92 U | |

| VIII | | | I | II | III | IV |
|---|---|---|---|---|---|---|
| 26 Fe | 27 Co | 28 Ni | 29 Cu | 30 Zn | 31 *Ga* | 32 *Ge* |
| 44 Ru | 45 Rh | 46 Pd | 47 Ag | 48 Cd | 49 *In* | 50 *Sn* |
| 76 Os | 77 Ir | 78 Pt | 79 Au | 80 Hg | 81 *Tl* | 82 *Pb* |

**Typical and transitional elements.**—In Part II an account has been given of Mendeléeff's " typical elements "

H, [He], Li, Be, B, C, N, O, F, [Ne],

and of the elements which correspond with them in their electronic structure, together with the " inert gases," He, Ne, etc , which were still unknown when Mendeléeff's table was constructed The principal feature of these " typical elements " is the building up, around the helium " duplet," of an " octet " of 8 outer electrons, which is completed in neon It has been shown that this octet is characteristic of *all* the inert gases except helium The periodic classification of the elements is therefore based fundamentally on the repetition of this process of octet-formation in successive shells of *L*, *M*, *N*, *O*, *P* electrons Thus the first two steps in the formation of a new octet give rise always to metals of the alkalis and of the alkaline earths, with 1 or 2 electrons only in the outer shell, whilst the penultimate step gives rise to a halogen, with 7 electrons in the outer shell

So far, the whole process is simple, and, if 8 electrons were the maximum capacity of all the other shells, as it is of the *L*-shell, we need go no further than Newland's system of octaves, expanded to include the inert

* The gap between 57 La and 72 Hf is filled by 14 tervalent elements of the rare earth series

gases, in order to construct a framework in which all the elements (after hydrogen and helium) would fall into place in a series of 8 columns, with a " typical element " at the head of each We have already seen, however, that the *M*-shell can hold 18 electrons, and the *N*-shell 32 electrons Competition may therefore arise between the claims of (i) an outer shell to build up an octet, and (ii) an inner shell, which has already secured 8 electrons, to expand its octet to a larger group of 18 or 32 electrons At certain stages these rival claims are balanced so evenly that it would be difficult or impossible to *predict* whether an additional electron would be bound more firmly in the outer or in an inner shell , but in practice it is possible to determine, from spectroscopic observations, the fate of each successive electron, and in this way to record the fact that the outer shell generally secures two electrons, and then has to wait for the third electron until the inner shell has been expanded from 8 to 18 or 32 electrons, as the case may be For this reason the " typical elements " which form a continuous series of 8 elements in the two short periods are interrupted in the subsequent long periods *after the elements of the alkaline earths*, as shown in Table 24 below This interruption, during which an inner shell is being expanded from 8 to 18 electrons, gives rise to 10 " transitional elements " in each of the two " long " periods of 18 elements, whilst a further expansion of the *N*-shell from 18 to 32 electrons accounts for intrusion of fourteen rare earths, which interrupt another sequence of 10 transitional elements in the following " very long " period of 32 elements

TABLE 24 —ELECTRONIC STRUCTURE OF TRANSITIONAL ELEMENTS

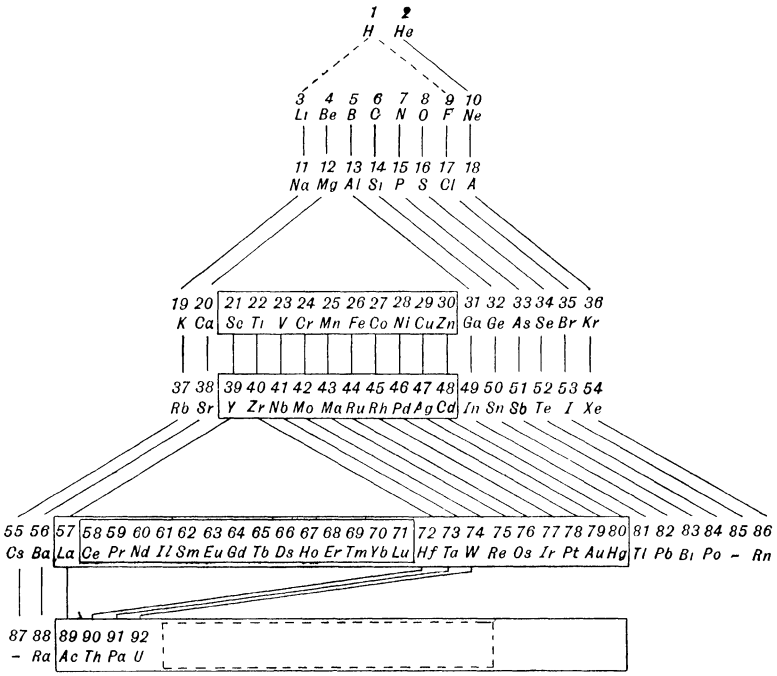
| | | *K* *L* *M* *N* | |
|---|---|---|---|
| Argon | $Z=18$ | 2 + 8 + 8 | Typical elements |
| Potassium | $Z=19$ | 2 + 8 + 8 + 1 | |
| Calcium | $Z=20$ | 2 + 8 + 8 + 2 | |
| **Scandium** | $Z=21$ | 2 + 8 + 9 + 2 | Transitional elements |
| **Titanium** | $Z=22$ | 2 + 8 + 10 + 2 | |
| **Vanadium** | $Z=23$ | 2 + 8 + 11 + 2 | |
| **Chromium** | $Z=24$ | 2 + 8 + 13 + 1* | |
| **Manganese** | $Z=25$ | 2 + 8 + 13 + 2 | |
| **Iron** | $Z=26$ | 2 + 8 + 14 + 2 | |
| **Cobalt** | $Z=27$ | 2 + 8 + 15 + 2 | |
| **Nickel** | $Z=28$ | 2 + 8 + 16 + 2 | |
| **Copper** | $Z=29$ | 2 + 8 + 18 + 1* | |
| **Zinc** | $Z=30$ | 2 + 8 + 18 + 2 | |
| Gallium | $Z=31$ | 2 + 8 + 18 + 3 | Typical elements |
| Germanium | $Z=32$ | 2 + 8 + 18 + 4 | |
| Arsenic | $Z=33$ | 2 + 8 + 18 + 5 | |
| Selenium | $Z=34$ | 2 + 8 + 18 + 6 | |
| Bromine | $Z=35$ | 2 + 8 + 18 + 7 | |
| Krypton | $Z=36$ | 2 + 8 + 18 + 8 | |

The way in which the successive periods are expanded from 2 to 8, 18 and 32 elements is shown very clearly in Table 25, which is based

* The irregularity of the sequence of numbers is an interesting reminder that chemistry is not a matter of simple algebra

upon Bohr's Periodic Table In this table, hydrogen is linked by dotted lines to lithium and to fluorine, since it yields ions either by losing or gaining one electron The two short periods are then shown with eight elements in each , but in the two long periods the sequence of 8 " typical elements " is interrupted by a series of 10 * " transitional elements " (beginning in each case with a tervalent element) which are enclosed in a frame Similarly in the " very long period " the sequence of 10

TABLE 25 --BASED UPON BOHR'S PERIODIC TABLE




transitional elements is interrupted in its turn by a series of 14 " rare earth elements " which are enclosed in an inner frame These rare earth elements ($Z = 58$ to 71) are *all* tervalent, like aluminium , but, since the preceding transitional element (lanthanum, $Z = 57$) is also tervalent, this cluster of " rare earth elements " includes 15 elements in all The four radioactive elements ($Z = 89$ to 92), which follow radium, are obviously all transitional elements , it is therefore a pure speculation whether a second " rare earth " series would appear if elements of higher atomic number could be studied

* In Bohr's original table only *eight* elements were enclosed in the panel

TABLE 26.—ATOMIC NUMBERS AND ATOMIC WEIGHTS

| | I | II | III | IV | V | VI | VII | O | VIII | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | 1 | 2 | | | |
| PERIOD (2 Elements) | | | | | | | **H** | **He** | | | |
| | | | | | | | 1 0081 | 4 002 | | | |
| | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | | | |
| PERIOD II | Li | Be | **B** | **C** | **N** | **O** | **F** | **Ne** | | | |
| (8 Elements) | 6 940 | 9 02 | 10 82 | 12 01 | 14 008 | 16 | 19 00 | 20 183 | | | |
| | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | | | |
| PERIOD III | Na | Mg | Al | Si | **P** | **S** | **Cl** | **A** | | | |
| (8 Elements) | 22 997 | 24 32 | 26 97 | 28 06 | 30 98 | 32 06 | 35 457 | 39 944 | | | |
| | 19 | 20 | 21 | 22 | 23 | 24 | 25 | | 26 | 27 | 28 |
| PERIOD IV | K | Ca | Sc | Ti | V | Cr | Mn | | Fe | Co | Ni |
| (18 Elements) | 39 096 | 40 07 | 45 10 | 47 90 | 50 95 | 52 01 | 54 93 | | 55 84 | 58 94 | 58 69 |
| | 29 | 30 | 31 | 32 | 33 | 34 | 35 | 36 | | | |
| | Cu | Zn | Ga | Ge | **As** | **Se** | **Br** | **Kr** | | | |
| | 63 57 | 65 38 | 69 72 | 72 60 | 74 91 | 78 90 | 79 916 | 83 7 | | | |
| | 37 | 38 | 39 | 40 | 41 | 42 | 43 | | 44 | 45 | 46 |
| PERIOD V | Rb | Sr | Y | Zr | Nb | Mo | Ma | | Ru | Rh | Pd |
| (18 Elements) | 85 44 | 87 63 | 88 92 | 91 22 | 92 91 | 96 0 | — | | 101 7 | 102 91 | 106 7 |
| | 47 | 48 | 49 | 50 | 51 | 52 | 53 | 54 | | | |
| | Ag | Cd | In | Sn | Sb | **Te** | **I** | **Xe** | | | |
| | 107 880 | 112 41 | 114 76 | 118 70 | 121 76 | 127 61 | 126 92 | 131 3 | | | |
| | 55 | 56 | 57–71 | 72 | 73 | 74 | 75 | | 76 | 77 | 78 |
| PERIOD VI | Cs | Ba | RARE | Hf | Ta | W | Re | | Os | Ir | Pt |
| (32 Elements) | 132 91 | 137 36 | EARTHS | 178 6 | 181 4 | 184 0 | 186 31 | | 191 5 | 193 1 | 195 23 |
| | 79 | 80 | 81 | 82 | 83 | 84 | 85 | 86 | | | |
| | Au | Hg | Tl | Pb | Bi | Po | ? | **Rn** | | | |
| | 197 2 | 200 61 | 204 39 | 207 22 | 209 00 | — | — | 222 | | | |
| | 87 | 88 | 89 | 90 | 91 | 92 | | | | | |
| PERIOD VII | ? | Ra | Ac | Th | Pa | U | | | | | |
| (? Elements) | — | 225 97 | — | 232 12 | 231 | 238 14 | | | | | |

Non-metals are printed in heavy type

A complete table showing the atomic weights of all the elements, except those of the rare earths, is reproduced for reference as Table 26, whilst an alphabetical list is reproduced for reference as Table 27

**Properties of the transitional elements**.—The physical properties of the principal elements of the transition series may be summarised as follows

(*a*) Since the outer electrons are not bound very strongly to the nucleus, the transition-elements are all *metals*, which are good *conductors of heat and electricity* and have a bright *metallic lustre*. Most of them are silvery white in colour, the principal exceptions being red copper and yellow gold

(*b*) The *densities* (Table 28) are usually high, but fall off at the beginning of the series, where the initial elements are not very much denser than the metals of the alkalis and alkaline earths which immediately precede them

TABLE 27.—ATOMIC WEIGHTS, 1939

| | Symbol | At No | At wt |
|---|---|---|---|
| Aluminium | Al | 13 | 26 97 |
| Antimony | Sb | 51 | 121 76 |
| Argon | A | 18 | 39 944 |
| Arsenic | As | 33 | 74 91 |
| Barium | Ba | 56 | 137 36 |
| Beryllium | Be | 4 | 9 02 |
| Bismuth | Bi | 83 | 209 00 |
| Boron | B | 5 | 10 82 |
| Bromine | Br | 35 | 79 916 |
| Cadmium | Cd | 48 | 112 41 |
| Cæsium | Cs | 55 | 132 91 |
| Calcium | Ca | 20 | 40 08 |
| Carbon | C | 6 | 12 01 |
| Cerium | Ce | 58 | 140 13 |
| Chlorine | Cl | 17 | 35 457 |
| Chromium | Cr | 24 | 52 01 |
| Cobalt | Co | 27 | 58 94 |
| Copper | Cu | 29 | 63 57 |
| Dysprosium | Dy | 66 | 162 46 |
| Erbium | Er | 68 | 167 2 |
| Europium | Eu | 63 | 152 0 |
| Fluorine | F | 9 | 19 00 |
| Gadolinium | Gd | 64 | 156 9 |
| Gallium | Ga | 31 | 69 72 |
| Germanium | Ge | 32 | 72 60 |
| Gold | Au | 79 | 197 2 |
| Hafnium | Hf | 72 | 178 6 |
| Helium | He | 2 | 4 003 |
| Holmium | Ho | 67 | 163 5 |
| Hydrogen | H | 1 | 1 0081 |
| Indium | In | 49 | 114 76 |
| Iodine | I | 53 | 126 92 |
| Iridium | Ir | 77 | 193 1 |
| Iron | Fe | 26 | 55 84 |
| Krypton | Kr | 36 | 83 7 |
| Lanthanum | La | 57 | 138 92 |
| Lead | Pb | 82 | 207 21 |
| Lithium | Li | 3 | 6 940 |
| Lutecium | Lu | 71 | 175 0 |
| Magnesium | Mg | 12 | 24 32 |
| Manganese | Mn | 25 | 54 93 |
| Mercury | Hg | 80 | 200 61 |
| Molybdenum | Mo | 42 | 95 95 |
| Neodymium | Nd | 60 | 144 27 |
| Neon | Ne | 10 | 20 183 |
| Nickel | Ni | 28 | 58 69 |
| Niobium | Nb | 41 | 92 91 |
| Nitrogen | N | 7 | 14 008 |
| Osmium | Os | 76 | 190 2 |
| Oxygen | O | 8 | 16 0000 |
| Palladium | Pd | 46 | 106 7 |
| Phosphorus | P | 15 | 30 98 |
| Platinum | Pt | 78 | 195 23 |
| Potassium | K | 19 | 39 096 |
| Praseodymium | Pr | 59 | 140 92 |
| Protactinium | Pa | 91 | 231 |
| Radium | Ra | 88 | 226 05 |
| Radon | Rn | 86 | 222 |
| Rhenium | Re | 75 | 186 31 |
| Rhodium | Rh | 45 | 102 91 |
| Rubidium | Rb | 37 | 85 48 |
| Ruthenium | Ru | 44 | 101 7 |
| Samarium | Sm | 62 | 150 43 |
| Scandium | Sc | 21 | 45 10 |
| Selenium | Se | 34 | 78 96 |
| Silicon | Si | 14 | 28 06 |
| Silver | Ag | 47 | 107 880 |
| Sodium | Na | 11 | 22 997 |
| Strontium | Sr | 38 | 87 63 |
| Sulphur | S | 16 | 32 06 |
| Tantalum | Ta | 73 | 180 88 |
| Tellurium | Te | 52 | 127 61 |
| Terbium | Tb | 65 | 159 2 |
| Thallium | Tl | 81 | 204 39 |
| Thorium | Th | 90 | 232 12 |
| Thulium | Tm | 69 | 169 4 |
| Tin | Sn | 50 | 118 70 |
| Titanium | Ti | 22 | 47 90 |
| Tungsten | W | 74 | 183 92 |
| Uranium | U | 92 | 238 07 |
| Vanadium | V | 23 | 50 95 |
| Xenon | Xe | 54 | 131 3 |
| Ytterbium | Yb | 70 | 173 04 |
| Yttrium | Y | 39 | 88 92 |
| Zinc | Zn | 30 | 65 38 |
| Zirconium | Zr | 40 | 91 22 |

(*c*) The *melting-points* are generally above 1000°, but fall abruptly from 1083°, 960° and 1063° in the triad Cu, Ag, Au to 419°, 321° and −39° in the triad Zn, Cd, Hg

TABLE 28.—DENSITIES AND MELTING-POINTS OF TRANSITIONAL ELEMENTS

| | 24 Cr | 25 Mn | 26 Fe | 27 Co | 28 Ni | 29 Cu | 30 Zn |
|---|---|---|---|---|---|---|---|
| Density - | - 7·1 | 7·2 | 7·86 | 8·9 | 8·9 | 8·9 | 7·1 |
| Melting-point | - 1615° | 1260° | 1530° | 1480° | 1452° | 1083° | 419° |

**Valency.**—(*a*) *Electrovalence*.—The transition-elements are too remote from the inert gases to show the intense chemical activity and sharply-defined negative or positive electrovalences of the typical elements which immediately precede and follow these gases. They are therefore relatively inert, but, in presence of electronegative elements such as chlorine, they lose electrons and form positively-charged cations. Since the binding force increases progressively with the charge on the ion, it is not easy to remove more than 2 or 3 electrons from any atom. Most of the transition-elements therefore form bivalent ions, *e g*

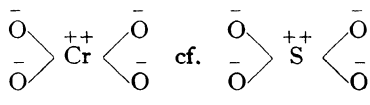
| $Cr^{++}$ | $Mn^{++}$ | $Fe^{++}$ | $Co^{++}$ | $Ni^{++}$ | $Cu^{++}$ | $Zn^{++}$ |
|---|---|---|---|---|---|---|
| blue | pink | green | red | green | blue | colourless |

These give double sulphates of the type, $K_2Fe(SO_4)_2,6H_2O$, isomorphous with SCHONITE, $K_2Mg(SO_4)_2,6H_2O$. Many of the metals also form tervalent ions, *e g*

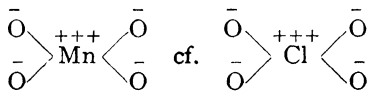
| $Cr^{+++}$ | $Mn^{+++}$ | $Fe^{+++}$ | $Co^{+++}$ |
|---|---|---|---|
| green | violet | yellow | blue |

These give rise to double sulphates of the type, $KFe^{\cdot\cdot}(SO_4)_2,12H_2O$, isomorphous with alum, $KAl(SO_4)_2,12H_2O$. The variable valency and wide range of colours exhibited by the above ions are noteworthy characteristics of the transitional elements.

(*b*) *Covalence*.—The transition-elements also form covalent compounds such as the METALLIC CARBONYLS, $Cr(CO)_6$, $Fe(CO)_5$, $Ni(CO)_4$, in which the valency of the central atom is apparently 12, 10 and 8, respectively, thus providing a remarkable extension of the variable valencies already noted in the ions. Higher valencies are also developed in the oxy-acids of chromium and manganese, the ions of which contain 8 electrons more than those of sulphur and chlorine, *e g*




where the central atom has a positive electrovalence of 2 and a covalence of 4




where the central atom has a positive electrovalence of 3 and a covalence of 4

The formation of these complex ions provides the principal (perhaps the

only) justification for classifying manganese with the halogens and chromium with sulphur, just as the univalency of silver and the occasional univalency of copper and gold provides the sole basis for classifying these metals with those of the alkalis

(*c*) *Coordination*.—Higher valencies are also developed in the coordination compounds, which are formed by the combination of the simple ions with water or ammonia, as well as with CO and NO. Thus the blue colour of the cupric salts is due to a hydrated cupric ion, perhaps $[Cu\ 4H_2O]$, since anhydrous copper sulphate is colourless, and the red and blue colours developed by cobaltous chloride (p. 347) have been attributed to ions of different colour such as $[Co\ 6H_2O]^{++}$ (red) and $[CoCl_4]^{--}$ (blue). The ions of the transition-elements are exceptionally ready to unite with *six* molecules of water or with *six* molecules of ammonia, as in

$$CrCl_3,6NH_3, \qquad CoCl_3,6NH_3, \qquad NiCl_2,6H_2O,$$

or $$[Cr\ 6NH_3]Cl_3, \quad [Co\ 6NH_3]Cl_3, \quad [Ni\ 6H_2O]Cl_2$$

In these coordination compounds an incomplete shell of M electrons,

$$\overset{+++}{Cr} = 2+8+11, \quad \overset{+++}{Co} = 2+8+14, \quad \overset{++}{Ni} = 2+8+16,$$

is enveloped by a shell of 12 shared electrons derived from 6 molecules of ammonia or of water. The central metallic ion is therefore hexacovalent, and again has a higher valency than in the simple ions

# CHAPTER XXIII

## THE COINAGE METALS

| | | |
|---|---|---|
| 29 | COPPER | Cu = 63·57 |
| 47 | SILVER | Ag = 107 880 |
| 79 | GOLD | Au = 197·2 |

**Classification** —The atoms of the coinage metals, copper, silver and gold, have the following electronic structures

| *K L M N O P* | *K L M N O* |
|---|---|
| Cu = 2 + 8 + 18 + 1 | Cu = 2 + 8 + 18 |
| Ag = 2 + 8 + 18 + 18 + 1 | Ag = 2 + 8 + 18 + 18 |
| Au = 2 + 8 + 18 + 32 + 18 + 1 | Au = 2 + 8 + 18 + 32 + 18 |

The table shows that these elements have a single electron in their outermost orbits, and therefore resemble the alkali metals in their tendency to lose an electron and form univalent salts such as $Cu^+ Cl^-$, cf $Na^+ Cl^-$

The univalent ions of the alkali metals are remarkably stable, since they have the electronic configuration of the inert gases which precede them in the periodic classification of the elements, and have therefore no tendency to form ions of higher valency On the other hand, the removal of an electron from an atom of copper, silver or gold, instead of disclosing the outer octet of an inert gas, results in the exposure of a much less stable shell of 18 electrons The instability of this shell is proved by the fact that the elements, Ni, Pd, Pt, which precede the coinage metals, are not inert gases, like those which precede the metals of the alkalis, but are themselves metals from which electrons can be removed to form metallic salts The coinage metals therefore differ profoundly from the alkali metals in almost every respect, not only in the metallic state and in their univalent compounds, but above all in their ability to form compounds of higher valency There is, therefore, no real justification for classifying them with these metals, and hence they are most appropriately placed in the series of transition-elements, thus

| | | |
|---|---|---|
| 28 Ni | 29 Cu | 30 Zn |
| 46 Pd | 47 Ag | 48 Cd |
| 78 Pt | 79 Au | 80 Hg |

This classification is justified by the strong resemblance of copper to nickel and zinc, especially in its bivalent compounds, and by the similarities which exist between palladium and silver, and between platinum and gold In particular it may be noted that copper is being displaced by

nickel in coins of small value, whilst palladium now provides an alternative to silver-plating and platinum competes with gold as a precious metal for use in jewellery. Since palladium and platinum are " noble metals " like silver and gold, and do not show any very close resemblance to nickel, it is convenient to refer briefly to their properties in the present chapter, which therefore deals with the elements Cu, Ag, Au, Pt, whilst nickel and cobalt, which are associated closely with copper in a horizontal transition series, are described together in Chapter XXV

**Physical properties.**—Copper, silver and gold are tough, malleable, ductile metals, which can be drawn into wire, rolled or hammered into thin sheet or foil, and pressed between dies to form coins and medals They melt at about 1000°, and show a gradation in density from 8 9 and 10 5 to 19 3 In these respects they are at the opposite extreme to the light and fusible metals of the alkalis, but resemble nickel, palladium and platinum, which melt at even higher temperatures (Ni 1452°, Pd 1555°, Pt 1755°) and are also rather denser than the coinage metals (Ni 8 9, Pd 12 0, Pt 21 4)

**Chemical properties.**—(*a*) *Electrode potentials* —The coinage metals are only feebly electropositive and are therefore almost the only metals which are found frequently in the native state In this respect also they are at the opposite extreme to the alkali metals, but resemble the preceding elements of the transitional series, since native iron and nickel are found in the metallic state in meteorites, and are believed to form the central metallic core of the earth, whilst the triads of metals (including platinum) which precede silver and gold in Table 26 are also found almost exclusively in the native state as precious metals

The three metals form an evenly-graded electrochemical series, since copper is more electropositive than silver, and precipitates it readily from its salts, whilst silver is more electropositive than gold They can therefore be separated very readily by electrolysis, when copper is dissolved at the anode, and silver and gold are left, whilst at a higher potential silver is dissolved and gold is left In this classification, nickel and cobalt approximate to iron, and are definitely more electropositive than copper, in the same way platinum is also rather more electropositive than gold, since it is left behind in solution, when gold is deposited by electrolysis

(*b*) *Action of acids* —Since copper, silver and gold are less electropositive than hydrogen, they do not liberate hydrogen from water or from dilute acids (contrast Na, K, etc ), although copper dissolves readily in hot dilute sulphuric acid *in presence of air*, when water is formed instead of hydrogen On the other hand copper and silver are dissolved by dilute nitric and concentrated sulphuric acid, with liberation of oxides of nitrogen and sulphur dioxide respectively, whilst gold and platinum are dissolved only by aqua regia

$$Cu + H_2SO_4 + \tfrac{1}{2}O_2 = CuSO_4 + H_2O,$$
$$Cu + 2H_2SO_4 = CuSO_4 + SO_2 + 2H_2O,$$
$$2Ag + 2H_2SO_4 = Ag_2SO_4 + SO_2 + 2H_2O,$$
$$Au + 4HCl + HNO_3 = HAuCl_4 + NO + 2H_2O,$$
$$3Pt + 18HCl + 4HNO_3 = 3H_2PtCl_6 + 4NO + 8H_2O.$$

In the last two cases, the noble metal is not converted into the *cation* of a metallic salt, but forms the central atom of the *anion* of a chloro-acid

(*c*) *Oxidation*.—Copper is oxidised in air to CuO (compare NiO) but yields $Cu_2O$ at high temperatures. Silver dissolves oxygen, probably in the form of $Ag_2O$, but spits it out again on solidification, since the free oxide is unstable at high temperatures. Gold and platinum are noble metals which do not oxidise in air.

(*d*) *Formation of salts*.—The valencies developed in the salts of copper, silver and gold are indicated, with those of nickel and platinum, in the following table:

| Univalent | Bivalent | Tervalent | Quadrivalent |
|---|---|---|---|
| CuCl | $CuCl_2$ | — | — |
| AgCl | $[Ag\ 4C_5H_5N](NO_3)_2$ | — | — |
| AuCl | — | $AuCl_3$ | — |
| — | $NiCl_2$ | — | — |
| PtCl | $PtCl_2$ | — | $PtCl_4$ |

They illustrate in a remarkable manner the variable valency which is so pronounced a characteristic of many of the transitional elements.

In accordance with the electronic structures of the atoms, copper, silver and gold all form *univalent* salts, which differ widely, however, from those of the alkali metals. Thus the *univalent* halide salts of copper, silver and gold are insoluble in water, *i e* the ionic aggregate, $Ag^+Cl^-$, etc., is not broken up by condensation of water round the ions in the same way as $Na^+Cl^-$. The three *sulphides*, $Cu_2S$, $Ag_2S$ and $Au_2S$ also differ diametrically from those of the alkali metals, since they are black and are insoluble in water and dilute acids. The *cyanides* likewise differ from those of the alkali metals in that they are insoluble in water, but they dissolve readily in excess of alkali cyanide to form double cyanides, *e g* $KAgC_2N_2$.

Since the removal of one electron from an atom of copper discloses a complete shell of 18 electrons, it might have been expected that copper would be exclusively univalent, like the alkali metals, or at least predominantly univalent like silver, even if we admit that a shell of 18 electrons may be less refractory than the outer octet of an inert gas. It is therefore remarkable that the salts of copper are predominantly *bivalent*. In this respect they resemble those of nickel and zinc, which precede and follow copper in the first transition series of metals. The bivalent ions have the following structures:

$$\overset{++}{Ni}\quad Z = 28 - 2 = 2 + 8 + 16,$$
$$\overset{++}{Cu}\quad = 29 - 2 = 2 + 8 + 17,$$
$$\overset{++}{Zn}\quad = 30 - 2 = 2 + 8 + 18$$

These ions are all extremely stable, but the cupric ion can be reduced to the cuprous state because the 17 outer electrons are less stable than a complete shell of 18 electrons.

The readiness of copper to form bivalent salts is also in marked contrast

to the rigid univalency of silver A few derivatives of bivalent silver have been prepared in recent years, but even these are only known as coordination compounds and the simple ion, $Ag^{++}$, corresponding with the ions $Cu^{++}$, $Ni^{++}$ and $Zn^{++}$, is therefore still unknown

Gold differs from copper and silver in that most of its compounds are *tervalent* The positive electrovalence of the element is very feeble, and the metal is very ready to form covalent derivatives of higher valency, in which it forms part of a *complex anion*, as in the aurichlorides,

$$Na^+ [Au\ Cl_4]^- \quad \text{and} \quad K^+ [Au\ Cl_4]^-$$

The evidence for the existence of the free ion, $Au^{+++}$, is therefore not very strong In the same way, although platinum forms bivalent and quadrivalent compounds, the most important salts are derived from *complex ions*, *e g* $K_2[PtCl_4]$ and $K_2[PtCl_6]$

## 29 COPPER Cu = 63 57

**History.**—Copper appears to have been known to the Egyptians for at least six thousand years, either alone or alloyed with tin in the form of BRONZE The Greeks and Romans obtained supplies of copper from Cyprus and gave the name *cuprum* to the metal Copper from Britain was probably known to the Phoenicians as early as 1000 B C, and copper from Anglesey was used by the Romans As recently as 1800 Great Britain produced as much as three-quarters of the world's output of copper, but supplies are now obtained mainly from North and South America and from the upper reaches of the Congo

**Occurrence** —Native copper occurs in enormous masses in the region of Lake Superior, where it forms veins in the red sandstone The chief ores are COPPER PYRITES, $CuFeS_2$, COPPER GLANCE, $Cu_2S$, RED COPPER ORE, $Cu_2O$, BLACK COPPER ORE, $CuO$, MALACHITE, $CuCO_3,Cu(OH)_2$, AZURITE, $2CuCO_3,Cu(OH)_2$, and BASIC COPPER SULPHATE

**Preparation of copper.**—(*a*) *Native copper* is very difficult to work on account of its toughness Small aggregates are melted with a little carbon and a flux to remove the siliceous material, and the impure product is refined by electrolysis Larger masses are sometimes extracted by electrolysis *in situ*

(*b*) *Oxide and carbonate ores* are crushed and heated to convert the carbonate and hydroxide into oxide The oxide is mixed with anthracite or coke, and a flux to remove earthy material, and heated in a reverberatory furnace, when crude copper is obtained

$$2CuO + C = 2Cu + CO_2$$

(*c*) *Sulphide ores* are smelted by a process of controlled oxidation, whereby the sulphur is eliminated as sulphur dioxide

$$2Cu_2S + 3O_2 = 2Cu_2O + 2SO_2,$$
$$2Cu_2O + Cu_2S = 6Cu + SO_2$$

This simple process is complicated, however, by the necessity for removing iron as well as sulphur from the ore This is done by taking advantage of

ne preferential oxidation of the baser metal and the greater affinity of s oxide for silica, as indicated by the equation

$$2FeS + 3O_2 + 2SiO_2 = 2FeSiO_3 + 2SO_2$$

The two processes used for this purpose are described below

**The Welsh process.**—(i) *Calcination* —The crude ore is roasted, when rsenic is volatilised as the oxide, $As_4O_6$, and part of the sulphur as sulphur ioxide, mainly by preferential oxidation of iron

$$2CuFeS_2 + 4O_2 = Cu_2S + 2FeO + 3SO_2$$

The sulphur dioxide is used for making sulphuric acid

(ii) *First fusion* —The roasted ore is mixed with material containing ilica (*e g* a copper ore which is free from sulphur) and fused at a high emperature on the hearth of a reverberatory furnace The iron oxide ombines with the silica to form a slag of ferrous silicate which only conains a small amount (0 5%) of copper The heavier layer of cuprous and errous sulphides is run off into water to granulate it The product, nown as COARSE METAL, contains about 30-34% Cu, 23% S, and conderable quantities of iron

(iii) *Second fusion* —A second calcination and fusion with a siliceous re (and with " refinery slags " from the later stages) gives a FINE METAL which consists mainly of cuprous sulphide, since it contains 70-80% Cu, 5-20% S This fine metal contains very little iron, but the slag of ferrous ilicate contains an appreciable quantity of copper, which is recovered by eturning it to process (ii)

(iv) *Roasting for metal* —Blocks of " fine metal " are roasted on the earth of a reverberatory furnace to oxidise cuprous sulphide partially to upric oxide

$$Cu_2S + 2O_2 = 2CuO + SO_2$$

The supply of air is then stopped and the temperature of the furnace aised so that the following reaction takes place

$$Cu_2S + 2CuO = 4Cu + SO_2$$

The metal separates as a liquid, together with a little " refinery slag," which is rich in copper and is therefore returned to process (iii) The nolten metal is run off into small moulds and is known as BLISTER COPPER, because the liberation of sulphur dioxide as it solidifies gives it a blistered ppearance

(v) *Refining* —The " blister copper " is purified by melting in a earth in a stream of air The remaining sulphur is oxidised to sulphur ioxide, arsenic is volatilised as $As_4O_6$, whilst iron, tin, etc , are converted nto their oxides and skimmed off, but the purified metal contains cuprous xide which renders it brittle The oxide is reduced by sprinkling the urface with powdered anthracite and stirring with a pole of green irchwood, when reducing gases are evolved, which convert the oxide to netal , the product contains 99½% Cu, and is known as TOUGH PITCH r MARKETABLE COPPER

**The Mansfield process** differs from the Welsh process in the use of a last furnace and Bessemer converter in place of a reverberatory furnace.

The roasted ore is mixed with coke and a siliceous material and yields in the blast furnace a *slag* of ferrous silicate and a *matte* of copper and iron sulphides, which corresponds to the " coarse metal " of the Welsh process This matte is run into a Bessemer converter (p 354) lined with siliceous material, the air-blast is turned on and crude copper is produced as in process (iv) and refined as in process (v) above

**Electrolytic refining of copper** —The copper produced by the above methods contains impurities such as arsenic, bismuth, lead, tin, iron and traces of silver and gold Pure copper, *e g* for electric cables, is prepared from it by electrolysis Heavy anodes of the crude metal are placed between thin cathodes of the pure metal in a bath containing about 15% $CuSO_4$ and 5% $H_2SO_4$ On electrolysis, copper dissolves from the anodes and is deposited on the cathodes , metallic silver and gold are left behind as an anode slime, together with lead in the form of sulphate, and tin, antimony and bismuth in the form of insoluble basic salts American copper yields almost sufficient silver (110 oz per ton) and gold ($\frac{1}{3}$ oz per ton), to pay for the cost of refining

**Physical and mechanical properties of copper** —Copper melts at 1083° and has a density of 8 945 It is a soft, tough metal with a high conductivity for heat and electricity It is therefore used for making cooking utensils and electric cables , but for the latter purpose it must be highly purified, since its conductivity is reduced disastrously by traces of impurity (*e g* 0 1% Bi) or by oxidation during casting

The mechanical properties of copper can be improved by alloying with tin to form BRONZE, or with zinc to form BRASS Thus CARTRIDGE BRASS (30% Zn) can be deformed to a remarkable extent by pressing or drawing before it begins to crack Copper coins contain 4% Sn, 1% Zn, whilst GUN-METAL, with 8-12% Sn, is used in place of iron and steel for instruments, gear-wheels, etc Finally, PHOSPHOR BRONZE (Sn 12%, Pb 4%, P 1 5%), which is a gun-metal deoxidised by the addition of phosphor-copper and alloyed with a little lead to check corrosion, is one of the strongest non-ferrous metals, and is used as a substitute for steel in bearings, valves, taps, etc , where rusting must be avoided

**Chemical properties of copper.**—Copper is stable in dry air at ordinary temperatures, but in moist air is slowly converted by the action of oxygen and carbonic acid into the **basic carbonate,** VERDIGRIS, $CuCO_3$, $Cu(OH)_2$ When heated in air, it unites with oxygen to form **cupric oxide,** CuO, but above 1100° **cuprous oxide,** $Cu_2O$, is formed It does not combine directly with hydrogen, and is attacked by steam only at a white heat, when slight oxidation takes place, perhaps as a result of the dissociation of water-vapour into hydrogen and oxygen

Dilute sulphuric and hydrochloric acids are without action on copper, but in the presence of air the metal dissolves slowly with formation of water instead of hydrogen

$$2Cu + 2H_2SO_4 + O_2 = 2CuSO_4 + 2H_2O$$

It also dissolves slowly in hot concentrated hydrochloric acid as represented by the equation

$$2Cu + 4HCl = 2HCuCl_2 + H_2.$$

Concentrated sulphuric acid also dissolves it, with the evolution of sulphur dioxide and formation of copper sulphate,

$$Cu + 2H_2SO_4 = CuSO_4 + 2H_2O + SO_2 ,$$

but an insoluble black sludge of cuprous and cupric sulphides is produced simultaneously by a reaction such as

$$5Cu + 4H_2SO_4 = Cu_2S + 3CuSO_4 + 4H_2O$$

Ordinary dilute nitric acid dissolves copper readily with evolution of nitric oxide and traces of other oxides

$$3Cu + 8HNO_3 = 3Cu(NO_3)_2 + 2NO + 4H_2O$$

This action appears to be initiated by *nitrous acid*, since, if this is removed by bubbling air through the dilute acid or by the addition of urea, the action can be arrested almost completely, but becomes very rapid as soon as fresh supplies of nitrous acid have been formed by the initial attack on the metal With concentrated nitric acid, copper gives mainly nitrogen peroxide

$$Cu + 4HNO_3 = Cu(NO_3)_2 + 2NO_2 + 2H_2O$$

Copper reduces a solution of ferric iron quantitatively to the ferrous state

$$Cu + Fe_2(SO_4)_3 = CuSO_4 + 2FeSO_4$$

The reaction is accelerated by using copper filings and heating

**Compounds of Copper.**—Copper forms univalent CUPROUS COMPOUNDS and bivalent CUPRIC COMPOUNDS The former are generally colourless and insoluble in water (cf mercurous compounds, p 338), whilst the latter, which are very similar to the corresponding compounds of nickel, are generally soluble and blue or green in colour Both series of compounds are remarkable for the number of addition compounds they form with ammonia, hydrochloric acid, etc

Cuprous salts are stable in dry air but slowly oxidise in the presence of moisture to basic cupric compounds Cuprous nitrate and sulphate are decomposed immediately by water into copper and a cupric salt, *e g*

$$Cu_2SO_4 = Cu + CuSO_4$$

It must not be inferred from this that cupric compounds are necessarily more stable than cuprous compounds, since cupric iodide, cyanide and sulphocyanide decompose spontaneously into the corresponding cuprous salts, whilst cupric oxide, sulphide, fluoride, chloride and bromide decompose similarly when heated

The instability of certain cupric salts is due to the fact that the cupric ion has a tendency to gain an electron, in order to acquire a complete outer shell of 18 $M$-electrons

$$Cu^{++} + e \rightarrow Cu^{+}$$

This change takes place most easily when the anion is only feebly electronegative, *e g* $CN^-$ The feeble electron affinity of the anion then favours the transfer of an electron to the cation, whilst the unchanged radicals of the anions unite in pairs to form covalent molecules

$$CN^- + Cu^{++} \rightarrow Cu^{+} + CN , \quad 2CN = (CN)_2.$$

The conversion of a cupric into a cuprous salt is also favoured when the cuprous salt is very insoluble Thus aqueous cupric iodide decomposes into cuprous iodide and iodine, because the extreme insolubility of cuprous iodide causes the removal of cuprous ions from the equilibrium

$$\underset{}{\overset{++}{Cu} + 2\overset{-}{I} \rightleftharpoons \underset{(ppt)}{\overset{+}{Cu}\overset{-}{I}} + I}, \quad I + I = I_2$$

On the other hand, the apparent instability of the cuprous ion, $Cu^+$, in aqueous solution (as shown by the spontaneous decomposition of soluble cuprous salts such as cuprous sulphate) may be attributed to the extreme insolubility of metallic copper Thus although the equilibrium,

$$2Cu^+ \rightleftharpoons Cu^{++} + Cu,$$

may be strongly in favour of the cuprous ion, the metal is so insoluble that it is precipitated from any but very dilute cuprous solutions, with the result that the above equilibrium is driven almost completely from left to right This explains why only the insoluble cuprous salts can be prepared in contact with water

The ready oxidation of cuprous salts by moist air can be attributed to the stability of the copper-hydroxide link, which is probably covalent Thus the hydroxide has to be heated to a very high temperature before all the water is expelled

## Cuprous Compounds

**Cuprous oxide**, $Cu_2O$, separates as a brilliant red powder when an alkaline solution of cupric tartrate, known as Fehling's solution, is warmed with a " reducing sugar " such as glucose This process is used to estimate such sugars, either gravimetrically (the cuprous oxide being oxidised to cupric oxide or reduced to metallic copper before weighing it) or volumetrically, using the blue colour of the cupric solution to indicate the end-point of the titration

$$2Cu(OH)_2 + C_6H_{12}O_6 = Cu_2O + 2H_2O + C_6H_{12}O_7$$

Expt 44 **Fehling's solution**

69 28 grams of copper sulphate, $CuSO_4,5H_2O$, are weighed out, dissolved in water, and made up to 1 litre Another solution is prepared, containing 120 grams of caustic soda and 350 grams of Rochelle salt (sodium potassium tartrate, $NaKC_4H_4O_6$, p 754), in 1 litre of water A mixture of equal volumes of these two solutions is known as Fehling's solution Since the solution is not very stable, it is usual to prepare the two component solutions separately and to mix them only when required for use Two experiments can now be carried out with the Fehling's solution

(*a*) *Preparation of cuprous oxide* —1000 c c of Fehling's solution is brought to the boil and then 5 grams of glucose, dissolved in a little water, is added with stirring The precipitated cuprous oxide is filtered on a Buchner funnel, washed with boiling water and alcohol, and dried in a vacuum desiccator

(*b*) *Estimation of glucose* —A mixture of 50 c c of Fehling's solution and 100 c c of water is heated to boiling in a conical flask A solution of glucose (about 5 grams per litre) is then added from a burette until the blue colour just disappears When the end-point is nearly reached it is best to wait for a few minutes until the red cuprous oxide settles 10 c c of the above Fehling's solution = 0 05 gram glucose

Cuprous oxide is a red solid, which is found as CUPRITE or " red copper ore " It is oxidised to cupric oxide when heated in air at temperatures below 1000°, but at higher temperatures it is the more stable oxide It dissolves in concentrated hydrochloric acid, forming a soluble addition compound of cuprous chloride and hydrogen chloride, $HCuCl_2$ With dilute sulphuric acid it gives copper and cupric sulphate

$$Cu_2O + H_2SO_4 = Cu + CuSO_4 + H_2O$$

It probably behaves in the same way with dilute nitric acid, but the copper is dissolved by the acid with evolution of nitric oxide

$$3Cu_2O + 14HNO_3 = 6Cu(NO_3)_2 + 2NO + 7H_2O$$

**Cuprous chloride**, CuCl or $Cu_2Cl_2$, is prepared by heating a mixture of cupric oxide and copper turnings with concentrated hydrochloric acid

$$CuO + Cu + 2HCl = 2CuCl + H_2O$$

On pouring the solution into a large volume of water a white precipitate of cuprous chloride separates It is also precipitated by passing sulphur dioxide through a solution of copper sulphate to which common salt has been added in equivalent proportions

$$2CuSO_4 + 2NaCl + 2H_2O + SO_2 = 2CuCl + 2NaHSO_4 + H_2SO_4$$

EXPT 45 **Preparation of cuprous chloride**

Cupric oxide (20 grams) and copper turnings (40 grams) are added to concentrated hydrochloric acid (200 c c ) in a flask The mixture is heated almost to the boiling-point in a fume chamber, and at the end of half an hour a further 100 c c of concentrated hydrochloric acid is added and heating is continued until the solution is almost colourless The solution is then poured into a litre of cold distilled water, which has previously been boiled to expel all dissolved oxygen, since cuprous chloride is readily oxidised Cuprous chloride is precipitated as a white powder and is rapidly filtered off on a Buchner funnel, washed with cold boiled distilled water, and dried in a vacuum desiccator

Cuprous chloride is a white solid, consisting probably of an ionic aggregate of cuprous and chloride ions, $Cu^+Cl^-$, compare $Ag^+Cl^-$, but it is often formulated as $Cu_2Cl_2$, since its vapour density at 1700° is only a little less than that calculated for this formula It is almost insoluble in water, but dissolves in concentrated hydrochloric acid, forming the complex **acid**, $HCuCl_2$, and in ammonia, forming the **ammine**, $CuCl,NH_3$ Both solutions are used for the absorption of carbon monoxide in gas-analysis, when the **carbonyl compound**, $CuCl,CO,2H_2O$, separates in

colourless crystals On exposure to the air cuprous chloride (which is colourless) is gradually converted into a green **basic cupric chloride**, $3CuO,CuCl_2,3H_2O$

**Cuprous iodide**, CuI, is precipitated as a white powder when potassium iodide is added to a solution of a cupric salt, since cupric iodide is unstable and decomposes into iodine and cuprous iodide

$$2CuSO_4 + 4KI = 2CuI + I_2 + 2K_2SO_4$$

This reaction takes place quantitatively in the absence of mineral acids and is used in the volumetric estimation of copper, the iodine set free being titrated with sodium thiosulphate (p 424) When preparing cuprous iodide, the free iodine is reduced by addition of sulphurous acid (p 254), so that the whole of the iodine is precipitated according to the equation

$$2CuSO_4 + 2KI + SO_2 + 2H_2O = 2CuI + 2KHSO_4 + H_2SO_4$$

**Cuprous cyanide**, CuCN, is formed (in a similar manner to cuprous iodide) by the addition of potassium cyanide to a cupric solution

$$2CuSO_4 + 4KCN = 2CuCN + C_2N_2 + 2K_2SO_4$$

It is a white solid which is insoluble in water but dissolves in excess of potassium cyanide, forming a stable **potassium cuprocyanide**, $KCuC_2N_2$, which does not give the ionic reactions of copper (cf the separation of copper from cadmium, p 401)

**Cuprous acetylide**, $Cu_2C_2$, is formed as a chocolate-brown powder when acetylene is passed into an ammoniacal solution of cuprous chloride In the dry state it is liable to explode, but it is quite safe when moist

**Cuprous sulphide**, $Cu_2S$, occurs naturally as COPPER GLANCE, and in combination with ferric sulphide as COPPER PYRITES, $CuFeS_2$ It is formed by reducing cupric sulphide, CuS, in a current of hydrogen, or by heating copper strongly with excess of sulphur in a crucible with a lid, when any cupric sulphide which may be formed simultaneously is decomposed by the high temperature

**Cuprous sulphate**, $Cu_2SO_4$, is formed in small quantities when copper is left in contact with a solution of copper sulphate It can be prepared by heating together molecular proportions of cuprous oxide and dimethyl sulphate, $(CH_3)_2SO_4$ (p 727), in the absence of moisture

$$(CH_3)_2SO_4 + Cu_2O = Cu_2SO_4 + (CH_3)_2O$$

It is a light grey powder which is instantly decomposed by water into copper and cupric sulphate

$$Cu_2SO_4 \xrightarrow{\text{water}} CuSO_4\ aq + Cu$$

## CUPRIC COMPOUNDS

**Cupric oxide**, CuO, can be prepared by heating the hydroxide, carbonate or nitrate, or by heating copper in air or oxygen at moderate temperatures, but when heated strongly it dissociates into cuprous oxide and oxygen

$$4CuO \rightleftharpoons 2Cu_2O + O_2$$

In a vacuum, this dissociation begins at about 350°, the oxide therefore parts with oxygen very readily, and is commonly used to oxidise organic compounds in the combustion furnace, when the oxide is reduced to metal, whilst the organic compound is burnt to water and carbon dioxide

**Cupric hydroxide**, $Cu(OH)_2$, is obtained as a light blue precipitate by adding sodium hydroxide or ammonia to a cold solution of a cupric salt, it does not dissolve in excess of sodium hydroxide (cf Ni and Zn) but dissolves in excess of ammonia, like nickel and zinc hydroxides, forming a deep blue solution of **tetrammine cupric hydroxide** $[Cu\ 4NH_3](OH)_2$ If warmed during precipitation, a black substance, having the composition $Cu(OH)_2,3CuO$ (not CuO), is produced, which is the parent of a series of crystalline BASIC SALTS such as **basic cupric chloride**, $3CuO,CuCl_2,3H_2O$

**Cupric carbonate**, $CuCO_3$, is not known in a pure state, but the **basic carbonate**, $CuCO_3,Cu(OH)_2$, occurs as MALACHITE, and a double carbonate can be prepared by adding a concentrated solution of potassium carbonate to a concentrated solution of copper sulphate A green basic carbonate separates, but this dissolves again, and the blue solution then slowly deposits **potassium copper carbonate**, $K_2CO_3,CuCO_3$

**Cupric chloride**, $CuCl_2$, is formed as a brown powder when copper is burnt in excess of chlorine The product is allowed to cool in chlorine because it dissociates into cuprous chloride and chlorine at temperatures above 400°

$$2CuCl_2 \rightleftharpoons 2CuCl + Cl_2$$

The chloride may also be prepared by dissolving the oxide or basic carbonate in dilute hydrochloric acid and evaporating, when green crystals of the **dihydrate**, $CuCl_2,2H_2O$, separate out Concentrated solutions of cupric chloride are brown in colour, but on dilution turn green and then blue The green solution is turned brown by the addition of concentrated hydrochloric acid or potassium chloride These changes of colour, which provide a striking contrast to the blue colour of the hydrated cupric ion, have been attributed to the formation of complexes such as $Cu[CuCl_4]$, $HCuCl_3$, etc

**Cupric bromide**, $CuBr_2$, is black, but forms a green **hydrate**, $CuBr_2$, $4H_2O$, in solution it shows the same colour changes as the chloride

**Cupric iodide** is unstable in the free state, but forms a blue **tetrammine**, $CuI_2,4NH_3,H_2O$

**Cupric cyanide**, $CuC_2N_2$, is formed as a yellow precipitate when potassium cyanide is added to a cold solution of copper sulphate, but it is extremely unstable and readily decomposes into cuprous cyanide and free cyanogen The yellow precipitate dissolves in excess of potassium cyanide to form **potassium cupricyanide**, $K_2Cu(CN)_4$, cf $K_2Ni(CN)_4$ and $K_2Zn(CN)_4$

**Cupric sulphide**, CuS, is obtained as a black precipitate when hydrogen sulphide is passed into a solution of a cupric salt It is insoluble in dilute hydrochloric acid and in yellow ammonium sulphide

**Cupric sulphate**, $CuSO_4,5H_2O$, or BLUE VITRIOL, is the most widely used salt of copper Large quantities of it are obtained as a by-product in the Mond nickel process (p 344) It is also prepared by spraying dilute sulphuric acid on to copper scrap or turnings in a lead-lined tower, whilst

a current of air is pumped in at the base to meet the descending stream of acid, the copper dissolves, and the solution is circulated until a sufficient concentration of sulphate is obtained

$$2Cu + 2H_2SO_4 + O_2 = 2CuSO_4 + 2H_2O$$

The blue **pentahydrate**, $CuSO_4,5H_2O$, loses four molecules of water when heated at 100° and forms the **monohydrate**, $CuSO_4,H_2O$ When heated to about 250° it yields the anhydrous salt, this is colourless and is used as a test for water, which converts it quickly into the blue pentahydrate

Commercial copper sulphate contains isomorphous ferrous sulphate, owing to the presence of iron in the original copper ore It can be purified by recrystallising from water in the presence of a little nitric acid, when the iron is oxidised to ferric sulphate, which is not isomorphous with copper sulphate, and therefore remains in solution Solutions of copper sulphate, containing only small amounts of ferrous sulphate, give mixed crystals of the **pentahydrate**, $[Cu,Fe]SO_4,5H_2O$, but if the iron predominates, crystals of the mixed **heptahydrate**, $[Fe,Cu]SO_4,7H_2O$, are formed, although the heptahydrate of copper sulphate is not known in the free state The **double sulphate**, $(NH_4)_2SO_4,CuSO_4,6H_2O$, is prepared by dissolving an equimolecular mixture of ammonium and copper sulphates in hot water and putting aside to crystallise

Copper sulphate is used in copper plating, in dyeing and in calico printing, and for preserving wood and hides It is also used as a germicide and fungicide in agriculture, *e g* potatoes and vines are sprayed with BORDEAUX MIXTURE (copper sulphate and lime stirred up with water)

**Cuprammonium compounds** —Many copper compounds combine with ammonia to form AMMINES Some of these, such as $CuCl_2,2NH_3$, resemble the ammonia compounds of mercury, silver and gold, whilst others, *e g* $[Cu\ \ 4NH_3](OH)_2$ and $[Cu\ \ 4NH_3]SO_4$, are similar to those of zinc and nickel Cuprammonium solutions dissolve cellulose, *e g* in the form of paper-pulp or cotton-wool, if this solution is then squirted into dilute acid, a thread of amorphous cellulose is produced, which is a variety of artificial silk

EXPT 46 **Preparation of cuprammonium sulphate**

Dissolve not more than 60 grams of copper sulphate in 200 c c of hot water in a beaker When cold, add concentrated ammonia until the precipitate of cupric hydroxide just dissolves, then float a filter paper, which just fits the beaker, on the top of this solution Add a thin layer (about ½″) of pure water above the paper by means of a pipette and then a layer (about 2″) of methylated spirits If the beaker is put away in a cupboard for a few days beautiful deep blue crystals of cuprammonium sulphate separate from the solution

**Estimation of copper** —Copper is estimated gravimetrically as the oxide, CuO, sulphide, $Cu_2S$, or metal (p 441), and volumetrically by means of the reaction between a cupric salt and potassium iodide (p 424)

## 47 SILVER Ag = 107 88

**Occurrence.**—Large quantities of native silver are obtained in the neighbourhood of the town of Cobalt in Ontario, from a vein of quartz heavily charged with the metal The most important ores are SILVER GLANCE, $Ag_2S$ (isomorphous with PbS), SILVER COPPER GLANCE, $[CuAg]_2S$ (isomorphous with $Cu_2S$), RUBY SILVER ORE, $Ag_3SbS_3$, and HORN SILVER, AgCl

**Preparation of metallic silver.**—The various processes by which silver is extracted from its ores may be considered under the following headings

(1) Lead processes
(2) Amalgamation processes
(3) Wet processes
(4) Electrolytic process

**Lead processes** —Galena, PbS, which is the principal source of lead, often contains appreciable amounts of silver sulphide, $Ag_2S$, as an isomorphous impurity When smelted, either alone or with added silver ore, it yields an argentiferous lead The silver which it contains is concentrated by Pattinson's, Rozan's or Parkes' processes, and the lead is then removed as oxide by " cupellation "

(*a*) *Pattinson's process* depends on the fact that argentiferous lead deposits crystals of pure lead, provided that the concentration of silver is less than that of the eutectic mixture, which contains 2% Ag (Fig 89)

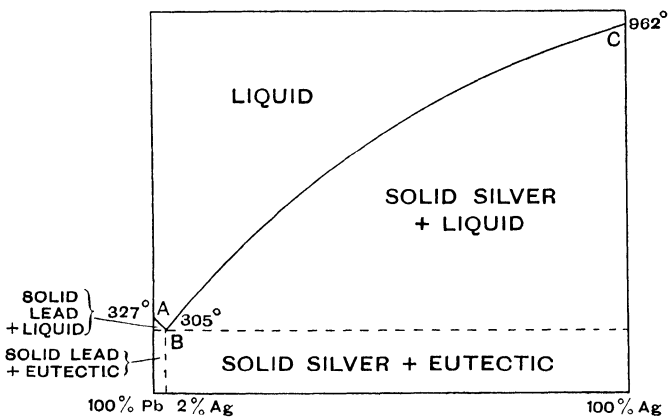



FIG 89 FREEZING-POINT DIAGRAM FOR LEAD AND SILVER

The argentiferous lead is therefore concentrated by removing in a perforated ladle the crystals of lead which first separate Since these cannot be separated completely from adhering liquid, the fractional crystallisation is repeated until the crystals contain about 0 001% Ag, whilst the concentrate contains about 1% Ag For this purpose a ring of

iron pots is used The crystals of lead are passed in one direction for remelting and recrystallisation, while the enriched argentiferous lead is left behind, and ultimately removed for cupellation

(*b*) In the *Luce Rozan process* the lead is crystallised out by blowing steam through the molten mass, whilst cold water is sprayed on the surface Only two pots are used, but the steam blast keeps the temperature much more uniform, so that the enriched silver lead alloy contains as much as 2% of silver before cupellation

(*c*) *Parkes' process* depends on the fact that silver can be extracted from lead by the addition of zinc These two metals float one upon the other, the composition of the two layers at 800° being as follows

| | | |
|---|---|---|
| Upper layer - - | Zn = 98 86 | Pb = 1 14% |
| Lower layer - - | Pb = 98 70 | Zn = 1 30% |

Any silver which may be present distributes itself in a fixed ratio between these, the concentration of silver in the upper layer of zinc being about 300 times as great as in the lower layer of lead Thus, if a ton of lead were stirred up with half a hundredweight of zinc, the zinc would take up about seven-eighths of the silver from the lead

In practice only 1% of zinc is used at a time Compounds of silver and zinc, *e g* AgZn, which melt at a higher temperature than zinc itself, then crystallise out and are skimmed off with a perforated ladle The operation is repeated until the lead contains only about 0 0005% of silver The zinc in the skimmings is removed by distillation in a retort (with a little charcoal to reduce any zinc oxide which may have been formed), leaving a residue containing about 10% Ag and 90% Pb, which is separated by cupellation The desilvered lead is freed from zinc by blowing steam through it, when the zinc is converted into oxide, which rises to the surface as a scum Parkes' process is used now in preference to Pattinson's process since it is easier to operate and gives a lead with less residual silver

(*d*) *Cupellation* —The argentiferous lead is placed in a cupel and heated in a blast of air, when the lead is oxidised to molten litharge, PbO, which is blown away by the blast, leaving a bright residue of molten silver

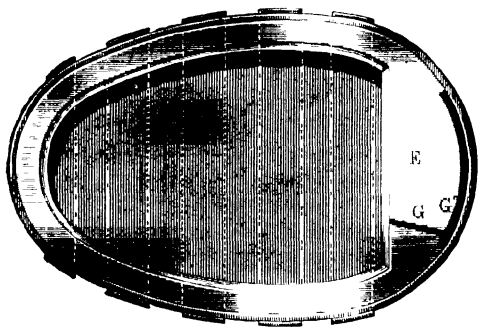



FIG 90 CUPEL

The cupel (Fig 90) is a flat dish of marl and bone ash or of Portland cement, supported in an iron framework It is heated in a reverberatory

furnace arranged so that the litharge can be blown away from the surface of the molten metal and drawn off through the groove, *GG'* Fresh argentiferous lead is added from time to time until sufficient silver has collected in the cupel The metal (99 7-99 8% Ag) remaining in the cupel is refined by cupellation at a higher temperature, when the last traces of copper, lead, and bismuth are oxidised and a FINE METAL containing 99 9% or more of pure silver is produced The traces of gold which remain in the fine silver can be recovered by electrolysis, when the gold remains behind as an anode slime

**Amalgamation processes.**—The Mexican process for extracting silver from its ores dates back to 1557, and was of special value in localities where fuel and water were scarce

The wet ore (containing silver sulphide, silver chloride and free silver) was crushed, mixed with about 5% of salt, and thoroughly incorporated by the treading of mules on a circular paved floor, with successive additions of mercury and of weathered pyrites containing copper and ferric sulphates. The sulphur was eliminated as copper sulphide and the chlorine as mercurous chloride, as represented by the following equations

$$CuSO_4 + 2NaCl = CuCl_2 + Na_2SO_4,$$
$$CuCl_2 + Ag_2S = 2AgCl^* + CuS,$$
$$2AgCl^* + 2Hg = Hg_2Cl_2 + 2Ag$$

The silver amalgam was separated and distilled to recover the mercury The residue of crude silver was refined by cupellation

**Wet processes.**—In the cyanide process, the ore is finely ground in ball mills and extracted with a dilute solution of sodium cyanide, the sludge being agitated by a stream of air The silver sulphide dissolves as sodium argentocyanide and the sodium sulphide, which tends to reverse the reaction, is oxidised by the stream of air to thiosulphate and sulphur The argentocyanide solution is filtered from the sludge and the silver precipitated by the addition of zinc or aluminium

$$Ag_2S + 4NaCN \rightleftharpoons 2NaAgC_2N_2 + Na_2S,$$
$$2NaAgC_2N_2 + Zn = 2NaCN + ZnC_2N_2 + 2Ag$$

**Electrolytic processes.**—Large quantities of silver are recovered from the anode slime formed in the electrolytic refining of copper. The " slime " is melted into ingots, from which the silver is dissolved out by sulphuric acid, leaving a residue of gold Metallic silver is then recovered from the sulphate by precipitation with copper or iron

**Properties and uses of silver.**—Silver has a density of 10 5 and melts at 960° It is very tough, malleable and ductile (1 gram can be drawn out to a length of over a mile); and it is the best of all metals as a conductor of heat and electricity. The metal is used extensively in coins and in jewellery Until 1919, British coinage contained 92 5% Ag, 7 5% Cu, the copper being added to increase the strength and toughness of the metal, and thus to improve the wear of the coins, but the standard has

* Dissolved in the aqueous salt solution

now been lowered to 50% Ag Silver salts are used in photography and in medicine

**Chemical properties of silver.**—(*a*) Silver melts without tarnishing when heated in air, but dissolves more than twenty times its own volume of oxygen This is expelled on cooling, probably because silver oxide, dissolved in the molten metal, is decomposed when thrown out of solution as the silver crystallises This explanation of the " spitting " of silver is supported by the fact that silver which has dissolved oxygen freezes 5° below the normal freezing-point

(*b*) The tarnishing of silver on exposure to air is due to the action of hydrogen sulphide, which forms the black sulphide, $Ag_2S$ , the tarnishing can be checked by alloying the metal with cadmium The metal is also attacked by chlorine, bromine and iodine, especially at temperatures above the melting-point of the product

(*c*) Silver is not acted on by dilute hydrochloric or sulphuric acids, since it is less electropositive than hydrogen , but it dissolves readily in hot concentrated sulphuric acid and in dilute nitric acid, with evolution of sulphur dioxide and oxides of nitrogen respectively

$$2Ag + 2H_2SO_4 = Ag_2SO_4 + SO_2 + 2H_2O$$

Hot strong hydrochloric acid slowly attacks silver, forming silver chloride, which is soluble in the strong acid , silver can also be converted into the chloride by heating in a current of hydrogen chloride The former action may depend (as in the case of copper) on the formation of a compound of the acid with the chloride , in the latter action, the metal is perhaps attacked by traces of chlorine, formed by dissociation of hydrogen chloride (p 270).

**Silverplating.**—(*a*) *Electroplating* —SHEFFIELD PLATE was made by welding together copper and silver and rolling the composite metal into sheets so as to produce a silver surface on a copper base , but this process has been replaced by the more economical operation of ELECTROPLATING The silver deposited from silver nitrate is too granular to be of any value, but a coherent film of silver can be deposited from a solution of **potassium argentocyanide**, $KAgC_2N_2$, prepared by adding an excess of potassium cyanide to a solution of silver nitrate

$$AgNO_3 + 2KCN = KAgC_2N_2 + KNO_3$$

The solution contains potassium ions, $K^+$, cyanide ions, $CN^-$, argentocyanide ions, $AgC_2N_2^-$ and a trace of ordinary silver ions produced by the dissociation of the complex ion

$$KAgC_2N_2 \rightleftharpoons K^+ + AgC_2N_2^- \rightleftharpoons K^+ + Ag^+ + 2CN^-$$

In order to carry out the process of electroplating, the article to be plated is made the cathode in a bath of the above solution, whilst silver plates or pieces of scrap silver are used as the anode On passing a current, silver ions are deposited at the cathode, whilst the cyanide ions attack the silver anode to form silver cyanide This dissolves in the excess of potassium cyanide, so that the strength of the plating bath is maintained

(*b*) *Silver mirrors* —Ammoniacal solutions of silver nitrate, containing silver oxide dissolved in an excess of ammonia, are able to oxidise many organic compounds, *e g* tartaric acid (as ammonium tartrate) and the sugars In this process the silver oxide is reduced to silver, and if the action takes place in a glass vessel a brilliant mirror of metallic silver may be produced

(*c*) *Oxidised silver* —" Oxidised " silver articles, which have a pleasant greyish appearance and do not tarnish in impure air, are prepared by dipping in a solution of an alkali sulphide, when a thin but very coherent film of silver sulphide is produced on the surface of the metal

## Compounds of Silver

**Univalent and bivalent salts** —Silver forms a series of univalent salts, many of which are insoluble in water and are therefore used for the detection of acid radicals in qualitative analysis In this respect silver stands at the opposite extreme to sodium and potassium, the salts of which are almost all freely soluble in water Bivalent compounds, corresponding with the cupric salts, can only be prepared by special methods, *e g* by electrolytic oxidation of silver nitrate in an anode compartment in presence of a nitrogenous base, such as pyridine The orange-red pyridine compound of **argentic nitrate**, $[Ag\ 4C_5H_5N](NO_3)_2$, is an oxidising agent, which liberates iodine from potassium iodide and oxidises chromium and manganese salts to chromates and permanganates

**Silver oxide**, $Ag_2O$, separates as a blackish-brown precipitate when a caustic alkali is added to aqueous silver nitrate, but is generally contaminated with silver carbonate The oxide decomposes when heated at 300°, and has been used as a source of pure oxygen, after mixing with a little caustic alkali to retain carbon dioxide

Silver oxide is only very slightly soluble in water, but the moist oxide has an alkaline reaction and behaves like **silver hydroxide**, AgOH, *e g* in replacing chlorine by hydroxyl in organic compounds (p 762) It dissolves in excess of ammonia to give a solution which on exposure to air deposits a black explosive compound called FULMINATING SILVER, $Ag_3N$

**Silver carbonate**, $Ag_2CO_3$, is a light yellow powder which is precipitated on mixing solutions of silver nitrate and an alkali carbonate in equivalent quantities With excess of potassium carbonate a white precipitate of the **double carbonate**, $K_2CO_3,Ag_2CO_3$, is formed

**Silver chloride**, AgCl, occurs naturally as HORN SILVER It is formed when chlorine is passed over silver at a dull red heat, or as a white curdy precipitate when a chloride is added to a solution of silver nitrate The precipitate is insoluble in dilute acids but soluble in ammonia, probably owing to the formation of an **ammine**, $2AgCl,3NH_3$, which can be crystallised out by slow evaporation Silver chloride also dissolves in solutions of sodium thiosulphate and of potassium cyanide

$$AgCl + Na_2S_2O_3 = NaAgS_2O_3 + NaCl.$$
$$AgCl + 2NaCN = NaAg(CN)_2 + NaCl$$

Silver chloride darkens on exposure to light, and on account of this

property (which it shares with the bromide and iodide) it is used in photography (see below)

**Silver bromide**, AgBr, resembles the chloride, but is less soluble in water and in aqueous ammonia, and is even more sensitive to light

**Silver iodide**, AgI, is obtained as a pale yellow precipitate by adding a soluble iodide to a solution of silver nitrate It is almost insoluble in ammonia, but dissolves in concentrated solutions of potassium iodide

**Silver fluoride**, AgF, differs from the other halides in being readily soluble in cold water, it is hygroscopic and absorbs 800 times its own volume of ammonia

**Silver thiosulphate**, $Ag_2S_2O_3$, is precipitated on adding sodium thiosulphate to a solution of silver nitrate, it decomposes readily into the sulphide

$$Ag_2S_2O_3 + H_2O = Ag_2S + H_2SO_4$$

With excess of thiosulphate, soluble **sodium silver thiosulphate**, $NaAgS_2O_3$, is formed

**Silver sulphate**, $Ag_2SO_4$, is formed by heating the finely-divided metal with concentrated sulphuric acid It is sparingly soluble in water, but dissolves readily in ammonia, forming the **ammine**, $Ag_2SO_4,2NH_3$ (cf copper)

**Silver nitrate**, $AgNO_3$, has been known since the earliest period of alchemy under the name of LUNAR CAUSTIC It is prepared by dissolving the metal in dilute nitric acid and concentrating the solution until crystallisation occurs It forms large, transparent, anhydrous plates, melts at a relatively low temperature (217°), and can easily be cast into sticks, in this form it is employed in surgery as a caustic It dissolves in less than an equal weight of water at 0°, and in one-ninth of its weight of water at 100° If excess of ammonia be added to a solution of silver nitrate and the solution evaporated, crystals of the **ammine**, $AgNO_3,2NH_3$, separate

Silver nitrate is used largely for the preparation of silver halides in photography, and to a lesser degree as a caustic

**Estimation of silver**—Silver may be estimated gravimetrically as the chloride (p 438) and volumetrically by titration with standard solutions of sodium chloride or ammonium thiocyanate as described in Chapter XXX.

## PHOTOGRAPHY

**Photography.**—The sensitivity to light of certain metallic salts, notably the halides of silver, has been utilised in photography The ordinary photographic film contains a suspension of **silver bromide** in gelatin When an image of an object is thrown on to this film by the lens of a camera, a "LATENT IMAGE" is produced, probably by the reduction to metallic silver of those silver ions on which the light falls The latent image is made visible by DEVELOPMENT, *i e* by immersing the exposed film in a solution of a reducing agent, such as **potassium ferrous oxalate**, which is capable of reducing silver bromide to metallic silver, but which

does so preferentially where the granules of silver bromide already carry a nucleus of metallic silver

$$K_2Fe(C_2O_4)_2 + AgBr = KFe^{\cdots}(C_2O_4)_2 + Ag + KBr.$$

The NEGATIVE thus produced inverts the light and dark portions of the original image It is made permanent and stable to light by FIXING, *i e* by dissolving the unchanged silver bromide in a bath of sodium thiosulphate or " hypo "

$$AgBr + Na_2S_2O_3 = NaBr + NaAgS_2O_3.$$

A POSITIVE print is obtained by prolonged exposure through the negative of a PRINTING PAPER, covered with an emulsion in gelatin of **silver chloride**, sensitised with **silver citrate** to facilitate the reduction of the chloride The print is fixed by thiosulphate, washed from adhering salts and dried Alternatively, the printing paper may be over-exposed and then TONED by immersion in a solution of **potassium aurichloride** (brown tone), or **potassium platinochloride** (grey tone), when some of the silver is replaced by gold or platinum

$$3Ag + KAuCl_4 = Au + KCl + 3AgCl,$$
$$2Ag + K_2PtCl_4 = Pt + 2AgCl + 2KCl$$

" Gas-light paper " contains **silver bromide** instead of silver chloride, the print is obtained by a very short exposure to light, followed by development and fixing, exactly as in the case of the negative

An ordinary negative does not give a faithful reproduction of light intensities, since silver halides are more sensitive to blue than to red light This fault is avoided by impregnating the gelatin with certain dyes, which increase the sensitiveness of the film to red light and thus make the plate " panchromatic "

## 79 GOLD Au = 197 2

**History.**—Gold has been known and valued since prehistoric times Egyptian rock carvings, dating from about 2500 B C , show the preparation of gold by the washing of auriferous sands and the subsequent purification of the metal by smelting The Legend of the Golden Fleece possibly had its origin in the use of sheep-skins to retain the heavy gold particles when auriferous sands were washed in running water

**Occurrence.**—Gold is nearly always found in the metallic form as NATIVE GOLD, but contains from 0 4 to 35% of silver Conversely, gold often occurs as an impurity in other metals and is a profitable by-product in the refining of lead, copper and silver In the Transvaal and elsewhere native gold is found in veins or reefs of quartz, the particles being so small as to be invisible to the eye The disintegration of these rocks gives rise to " alluvial gold " in the sand or gravel of river-beds, as in California The proportion of gold in the ore varies from about 1 part in 50,000 in gold quartz to 1 part in 1 to 15 millions in alluvium, but nuggets of gold, formed by the segregation and welding together of gold-particles in the river-beds, have been found, especially in Australia, weighing from a few ounces to 184 lb

**Extraction of Gold.**—(*a*) *Washing and amalgamation*—The coarse particles of alluvial gold (which are larger than the particles in the original rock) can be separated by taking advantage of its high density, varying from 19 to 17 according to the proportion of silver which it contains, as compared with the low density, about 2·7, of the sand or gravel with which it is mixed For this purpose the material is washed in a "pan" or "cradle," consisting of an inclined trough mounted on rockers, the trough being furnished with bars of wood to hold back the particles of gold as they settle out from the sand or gravel Finer particles may be retained by making use of mercury, which forms an AMALGAM from which the gold can be recovered by distilling off the mercury

(*b*) *Cyanide process*—The gold in quartz rock, which is too fine to be separated by washing, is dissolved in a dilute (0 35%) solution of potassium or sodium cyanide in presence of atmospheric oxygen

$$4Au + 8KCN + O_2 + 2H_2O = 4KAu(CN)_2 + 4KOH.$$

The metal is precipitated by passing the solution of potassium aurocyanide through wooden boxes containing zinc turnings

$$2KAu(CN)_2 + Zn = K_2Zn(CN)_4 + 2Au$$

The surplus zinc is removed with dilute sulphuric acid and the precipitated gold is then washed, dried, and melted with a flux,to give a product containing 85 to 90% Au Alternatively, the gold may be deposited from the cyanide solution by electrolysis, with an iron anode and lead cathode, when the gold is deposited on the cathode and separated from the lead by cupellation

**Refining of Gold.**—The gold extracted by the above processes is accompanied by silver, which can be separated by three processes as follows

(*a*) *Parting by chlorine*—The bullion is melted in a crucible and chlorine is forced through it Silver chloride is formed and floats to the surface, and traces of other metals (such as zinc, mercury, bismuth and arsenic) are volatilised as chlorides, whilst the gold is unaffected, since its chlorides decompose when heated

(*b*) *Parting by acids*—If the proportion of gold does not exceed one-third, the silver may be dissolved out by concentrated nitric or sulphuric acids, and the residual gold washed and melted into an ingot If necessary, silver is added to the bullion to reduce the content of gold to one-third

(*c*) *Electrolytic refining*—Gold and silver are left behind in the anode slime in the electrolytic refining of copper They can be separated by electrolysis of the crude silver in a solution of silver nitrate, when the gold is left behind in the anode slime Finally, gold itself may be refined by electrolysis in a hot solution of auric chloride, made strongly acid with hydrochloric acid and containing a little sulphuric acid to precipitate lead as sulphate The silver and lead are converted into a slime of AgCl and $PbSO_4$, whilst the gold is deposited in a pure state at the cathode, leaving behind in solution any platinum which may be present

**Properties of gold.**—(*a*) *Physical properties* —The physical and chemical properties of gold are related most closely to those of platinum, the metal which immediately precedes it in the periodic classification of the elements, its relation to mercury is much less obvious It is a bright yellow lustrous metal which has a density of 19 3, as compared with 21 4 for platinum It melts at 1063°, and this temperature is so well defined that it is used as a " fixed point " for standardising pyrometers. Gold is very malleable and ductile, it can be beaten out into leaf of a thickness of 0·0001 mm and 1 gram of the metal can be drawn out into 3240 metres of wire After silver and copper, gold is the best conductor among metals of heat and electricity.

(*b*) *Alloys of gold* —Pure gold is too soft to be used in coinage, in English coins an alloy of 22 parts of gold and 2 parts of copper, known as 22 carat gold, is used In Australian coinage, silver takes the place of copper and the metal is of a pale yellow colour.

(*c*) *Colloidal gold* —A *red* suspension of colloidal gold is obtained by reducing a dilute solution of a gold salt with formaldehyde, on adding alcohol the gold is precipitated in a form which disperses again in water A *blue* colloidal suspension is obtained when hydrazine hydrate is used as the reducing agent. The colour of these colloidal suspensions depends upon the size of the particles of gold When a mixture of stannous and stannic chlorides is added drop by drop to a solution of a gold salt, a *purple* precipitate is obtained, which is known as PURPLE OF CASSIUS, and probably consists of stannic hydroxide and colloidal gold

(*d*) *Chemical properties of gold* —Like platinum, gold is insoluble in nitric and sulphuric acids, but is dissolved by chlorinating agents, such as aqua regia

$$Au + 4HCl + HNO_3 = HAuCl_4 + NO + 2H_2O,$$
$$3Pt + 18HCl + 4HNO_3 = 3H_2PtCl_6 + 4NO + 8H_2O.$$

The products are not simple chlorides, but chloro-acids from which salts such as $NaAuCl_4$ and $K_2PtCl_6$ can be derived

Gold is not affected by oxygen, sulphur or water, nor by fusion with potassium chlorate, but is attacked by fused alkalis or nitrates It is attacked rapidly by chlorine and by bromine at atmospheric temperatures, and is dissolved by an aqueous solution of potassium or sodium cyanide in presence of air Like platinum, it forms two series of compounds, namely univalent AUROUS COMPOUNDS of the type, AuCl, and tervalent AURIC COMPOUNDS of the type, $AuCl_3$, these chlorides differ in valency from platinous and platinic chlorides, $PtCl_2$ and $PtCl_4$, but resemble them in being easily decomposed by heat, with separation of the free metal

**Compounds of gold.**—**Aurous oxide,** $Au_2O$, is prepared by drying at 100° the **hydroxide,** AuOH, formed by the action of an alkali on a soluble aurous salt. It decomposes at 250° into gold and oxygen and when acted on by hydrochloric acid it gives gold and auric chloride:

$$3Au_2O + 6HCl = 2AuCl_3 + 4Au + 3H_2O.$$

**Aurous chloride,** AuCl, is formed by heating auric chloride, $AuCl_3$, at 180°; it is insoluble in cold water and is decomposed by hot water, forming

soluble auric chloride and gold **Auric chloride,** $AuCl_3$, is obtained by the action of chlorine on gold at room temperature, or of liquid chlorine in a sealed tube at 100° It is soluble in water, from which it separates as the **dihydrate,** $AuCl_3,2H_2O$, but it can be dehydrated by drying at 150° It also combines with hydrochloric acid to form yellow needles of **aurichloric acid,** $HAuCl_4,4H_2O$, from which salts such as **potassium aurichloride,** $KAuCl_4$ (cf $K_2PtCl_6$), can be prepared

## 78 PLATINUM Pt=195 23

**Occurrence and uses.**—Platinum is found in the native state, *e g* in the Ural mountains It is a grey-white noble metal, of density 21 4, and melts at 1755° It is therefore used as a refractory metal in the form of wire or foil, and for making crucibles, etc , for use in chemical operations at high temperatures Finely-divided platinum, precipitated in the form of PLATINUM BLACK or SPONGY PLATINUM, absorbs both hydrogen and oxygen, and is used as a catalyst to ignite hydrogen or coal-gas When precipitated on asbestos or on magnesium sulphate it is used as a catalyst to promote the combination of sulphur dioxide and oxygen (p 259), whilst platinum gauze is used to promote the oxidation of ammonia to oxides of nitrogen (p 196)

**Chemical properties** —Platinum (like gold) is not oxidised in air, but is attacked by chlorine It is insoluble in dilute acids but dissolves in aqua regia It forms bivalent PLATINOUS COMPOUNDS and quadrivalent PLATINIC COMPOUNDS

**Platinous chloride,** $PtCl_2$, is formed by the action of chlorine on spongy platinum at 250°, or by heating chloroplatinic acid at 300°

$$Pt + Cl_2 = PtCl_2 \qquad H_2PtCl_6 = PtCl_2 + 2HCl + Cl_2$$

It forms a series of CHLOROPLATINITES or PLATINOCHLORIDES, *e g* **potassium platinochloride,** $K_2PtCl_4$ **Chloroplatinic acid,** $H_2PtCl_6$, formed by the action of aqua regia on platinum, yields **platinic chloride,** $PtCl_4$, when heated in hydrogen chloride at 165°, or in chlorine at 369°

$$H_2PtCl_6 = PtCl_4 + 2HCl$$

**Sodium platinichloride,** $Na_2PtCl_6$, is soluble in water, but **ammonium platinichloride,** $(NH_4)_2PtCl_6$, and **potassium platinichloride,** $K_2PtCl_6$, are precipitated on adding platinic chloride to solutions of ammonium and potassium salts

# CHAPTER XXIV

## THE MERCURY GROUP

| | | |
|---|---|---|
| 30 | ZINC | Zn = 65 38 |
| 48 | CADMIUM | Cd = 112 41 |
| 80 | MERCURY | Hg = 200 61. |

**Classification.**—(*a*) The three elements

*zinc*, *cadmium*, *mercury*,

follow the coinage metals,

*copper*, *silver*, *gold*,

and form a similar group of transition-elements They are *bivalent metals*, since they contain two electrons in an outer shell, like the alkaline earths , moreover, like the alkaline earths, they have no tendency to assume a higher electrovalency, since the removal of these outer electrons discloses a series of complete groups or sub-groups of electrons, as shown in the following scheme

| | *K L M N O P* | ++ *K L M N O* |
|---|---|---|
| Zn | $Z = 30 = 2 + 8 + 18 + 2$ | $Zn^{++}$ $2 + 8 + 18$ |
| Cd | $Z = 48 = 2 + 8 + 18 + 18 + 2$ | $Cd^{++}$ $2 + 8 + 18 + 18$ |
| Hg | $Z = 80 = 2 + 8 + 18 + 32 + 18 + 2$ | $Hg^{++}$ $2 + 8 + 18 + 32 + 18$ |

The three metals are therefore predominantly bivalent, and except in the case of mercury (the univalency of which is open to question, see p 331) they exhibit only in a secondary degree the property of *variable valency*, which is so marked a characteristic of the transition-elements as a whole They are in fact the last members of the transition series of the three long periods, and differ from the bivalent elements of the typical series only in that the outer shell of the bivalent ions contains 18 instead of 8 electrons

(*b*) *Magnesium and zinc* show an unusually close resemblance to one another (p 112), in spite of the fact that the former is a " typical element " and the latter a " transitional element " This resemblance may be illustrated by the similarity of zinc sulphate, $ZnSO_4,7H_2O$, to Epsom salts, $MgSO_4,7H_2O$, by the deliquescence and hydrolysis of the chlorides, etc It has, however, little or nothing to do with the periodic classification or with the electronic structure of the bivalent ions, since the principal factor appears to be the similar radii of the ions, $Mg^{++} = 0\ 78$, $Zn^{++} = 0{\cdot}83$ A U

The isomorphism of the bivalent sulphates of the transition-elements can be explained in the same way by the fact that the radii of their bivalent ions are almost constant at about 0 8 A U

(*c*) *Copper and mercury* differ widely in physical properties (mercury melts at $-39°$ and copper at 1083°), but exhibit an unexpected similarity in their behaviour towards acids, and in forming univalent and bivalent salts, as set out in the following table

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Cuprous compounds | | $Cu_2O$ | $Cu_2S$ | $Cu_2Cl_2$ | $Cu_2I_2$ | — | $Cu_2SO_4$ |
| Cupric | ,, | CuO | CuS | $CuCl_2$ | $[CuI_2]$ | $Cu(NO_3)_2$ | $CuSO_4$ |
| Mercurous | ,, | $Hg_2O$ | — | $Hg_2Cl_2$ | $Hg_2I_2$ | $Hg_2(NO_3)_2$ | $Hg_2SO_4$ |
| Mercuric | ,, | HgO | HgS | $HgCl_2$ | $HgI_2$ | $Hg(NO_3)_2$ | $HgSO_4$ |

This similarity is enhanced by the fact that cuprous chloride and mercurous chloride are insoluble in water, whereas cupric chloride and mercuric chloride are both soluble Nevertheless the resemblance in question is largely superficial, since the cuprous salts contain the *monatomic ion* $Cu^+$, whilst the mercurous salts are composed of *covalent molecules*, as in crystalline calomel, Cl – Hg – Hg – Cl, or of *diatomic ions*, $\overset{+}{Hg}—\overset{+}{Hg}$, as in aqueous solutions of mercurous nitrate Again, the cupric salts give blue or green solutions, which are good conductors of electricity, whilst solutions of mercuric salts are colourless and are often very poor conductors of electricity on account of the remarkable readiness of mercury (like hydrogen) to form covalent molecules, *e g*

$$Cl - Hg - Cl \rightleftharpoons \overset{++}{Hg} + 2\overset{-}{Cl}$$

**Physical properties** —The two most striking physical properties of the three metals are their volatility and their splendid spectra Comparative data for the physical properties of magnesium and copper are included in Table 29

TABLE 29 —PHYSICAL PROPERTIES OF THE ELEMENTS OF THE MERCURY GROUP

| | Density | Melting-point | Boiling-point |
|---|---|---|---|
| *Mg* | 1 74 | 651° | 1110° |
| Zn | 7 1 | 419° | 907° |
| Cd | 8 6 | 321° | 767° |
| Hg | 13 6 | −39° | 357° |
| *Cu* | 8 9 | 1083° | — |

**Chemical properties** —(*a*) On passing from magnesium through zinc and cadmium to mercury, there is a rapid decrease in the electropositive character of the elements Thus zinc burns in air (magnesium will also burn in steam) and dissolves readily in dilute acids, since it is more electropositive than hydrogen Cadmium also dissolves in dilute acids with the liberation of hydrogen and can be burnt to the oxide , but mercury is almost a " noble metal," since the oxide is only formed at moderate temperatures (*e g* below the boiling-point at 357°), and is

decomposed by heating to a temperature below 500° Mercury is also insoluble in dilute hydrochloric and sulphuric acids, but dissolves like copper and silver in oxidising acids such as dilute nitric and concentrated sulphuric acid

## 30 ZINC Zn = 65 37

**Occurrence.**—**Zinc sulphide** or BLENDE, ZnS, is found in mineral veins in various parts of England and Wales, and in very large quantities at Broken Hill, in Australia, where it is mixed with galena, PbS Less important ores are CALAMINE or **zinc carbonate**, $ZnCO_3$, and FRANKLINITE, $ZnFe_2O_4$

**Preparation of metallic zinc.**—The ore is roasted in order to convert sulphide or carbonate into oxide

$$ZnCO_3 = ZnO + CO_2, \quad 2ZnS + 3O_2 = 2ZnO + 2SO_2$$

The roasting of blende sets free large quantities of sulphur dioxide, which are used for the production of sulphuric acid The roasted ore is then mixed with about half its weight of powdered coke or anthracite and a

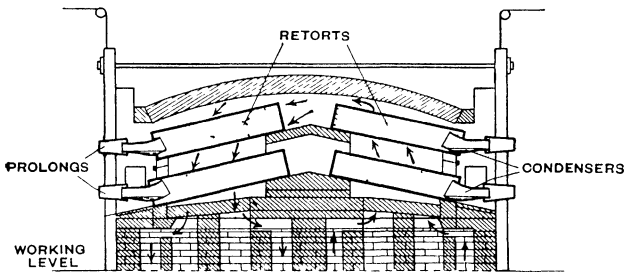



FIG 91 DISTILLATION OF ZINC

The brickwork chambers for regenerative heating of the air and gas, which extend about 15 feet below ground-level, are not shown

little salt and heated in fireclay retorts (Fig 91), when the metal distils and is collected in a clay condenser luted on to the front of the retort

$$ZnO + C = Zn + CO$$

The carbon monoxide burns at the mouth of the condenser with a flame which is coloured yellow by the slow vaporisation of salt, if the flame is coloured green by burning zinc-vapour a sheet-iron "prolong" is added to complete the condensation The temperature of distillation is about 1400° and the recovery of zinc is about 75% Any cadmium that may be present in the ore comes over with the first portions of the distillate, and most of the lead is also carried over as metal

Crude ZINC or SPELTER contains about 98% of zinc The principal impurities are lead, cadmium, iron, arsenic and carbon It is purified by remelting with a little nitre, if necessary after separating from a layer of molten lead, the nitre oxidises the lead and other impurities, which

rise to the surface as a scum Zinc can be freed from arsenic by adding sodium and heating for several hours, when the arsenide is converted into an arsenate

Very pure commercial zinc is obtained by electrolysis For this purpose, zinc sulphide is roasted in such a way as to give a maximum yield of sulphate , the remainder of the oxidised ore is then converted into sulphate by the action of sulphuric acid The solution of zinc sulphate is freed from all nobler metals, *e g* cadmium, cobalt, nickel, copper, silver, etc , by contact with zinc powder, and is then electrolysed so as to give a deposit of pure zinc (99 5% Zn) on an aluminium cathode, whilst sulphuric acid is regenerated at a lead anode

**Properties of metallic zinc** —(*a*) *Physical properties* —Zinc is a white metal, of density 7 1, as compared with 7 8 for iron , it melts at 419° and boils at 907° Commercial zinc is brittle at the temperature of the air, but malleable at about 120°, at which temperature it can be rolled into sheets and drawn into wire , at 200° it again becomes very brittle and can be powdered in a mortar Highly purified zinc, on the other hand, does not show this behaviour and is malleable at all temperatures

(*b*) *Chemical properties* —Commercial zinc dissolves rapidly in dilute acids The purity of zinc may, indeed, be gauged roughly by the rate at which it dissolves in dilute sulphuric acid, highly purified zinc hardly dissolving at all, whilst ordinary zinc rapidly liberates hydrogen

$$Zn + H_2SO_4 = ZnSO_4 + H_2$$

Zinc also dissolves in dilute hydrochloric acid, forming zinc chloride and hydrogen, whilst with dilute nitric acid it gives a mixture of nitric oxide, nitrous oxide, and ammonia, in different proportions according to the conditions

Zinc does not oxidise in purified air at atmospheric temperatures, but it is attacked slowly by moist air containing carbon dioxide, a white film of carbonate or oxide being formed It is less readily corroded than iron, since the carbon dioxide is retained and not set free again by oxidation (p 357) , zinc is therefore used to protect that metal from atmospheric corrosion or rusting GALVANISED IRON is sheet-steel coated with a thin layer of zinc by immersing it, after thoroughly cleaning its surface with dilute hydrochloric acid, in a bath of molten zinc Zinc, unlike tin, is more electropositive than iron and therefore protects the iron even when the film of metal is scratched or partly worn away

When zinc is heated strongly in air, it ignites and burns with a greenish-white flame, forming **zinc oxide**, ZnO

$$2Zn + O_2 = 2ZnO$$

It also combines directly with chlorine, forming **zinc chloride**, $ZnCl_2$ It does not combine directly with hydrogen, nitrogen, or carbon, but a **zinc nitride**, $Zn_3N_2$, corresponding with magnesium nitride, $Mg_3N_2$, has been prepared by heating zinc in a current of ammonia

$$3Zn + 2NH_3 = Zn_3N_2 + 3H_2$$

Zinc differs from magnesium, but resembles aluminium in dissolving in

solutions of alkali hydroxides, liberating hydrogen and forming a solution of an alkali zincate

$$Zn + 2NaOH = \underset{\text{Sodium zincate}}{Zn(ONa)_2} + H_2$$

(*c*) *Uses of zinc* —The principal uses of zinc are for galvanising iron and for alloying with copper to make brass (p 313) Zinc oxide is used as a paint, under the name of ZINC WHITE, and precipitated zinc sulphide, combined with precipitated barium sulphate, is used as a paint under the name of LITHOPONE (p 124) Zinc chloride is used to clean metals before soldering and in various industries

## COMPOUNDS OF ZINC.

**Zinc oxide**, ZnO, is manufactured on a large scale by distilling zinc in a current of air or steam The product is used as a paint under the name of ZINC WHITE , it has not such good " covering powers " as white lead, but is not blackened by hydrogen sulphide, since zinc sulphide is white, whereas lead sulphide is black The oxide prepared by heating the precipitated carbonate is used to prepare zinc ointment in pharmacy

**Zinc hydroxide**, $Zn(OH)_2$, is precipitated by the addition of the correct amount of alkali to a solution of a zinc salt, but is not precipitated by ammonia and ammonium chloride It is an amphoteric compound, since it dissolves in acids to form bivalent zinc salts, and in alkalis to form zincates

$$ZnSO_4 + 2NaOH = Zn(OH)_2 + Na_2SO_4$$
$$Zn(OH)_2 + 2NaOH = Na_2ZnO_2 + 2H_2O$$

The hydroxide also dissolves in ammonia to form the colourless complex, $[Zn \cdot 4NH_3](OH)_2$, compare blue, $[Cu \ 4NH_3](OH)_2$

**Zinc carbonate**, $ZnCO_3$, is formed when a solution of a zinc salt is precipitated with sodium bicarbonate, while sodium carbonate gives a basic carbonate

**Zinc chloride**, $ZnCl_2$, is prepared as a deliquescent white solid by passing chlorine or hydrochloric acid over heated zinc When a solution of zinc chloride (prepared by dissolving zinc in excess of hydrochloric acid) is evaporated, the **hydrate**, $ZnCl_2,H_2O$, crystallises out , but this cannot be converted into the anhydrous salt by heating, since hydrochloric acid is lost and a basic chloride is formed

$$ZnCl_2 + H_2O \rightleftharpoons Zn(OH)Cl + HCl$$

Zinc chloride is used as a dehydrating agent and as a catalyst in certain organic reactions (p. 724) It is applied in surgery as a caustic, and by plumbers under the name of " killed spirits " for cleaning metals before soldering, owing to the solvent action of the hydrochloric acid set free by hydrolysis.

**Zinc sulphide**, ZnS, occurs naturally as BLENDE, and can be prepared by heating sulphur and zinc filings The sulphide is a white substance which is insoluble in water and acetic acid, but soluble in dilute mineral acids In the presence of traces of certain impurities, *e g* bismuth sulphide, it becomes phosphorescent It is used as a white paint, especially in France, where paints containing lead are not allowed.

**Zinc sulphate**, $ZnSO_4$, may be prepared by dissolving zinc in dilute sulphuric acid, on evaporating, the solution deposits a **heptahydrate**, $ZnSO_4,7H_2O$ This is isomorphous with Epsom salts, $MgSO_4,7H_2O$, and forms similar double sulphates, *e g* $(NH_4)_2SO_4$, $ZnSO_4$, $6H_2O$ When heated strongly it loses sulphur dioxide and oxygen and is converted into zinc oxide

$$2ZnSO_4 = 2ZnO + 2SO_2 + O_2$$

**Estimation.**—Zinc may be estimated gravimetrically by precipitating as the carbonate and igniting to the oxide, ZnO (p 441) It may also be precipitated and weighed as the sulphide, ZnS

## 48 CADMIUM Cd = 112 41

**Occurrence.**—Cadmium accompanies zinc in its ores, in amounts varying from 1 to 5% **Cadmium sulphide,** CdS, occurs alone as the rare mineral GREENOCKITE

**Preparation.**—Cadmium is more volatile than zinc and its oxide is more readily reduced It is therefore concentrated in the dust which collects first in the condensers in the preparation of zinc This is redistilled with coal and the first portions are separated until cadmium of sufficient purity is obtained Cadmium is also separated by the action of zinc on solutions of crude zinc sulphate, when the less electropositive metals, such as cadmium, copper, lead and arsenic, are precipitated

**Properties.**—Cadmium is a white metal, which melts at 321°, boils at 767° and has a density of 8 6 In its chemical properties it resembles zinc but is less active (p 331) It also differs from zinc and resembles mercury in forming (i) univalent compounds, such as $Cd_2O$, (ii) a hydroxide which is not amphoteric, (iii) halogen salts which are not deliquescent and readily yield complex salts, (iv) a sulphate, $3CdSO_4,8H_2O$, which is not a vitriol

Cadmium is used with lead, tin and bismuth in the preparation of FUSIBLE ALLOYS (p 228), and with cadmium sulphate in the Weston Cell, which is employed as a standard of E M F

**Cadmium oxide**, CdO, is prepared like zinc oxide by burning the metal, but is brown instead of white

**Cadmium hydroxide**, $Cd(OH)_2$, is precipitated as a white powder on adding sodium or potassium hydroxide to a solution of a cadmium salt, like magnesium hydroxide, it is insoluble in alkali hydroxides, but, like zinc hydroxide, it dissolves readily in ammonium hydroxide

**Cadmium salts** are colourless and poor conductors of electricity in solution, although this is not so marked as in the case of mercury, *e g* $M/4CdCl_2$ is 25% ionised compared with 1% for $HgCl_2$ The poor conductivity of these solutions is attributed to the formation of covalent molecules as well as complex ions Thus the following equilibria occur together in solutions of cadmium chloride

$$CdCl_2 \rightleftharpoons Cd^{++} + 2Cl^-,$$
$$2Cl^- + CdCl_2 \rightleftharpoons CdCl_4^{--} \quad ,,$$

**Cadmium sulphide**, CdS, unlike zinc sulphide, is insoluble in dilute hydrochloric acid, but will dissolve in concentrated hydrochloric acid The precipitation of cadmium sulphide is therefore a reversible process

$$CdCl_2 + H_2S \rightleftharpoons CdS + 2HCl,$$

contrast

$$ZnCl_2 + H_2S \leftarrow ZnS + 2HCl,$$

and

$$HgCl_2 + H_2S \rightarrow HgS + 2HCl$$

**Cadmium sulphate** does not form a heptahydrate like zinc sulphate, $ZnSO_4,7H_2O$, but crystallises from water as $3CdSO_4,8H_2O$, whilst mercuric sulphate forms no hydrate

## 80 MERCURY Hg = 200 61

**Occurrence.**—Mercury occurs sometimes in the free state, but is nearly all extracted from **mercuric sulphide** or CINNABAR, HgS The Almaden mine in Spain, which has been worked since 415 B C , is still the chief producer

**Preparation of metallic mercury.**—The extraction of mercury depends on the instability of its oxide , thus, when an ore containing mercury sulphide is heated in a stream of air, it gives the free metal and not the oxide as in the case of zinc and cadmium

$$HgS + O_2 = Hg + SO_2$$

The roasting is effected (i) by burning a mixture of the crushed ore with charcoal in a blast furnace, or (ii) by passing finely-powdered ore down a series of sloping shelves in a shaft up which the gases from a furnace are passed The mercury vaporises and is condensed either by air or by water These processes are remarkable in that ores containing as little as 0 2% can be used without concentration, provided that they are well dried before roasting

**Purification of mercury.**—Mercury is purified by distillation in an iron retort with a little chalk or iron to decompose any compounds of mercury, and by filtering it through wash leather In the laboratory it can be freed from baser metals such as copper, lead, zinc, and bismuth, by being dropped in small globules through dilute nitric acid of density 1 1 It can also be purified by being made the anode in an electrolytic cell, when the baser metals pass into solution before the mercury The most effective method of purification, however, is by continuous distillation in a vacuum in an apparatus arranged so that the distilled mercury acts as a barometric column (Fig 92)

**Properties and uses of metallic mercury.**—(*a*) *Physical properties* — Mercury is a silvery liquid having a density of 13 595 at 0°, and is the heaviest liquid known at atmospheric temperatures It freezes at − 38 85°, and boils at 357 25° The vapour density shows that the metal is mainly monatomic, like zinc and cadmium, but spectroscopic evidence (namely the occurrence of the " band spectra " of molecules with the " line spectra " of atoms) proves the presence in the vapour of polyatomic molecules, to which the formula $Hg_2$ is assigned When pure, mercury

does not tarnish in air or in oxygen, and retains its lustre indefinitely, but, when it contains traces of baser metals such as zinc or lead, it becomes coated with a grey film of oxides, and leaves a " tail " when allowed to run over a porcelain or glass surface

(*b*) *Amalgams* — Mercury dissolves many metals, forming AMALGAMS It does not dissolve the metals of the iron group and is therefore commonly kept in iron bottles From some amalgams crystalline compounds have been obtained, *e g* sodium gives $NaHg_2$ (m -pt 360°) The plastic amalgam of tin is used in coating mirrors, and sodium amalgam (prepared by pressing small slices of sodium under mercury with a pestle in a mortar) is often used in place of sodium as a reducing agent An amalgam of mercury with a silver-tin alloy is used in dentistry for filling teeth, since the soft plastic mixture sets and becomes hard as a result of chemical changes such as that shown in the equation

$$5Ag_3Sn + 24Hg = 3Ag_5Hg_8 + 5Sn$$

(*c*) *Chemical properties* —Mercury is only less inactive than the noble metals It is therefore used to collect many gases which are soluble in water ; but it is attacked by chlorine, nitrogen peroxide and ozone When heated in air or oxygen below its boiling-point, mercury absorbs oxygen, forming red **mercuric oxide**, HgO, which decomposes again into its constituents when the temperature is raised to about 500°

Mercury is not attacked by hydrochloric acid, but dissolves in hot concentrated sulphuric acid, giving mercuric sulphate and sulphur dioxide

$$Hg + 2H_2SO_4 = HgSO_4 + SO_2 + 2H_2O$$

It dissolves readily in dilute nitric acid, giving oxides of nitrogen and **mercurous nitrite**, $Hg_2(NO_2)_2$, from which, by the further action of nitric acid, **mercurous nitrate**, $Hg_2(NO_3)_2$, various basic salts, and finally **mercuric nitrate**, $Hg(NO_3)_2$, are formed Unlike zinc, the metal is not attacked by alkalis.

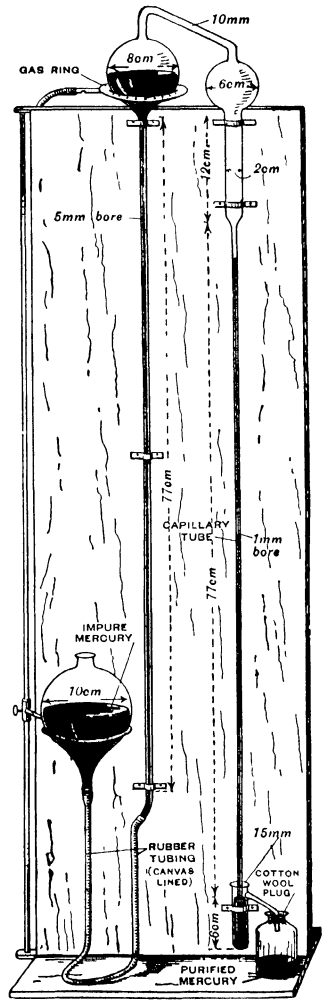



FIG 92 APPARATUS FOR PURIFYING MERCURY BY DISTILLATION

(*d*) *Uses* —Mercury is used in the extraction of silver and gold, in the manufacture of mercurial drugs and of mercury fulminate for detonators,

and in the construction of physical apparatus (barometers, thermometers, vacuum pumps, etc ), where a liquid of high density, good thermal conductivity, and low vapour pressure is required

(*e*) *Mercurous and mercuric salts* —Like copper, mercury forms two series of compounds, viz MERCUROUS COMPOUNDS, in which the metal is apparently univalent (p 331), and MERCURIC COMPOUNDS, in which the metal is bivalent

Many of the mercurous salts are insoluble in water, like the corresponding cuprous and silver salts On the other hand, mercuric salts are usually soluble in water like the cupric salts , but the black sulphide is insoluble in water and in dilute acids like cupric sulphide

## MERCUROUS COMPOUNDS

**Mercurous oxide**, $Hg_2O$, or grey oxide of mercury, is precipitated as a blackish-brown powder on adding a solution of a caustic alkali to a solution of a mercurous salt, *e g*

$$Hg_2(NO_3)_2 + 2KOH = Hg_2O + H_2O + 2KNO_3$$

It is decomposed by light, $Hg_2O = Hg + HgO$,

but when heated at 100° it combines with oxygen to form the red oxide

**Mercurous chloride**, or CALOMEL, $Hg_2Cl_2$, is obtained by heating an intimate mixture of mercuric chloride and mercury, when calomel sublimes

$$HgCl_2 + Hg = Hg_2Cl_2$$

Another method consists in subliming a mixture of mercuric sulphate, mercury, and common salt

$$HgSO_4 + Hg + 2NaCl = Hg_2Cl_2 + Na_2SO_4$$

In both cases the sublimate must be washed thoroughly with water to remove any mercuric chloride which may have sublimed with it It can also be prepared by adding dilute hydrochloric acid to a solution of a mercurous salt, when the chloride is precipitated

Mercurous chloride is a white powder which is almost insoluble in water, about 4 mg per litre at 20° as compared with 1 5 mg of silver chloride When heated it volatilises without melting Under ordinary conditions, the vapour will amalgamate gold-leaf, and the vapour density shows that the mercurous chloride has dissociated into a mixture of mercuric chloride and mercury

$$Hg_2Cl_2 = Hg + HgCl_2$$

When, however, the mercurous chloride has been dried carefully, and all precautions are taken to exclude traces of moisture, the mercurous chloride volatilises as such, and the vapour density corresponds with the formula $Hg_2Cl_2$ Further drying appears to prevent the compound from vaporising at the usual temperature

Calomel is used in medicine as a purgative and, unlike mercuric chloride (corrosive sublimate), is not poisonous in moderate doses

**Mercurous bromide**, $Hg_2Br_2$, which is white, and the **iodide**, $Hg_2I_2$, which is yellow, are similar in properties to the chloride The iodide, prepared by triturating iodine and excess mercury in a mortar, is green, owing to the presence of finely-divided mercury, as also is the precipitate which is obtained when potassium iodide is added to a solution of a mercurous salt

**Mercurous nitrate**, $Hg_2(NO_3)_2$, prepared by the action on mercury of cold dilute nitric acid of density 1 14 (hot concentrated nitric acid gives mercuric nitrate), crystallises as the **dihydrate**, $Hg_2(NO_3)_2,2H_2O$, but is decomposed by an excess of water, forming basic nitrates, the composition of which depends upon the conditions In presence of sulphuric acid, mercury reduces nitric acid quantitatively to nitric oxide

$$6Hg + 3H_2SO_4 + 2HNO_3 = 3Hg_2SO_4 + 2NO + 4H_2O ,$$

this reaction is used in the LUNGE NITROMETER (p 202) to estimate nitric acid

**Mercurous sulphate**, $Hg_2SO_4$, prepared by heating concentrated sulphuric acid with an excess of mercury, is easily soluble in the hot concentrated acid, but sparingly so in water, and is precipitated as a white powder on diluting the acid solution It is decomposed by water, like cuprous sulphate, giving mercury, mercuric sulphate, and a basic sulphate, $3HgO,SO_3$

## MERCURIC COMPOUNDS

**Mercuric oxide**, HgO, also known as RED OXIDE OF MERCURY or RED PRECIPITATE, is formed on heating mercury at a temperature slightly below its boiling-point for several weeks in a glass vessel containing air It is prepared on a large scale by heating a mixture of mercury and mercuric nitrate

$$Hg + Hg(NO_3)_2 = 2HgO + 2NO_2$$

When prepared in this way it forms a bright red crystalline powder , it can, however, be obtained as a yellow precipitate by adding potassium hydroxide to a solution of mercuric chloride

$$HgCl_2 + 2KOH = HgO + H_2O + 2KCl$$

This difference in colour is probably due to a difference in the fineness of sub-division of the particles, and not to dimorphism, as was formerly supposed It is also noteworthy that mercuric oxide becomes almost black when heated, but regains its original red colour on cooling When the oxide is heated above 500° it decomposes into mercury and oxygen

Mercuric oxide is a base, which interacts with acids to give mercuric salts When acted on by dilute ammonia, it is converted into a pale yellow powder having the empirical formula $2HgO,NH_4OH$, which explodes when heated and is known as MILLON'S BASE

**Mercuric chloride**, or CORROSIVE SUBLIMATE, $HgCl_2$, is prepared by heating mercury in chlorine or by heating a dry mixture of common salt and

mercuric sulphate, a little manganese dioxide being added as an oxidising agent to prevent the formation of calomel

$$HgSO_4 + 2NaCl = HgCl_2 + Na_2SO_4$$

It sublimes in needles, melts at 277°, and boils at 303°

Mercuric chloride, in common with other mercuric salts, except the fluoride and the salts of strong oxy-acids, is remarkable in that it has the properties of a covalent compound rather than those of a salt Thus it has a low boiling-point, is more soluble in ether than in water, and is only ionised to a very small extent in aqueous solution

Mercuric chloride interacts with ammonia to give a variety of compounds such as $NH_2HgCl$, which is formed by the addition of aqueous ammonia to a solution of mercuric chloride

$$2NH_3 + HgCl_2 = NH_2HgCl + NH_4Cl$$

Mercuric chloride is not usually classed as an oxidising agent, but it is readily reduced to calomel and then to mercury by reducing agents such as stannous chloride, oxalic acid and sulphur dioxide, *e g*

$$HgCl_2 + SnCl_2 \rightarrow SnCl_4 + Hg$$

Mercuric chloride is a powerful poison, but is used in medicine and in surgery as an antiseptic It is also used for preserving wood, skins and furs against insect pests

**Mercuric iodide**, $HgI_2$, is precipitated on adding a solution of potassium iodide to a solution of mercuric chloride , when it first separates it is yellow in colour but quickly becomes red Mercuric iodide is in fact dimorphous, with a well-defined transition temperature, the scarlet form being stable below 126°, whilst the yellow variety is stable above this temperature When the iodide is sublimed, the vapour usually condenses in yellow crystals, which gradually revert to the scarlet form at room temperatures , this change is accelerated by scratching or rubbing, a line of scarlet appearing where the crystals are touched

Mercuric iodide dissolves readily in an excess of potassium iodide, forming a solution from which the complex salt **potassium mercuri-iodide**, $K_2HgI_4$, can be crystallised This salt is not decomposed by potassium hydroxide, although the mercury can be precipitated by hydrogen sulphide The solution obtained by adding potassium hydroxide to the double salt is known as NESSLER'S REAGENT and forms a very delicate test for minute traces of ammonia, which produce a brown coloration or precipitate of **mercury hydroxyiodoamide**, HO Hg NH HgI

**Mercuric sulphide**, HgS, occurs in beautiful red crystals as CINNABAR and is the principal ore of mercury (p 336) It is obtained in a black form, either by precipitating a solution of mercury with hydrogen sulphide, or by triturating mercury with sulphur and a little caustic potash solution When the black sulphide is heated in a retort it sublimes as a brilliant red pigment and is known as VERMILION

Mercuric sulphide is insoluble in hot dilute nitric acid or hydrochloric acid, but dissolves readily in aqua regia

**Mercuric sulphate**, $HgSO_4$, is obtained by heating mercury with concentrated sulphuric acid, and crystallises from the strong acid in small silvery plates

$$Hg + 2H_2SO_4 = HgSO_4 + SO_2 + 2H_2O$$

It is decomposed by water, which precipitates a lemon-coloured **basic sulphate**, $2HgO,HgSO_4$

**Mercuric nitrate**, $Hg(NO_3)_2$, is formed when mercury is dissolved in an excess of nitric acid By dissolving mercuric oxide in concentrated nitric acid, a syrupy liquid is obtained, from which on adding strong nitric acid a crystalline but deliquescent precipitate separates having the composition $Hg(NO_3)_2,H_2O$ This salt is decomposed by water at 25°, giving an insoluble white basic nitrate, which is decomposed still further by heating with water, until finally mercuric oxide is obtained

**Mercuric cyanide**, $HgC_2N_2$, prepared by dissolving mercuric oxide in prussic acid, decomposes into mercury and cyanogen when heated

$$Hg(CN)_2 = Hg + C_2N_2$$

It appears to consist exclusively of covalent molecules, since even in aqueous solutions it is not an electrolyte and does not give the usual reactions of a mercuric salt with potassium hydroxide or potassium iodide

**Estimation of mercury**.—Mercury may be estimated by precipitating as the sulphide, HgS, or less accurately by distilling the material containing it in a glass tube with sodium carbonate, and condensing and weighing the metal which is formed

$$2HgCl_2 + 2Na_2CO_3 = 2Hg + 4NaCl + 2CO_2 + O_2$$

# CHAPTER XXV

## NICKEL AND COBALT

27 COBALT Co = 58 94
28 NICKEL Ni = 58 69

**Classification.**—After the copper and zinc families, it is convenient to consider the elements of the preceding triad,

26 IRON, 27 COBALT, 28 NICKEL,

which are predominantly bivalent or tervalent Iron, however, occupies such an unique position amongst the elements as to merit a separate chapter, and for this reason nickel and cobalt are now considered alone

These two elements have atomic weights which are almost the same but are in the wrong sequence when compared with their atomic numbers This irregularity is due to the fact that nickel is a mixture of isotopes, $^{58}_{28}$Ni and $^{60}_{28}$Ni, in which the lighter isotope predominates, so that the average atomic weight of the complex element is below that of the simple element $^{59}_{27}$Co Even before the atomic numbers had been determined, however, the correct sequence was established by the fact that there is a closer resemblance between iron and cobalt, and between nickel and copper, than is found when these two elements are interchanged

**General properties of nickel and cobalt.**—Nickel and cobalt are hard, white, steel-forming metals, which resemble iron and differ widely from copper and zinc in appearance and in mechanical properties, as well as in melting-point, although their densities are substantially the same as that of copper

| | Fe | Co | Ni | Cu | Zn |
|---|---|---|---|---|---|
| Melting-points, - | 1530° | 1480° | 1452° | 1083° | 419° |
| Densities, - - | 7 86 | 8 9 | 8 9 | 8 9 | 7 1 |

They also resemble iron in being polymorphic, since iron is magnetic below 766°, cobalt below 1150°, and nickel below 320° Their chemical properties are often quite distinct from those of iron, *e g* they do not corrode in air, and so can be used to protect iron from rusting

There is a close resemblance between the salts of nickel, which are exclusively *bivalent*, and the bivalent salts of copper This similarity extends to the bivalent salts of cobalt , but cobalt also forms simple *tervalent* salts analogous to those of iron, although they differ from the latter in that (i) they are unstable and have to be prepared by special methods, and (ii) they readily form very stable coordination compounds The pale green, red, green and blue ions of bivalent iron, cobalt, nickel

and copper, which all contain an incomplete shell of *M* electrons, therefore form a natural group, and may be contrasted with the colourless ions of zinc, where the *M* shell of 18 electrons is at last complete The formulae of some of the principal compounds of this cluster of elements are set out in Table 30

TABLE 30 —COMPOUNDS OF TRANSITIONAL ELEMENTS

| | IRON | COBALT | NICKEL | COPPER | ZINC |
|---|---|---|---|---|---|
| **Oxides** | — | — | — | **$Cu_2O$** | — |
| | FeO | CoO | **NiO** | CuO | **ZnO** |
| | **$Fe_3O_4$** | **$Co_3O_4$** | $Ni_2O_4$ | — | — |
| | $Fe_2O_3$ | $Co_2O_3$ | $Ni_2O_3$ | — | — |
| | $FeO_2$ (in $BaFeO_3$) | $CoO_2$ | $NiO_2$ | — | — |
| | $FeO_3$ (in $BaFeO_4$) | — | — | — | — |
| | (The oxides which are stable at high temperatures are shown in heavy type ) | | | | |
| **Chlorides** | — | — | — | $Cu_2Cl_2$ | — |
| | $FeCl_2,4H_2O$ | $CoCl_2,6H_2O$ | $NiCl_2,6H_2O$ | $CuCl_2,2H_2O$ | $ZnCl_2,H_2O$ |
| | $FeCl_3,6H_2O$ | $CoCl_3,6NH_3$ | — | — | — |
| **Sulphates** | — | — | — | $Cu_2SO_4$ | — |
| | $FeSO_4,7H_2O$ | $CoSO_4,7H_2O$ | $NiSO_4,7H_2O$ | $CuSO_4\,5H_2O$ | $ZnSO_4,7H_2O$ |
| | and double sulphates of the Schonite type, $K_2M''(SO_4)_2,6H_2O$ | | | | |
| | $Fe_2(SO_4)_3,xH_2O$ | $Co_2(SO_4)_3,18H_2O$ (compare Al) | — | — | — |
| | and alums of the type | | | | |
| | $KFe(SO_4)_2\,12H_2O$ | $KCo(SO_4)_2,12H_2O$ | — | — | — |
| **Carbonyls** | $Fe(CO)_5$ | $Co_2(CO)_9$ | — | — | — |
| | $Fe_2(CO)_9$ | $Co_2(CO)_8$ | — | — | — |
| | $Fe(CO)_4$ | — | $Ni(CO)_4$ | — | — |
| **Double cyanides** | — | — | — | $KCuC_2N_2$ | — |
| | $K_4FeC_6N_6$ | $K_4CoC_6N_6$ | $K_2NiC_4N_4$ | $K_2CuC_4N_4$ | $K_2ZnC_4N_4$ |
| | $K_3FeC_6N_6$ | $K_3CoC_6N_6$ | — | — | — |

## 28 NICKEL Ni = 58 69

**Occurrence.**—Metallic nickel is found with iron in meteorites, which usually contain about 8% of nickel Traces of nickel are found in igneous rocks, perhaps as $Ni_2SiO_4$, which by weathering yields the **hydrated nickel silicate** GARNIERITE, $Ni_2H_4Si_3O_{10}$ The principal source of nickel is an igneous dyke at Sudbury, Ontario, where nickel has separated from a siliceous magma in combination with sulphur as NICKELIFEROUS PYRRHOTITE, $[Ni,Fe]_3S_4$. It is also found as NiS, NiAs, NiSb, NiSAs, and $NiAs_2$

**Preparation.**—The sulphide ores of nickel contain iron and copper, which are removed as follows (*a*) The *iron* is removed by selective oxidation, exactly as in the metallurgy of copper (p. 312)

For this purpose the ore is (i) roasted, (ii) melted in a small blast furnace to a slag of ferrous silicate and a CRUDE MATTE of sulphides, which still contains more iron than nickel, (iii) it is then subjected to an air-blast in a Bessemer converter (p 354) with a siliceous lining, giving a slag of ferrous silicate, which contains 2-10% Ni and is returned to process (ii), and a REFINED MATTE of $Cu_2S$ and NiS, with only about 0 5% Fe

(*b*) The *copper* in the " refined matte " may be separated by melting with sodium sulphate and coal, when much of the copper and iron pass into the upper layer of sodium sulphide or " tops," whilst the **nickel sulphide** remains in the lower layer or " bottoms "

(*c*) In the MOND PROCESS nickel is extracted from this enriched sulphide ore by a series of operations in which **nickel carbonyl**, $Ni(CO)_4$, is formed and decomposed again into nickel and carbon monoxide

$$Ni + 4CO \rightleftharpoons Ni(CO)_4$$

(i) The matte of *sulphides* from (*a*) or (*b*) is roasted to remove the whole of the sulphur, and the resulting mass of *oxides* is ground, sieved and extracted with dilute sulphuric acid to remove some of the copper and iron as *sulphate*, leaving a residue containing 50% Ni as NiO

(ii) The *oxides* are then reduced by means of " water-gas " at 300°, giving a finely-divided mixture of nickel and copper with ferrous oxide, and a gas consisting mainly of carbon monoxide

(iii) The *metal* is then volatilised at 80° in the carbon monoxide from the reducers, after heating this gas with charcoal to reduce $CO_2$ to CO

(iv) The *carbonyl* thus produced (about 2% by volume of the gas) is decomposed at 180° in a tower containing pellets of pure nickel, these are allowed to grow to about $\frac{1}{4}''$ before the tower is refilled with smaller shot

(v) The nickel content is maintained by returning the metal to the roaster and extracting copper oxide as *sulphate*, the copper sulphate is a valuable by-product, which helps to cover the cost of refining After passing through the plant about six times, the residues are also an important source of precious metals, Ag, Au, Pd, Pt, etc

**Properties and uses of nickel.**—Nickel resembles iron, but its density (8 9) is higher and its melting-point (1452°) is lower It does not rust and is only slowly attacked by steam at high temperatures or by dilute acids, and is not attacked by molten alkalis It is therefore used in the laboratory in the form of nickel crucibles, spatulas, tongs, etc It is also used, like copper, for electroplating (but is being displaced by chromium, which has the merit of remaining bright, whereas nickel gradually becomes fogged on exposure to air), and for coins of small value When finely divided, it is of special value as a catalyst for promoting hydrogenation, *e g* unsaturated oils (p 718) combine directly with hydrogen at 250°, in the presence of finely-divided nickel, to form solid fats which are used for margarine, etc

Nickel is alloyed with *iron* to form NICKEL STEEL, *e g* for armour plate, with *chromium* and *iron* to form NICHROME wire (p 366) for winding electric furnaces, with *copper* (60%) to form CONSTANTAN wire for electric resistances, and with *brass* (Cu 50%, Zn 20%) to form GERMAN SILVER as a base for electroplated goods

## COMPOUNDS OF NICKEL

**Nickel hydroxide**, $Ni(OH)_2$, formed as an apple-green precipitate by the action of an alkali on a nickel salt, is insoluble in excess of alkali but dissolves in ammonia to form a blue complex, $[Ni(NH_3)_4](OH)_2$, compare

$[Cu(NH_3)_4](OH)_2$ On heating it yields green **nickel monoxide**, NiO The **sesquioxide**, $Ni_2O_3$, can be prepared as a black powder by gently roasting the bivalent nitrate, but yields the monoxide when heated more strongly The black precipitate formed by the action of an alkaline hypochlorite on a nickel salt is probably a mixture of the **trihydroxide**, $Ni(OH)_3$, with a hydrated **dioxide**, $NiO_2$, neither of these compounds yields salts with acids

**Nickel monosulphide**, NiS, cannot be precipitated in acid solution, but separates as a black precipitate by the action of an alkaline sulphide on a nickel salt If this is boiled with water, it is converted, like cobalt sulphide, into a form which is insoluble in dilute acids Use is made of this fact to separate nickel and cobalt from manganese and zinc in qualitative analysis (p 403).

**Nickel chloride**, $NiCl_2$, is formed in golden scales by the action of chlorine on nickel, it sublimes unchanged in the absence of oxygen, but when heated in air it liberates chlorine and leaves a residue of oxide

$$2NiCl_2 + O_2 = 2NiO + 2Cl_2$$

The chloride can also be prepared by dissolving the oxide or carbonate in hydrochloric acid, on evaporation, it separates from water in green crystals of the **hexahydrate**, $[Ni\ 6H_2O]Cl_2$ It yields the anhydrous chloride when evaporated in acid solutions and absorbs ammonia, forming the almost colourless **hexammine**, $[Ni\ 6NH_3]Cl_2$

**Nickel cyanide**, $NiC_2N_2$, is an apple-green precipitate, which dissolves in an excess of potassium cyanide, forming a **potassium nickelicyanide**, $K_2NiC_4N_4$ (compare cobalt and copper), which is decomposed at once by dilute acids

**Nickel sulphate**, $NiSO_4$, can be prepared by the action of dilute sulphuric acid on the metal, oxide or carbonate, but is obtained as a by-product in the Mond nickel process Below 32° it separates from water as a green **heptahydrate**, $NiSO_4,7H_2O$, but a blue and a green **hexahydrate** separate at higher temperatures When heated to 280°, it gives a yellow **anhydrous sulphate**, which unites with ammonia to form a violet **hexammine**, $[Ni\ 6NH_3]SO_4$ The **double sulphate**, $(NH_4)_2Ni(SO_4)_2,6H_2O$, compare $K_2Mg(SO_4)_2,6H_2O$, is used in electroplating

**Nickel nitrate**, $Ni(NO_3)_2,6H_2O$, prepared by dissolving nickel in boiling dilute nitric acid and evaporating to crystallisation, is a green deliquescent salt

**Nickel carbonate** is usually precipitated as a basic salt, but the normal carbonate, $NiCO_3$, and the hydrate, $NiCO_3,6H_2O$, have been prepared in a crystalline form by the action of sodium bicarbonate and carbon dioxide on a solution of the nitrate

**Nickel carbonyl**, $Ni(CO)_4$, formed by direct combination of nickel with carbon monoxide at temperatures below 100°, is a liquid which boils at 43° and freezes at −25° The vapour, which is very poisonous, decomposes at 180°-200°, depositing nickel and liberating carbon monoxide

## 27 COBALT Co = 58·94

**Occurrence and preparation of cobalt.**—In the copper mines of the Hartz Mountains an ore was found which looked like copper ore, but gave no copper This deception was attributed to an evil spirit, Kobold, which lived in the mine, and the " false ore " (an impure arsenide of cobalt) was called **cobalt** Cobalt occurs with nickel in meteoric iron and in sulphide and arsenide ores The principal cobalt minerals are SMALTITE, $CoAs_2$, and COBALT GLANCE, CoSAs, both isomorphous with pyrites The silver vein near Cobalt in Ontario, which is the largest source of silver in the world, is also the principal source of cobalt, which occurs (with nickel) as sulphide and arsenide Cobalt is separated by wet methods from ores which have been worked in the same way as for nickel, the oxide is finally precipitated with sodium hypochlorite or bleaching powder, and reduced with charcoal The pure metal is obtained by electrolysis or by igniting the oxalate $CoC_2O_4$

**Properties and uses.**—Cobalt is a silvery-white metal, its density (8 9) is similar to that of nickel and copper, and its melting-point (1480°) is intermediate between those of iron and nickel It has been used as a substitute for nickel in electroplating, and as a substitute for tungsten in making steel for permanent magnets The alloy STELLITE (Co 55, W 25, Cr 15, Mo 5) can be hardened without expansion, shrinkage or distortion, and is therefore used in making cutting tools for screw-threads, etc, where accurate dimensions are essential

**Chemical properties.**—Cobalt does not rust in air, but can be burnt to the **oxide**, $Co_3O_4$, compare $Fe_3O_4$, when heated to redness it also decomposes steam, giving the **monoxide**, CoO, compare NiO It dissolves slowly in dilute hydrochloric and sulphuric acids, liberating hydrogen, and much more rapidly in nitric acid with evolution of oxides of nitrogen Like nickel and iron, the metal is rendered " passive " by concentrated nitric acid (p 356) The solutions obtained by the action of acids on the metal contain bivalent COBALTOUS SALTS, which differ from those of nickel mainly in being pink instead of green By electrolytic oxidation, tervalent COBALTIC SALTS are produced, and these are also produced spontaneously in the form of stable AMMINES by atmospheric oxidation in presence of ammonia When heated under pressure with carbon monoxide, cobalt forms a **carbonyl**, $Co_2(CO)_8$, which melts at 51° and decomposes at higher temperatures

### COBALTOUS COMPOUNDS.

**Cobaltous oxide**, CoO, is formed as a light brown powder by reducing the higher oxides with hydrogen at 300° (compare the reduction of $Fe_2O_3$ to FeO) A rose-red **hydroxide**, $Co(OH)_2$, is obtained by adding an excess of caustic alkali to a cobaltous salt and boiling to decompose the bluish basic salt which is first precipitated, on exposure to the air it absorbs oxygen and becomes brown The black **sulphide**, CoS, is precipitated by the addition of an alkaline sulphide to a cobaltous salt, it resembles nickel sulphide in its properties

**Cobaltous chloride**, $CoCl_2$, is formed in blue scales by burning the metal

in chlorine, whilst a pink **hexahydrate**, $CoCl_2,6H_2O$, separates from the aqueous solutions obtained by dissolving the metal, oxide or carbonate in dilute hydrochloric acid The pink solutions, which probably contain the hydrated ion, $[Co\ 6H_2O]^{++}$, become blue on concentrating, heating or evaporating to dryness, or on adding hydrochloric acid, potassium chloride or calcium chloride , but the addition of water, or of mercuric or zinc chloride, causes a change from blue to pink The development of a blue colour has therefore been attributed to the formation of a blue anion such as $[CoCl_4]^{--}$ The production of a blue colour by calcium chloride and of a pink colour by mercuric chloride can then be explained by the greater readiness of calcium to form a cation and of mercury to form an anion, thus

$$\underset{\text{blue}}{Ca^{++}[CoCl_4]^{--}} \qquad \underset{\text{pink}}{Co^{++}[HgCl_4]^{--}}$$

A dilute solution of cobaltous chloride can be used as an " invisible ink," since the colour of the writing is too faint to be seen , when the paper is dried the colour of the blue anhydrous salt is clearly visible, but disappears as this reabsorbs moisture from the air

**Cobaltous sulphate**, $CoSO_4,7H_2O$, resembles nickel sulphate, but is pink in colour , it is isomorphous with ferrous sulphate, and forms double sulphates of the usual type, *e g* $K_2Co(SO_4)_2,6H_2O$

**Cobaltous cyanide**, $CoC_2N_2$, is formed as a pink precipitate by adding potassium cyanide to a solution of a cobaltous salt It dissolves in an excess of cyanide to form a **potassium cobaltocyanide**, $K_4CoC_6N_6$ (compare $K_4FeC_6N_6$), which oxidises to the **cobalticyanide**, $K_3CoC_6N_6$, so readily that it liberates *hydrogen* from an acid, just as if it were a metal

$$2K_4CoC_6N_6 + 2HCl = 2K_3CoC_6N_6 + 2KCl + H_2$$

## Cobaltic Compounds

**Cobaltic oxide**, $Co_2O_3$, is formed as a dark brown powder by igniting cobaltous nitrate

$$4Co(NO_3)_2 = 2Co_2O_3 + 8NO_2 + O_2$$

On heating more strongly it is converted into **cobalto-cobaltic oxide**, $Co_3O_4$, compare $Fe_3O_4$

**Cobaltic hydroxide**, $Co(OH)_3$, is precipitated as a brownish-black powder by the action of a hypochlorite, or of bleaching powder, on a cobaltous salt,

$$2CoCl_2 + NaOCl + 4NaOH + H_2O = 2Co(OH)_3 + 5NaCl\ ,$$

but the precipitate often contains more oxygen than this and may contain a certain amount of hydrated **dioxide**, $CoO_2$ aq

**Cobaltic sulphate**, $Co_2(SO_4)_3,18H_2O$, prepared by the electrolytic oxidation of cobaltous sulphate in a divided cell (cf persulphates, p 264), crystallises in blue silky needles and forms a series of cobaltic alums, *e g*

$$(NH_4)Co(SO_4)_2,12H_2O$$

**Coordination compounds.**—The cobaltic ion $Co^{+++}$ very readily combines with 6 molecules of water or of ammonia or with 6 cyanide or nitrite ions to form complex ions such as

$[Co\ 6H_2O]^{+++}$ $[Co\ 6NH_3]^{+++}$ $[Co\ 6CN]^{---}$ $[Co\ 6NO_2]^{---}$

in salts, such as

$CoCl_3,6H_2O$, $CoCl_3,6NH_3$, $K_3CoC_6N_6$, $K_3Co(NO_2)_6$

In these compounds the cobaltic ion, with $27 - 3 = 24$ electrons, acquires a share of six pairs of electrons belonging to other molecules or ions, and thus becomes linked with a total of 36 electrons, as in krypton The metallic carbonyls, formed by the action of carbon monoxide on nickel, cobalt or iron, are of similar type, as may be seen from the following table

| | | |
|---|---|---|
| Kr | $Z = 2 + 8 + 18 + 8$ | $= 36$ |
| Fe | $Z = 2 + 8 + 14 + 2$ | $= 26$ |
| $Fe(CO)_5$ | $Z = 2 + 8 + 16 + 10$ (shared) | $= 36$ |
| Co | $Z = 2 + 8 + 15 + 2$ | $= 27$ |
| $-Co(CO)_4$ | $Z = 2 + 8 + 16^* + 10$ (shared) | $= 36$ |
| Ni | $Z = 2 + 8 + 16 + 2$ | $= 28$ |
| $Ni(CO)_4$ | $Z = 2 + 8 + 18 + 8$ (shared) | $= 36.$ |

The radical $Co(CO)_4$ has one electron less than $Ni(CO)_4$, and therefore unites with a similar radical to form the molecule, $(CO)_4Co - Co(CO)_4$, in which two electrons are shared by two atoms of cobalt

These coordination compounds are held together by bonds, and are often extremely stable Thus silver nitrate will only precipitate *two* of the chlorine atoms in the pentammine, $CoCl_3,5NH_3$, which is therefore formulated as $[Co\ 5NH_3\ Cl]^{++}\ Cl_2^{--}$, where five ammonia molecules and one chlorine atom are coordinated to the cobalt atom The extraordinary stability of the complex cation is shown by the fact that cold concentrated sulphuric acid converts this salt into the sulphate,

$$[Co\ 5NH_3\ Cl]SO_4,$$

without evicting the ammonia For similar reasons the yellow **sodium cobaltinitrite**, $Na_3[Co\ 6NO_2]$, does not give the usual reactions of cobalt, and does not liberate nitrous fumes when dilute acids are added to it On the contrary, it behaves as a simple sodium salt and gives a precipitate of **potassium cobaltinitrite**, $K_3[Co\ 6NO_2]$, by double decomposition with soluble potassium salts It is therefore used as a reagent for detecting potassium

The coordination compounds of other elements, however, are often much less stable, and some of them ionise so readily that it is not easy to prove their existence and establish their structure Thus, whilst **potassium ferrocyanide**, $K_4[FeC_6N_6]$, and **potassium ferricyanide**, $K_3[FeC_6N_6]$, give no indication of the presence of iron or of cyanogen in the ordinary wet tests, **potassium argentocyanide**, $K[AgC_2N_2]$, gives precipitates of AgCl

* Two shared with a second atom of cobalt

on the addition of hydrochloric acid, and of $Ag_2S$ on the addition of sulphuretted hydrogen

EXPT 47 **Preparation of chloropentammine cobaltic chloride,** $[Co\ 5NH_3\ Cl]\ Cl_2$

Cobalt carbonate (20 grams) is dissolved in the minimum of dilute hydrochloric acid, filtered, and mixed when cold with 10% $NH_3$ (250 c c ), and a solution of ammonium carbonate (50 grams in 250 c c ) The product, after oxidation by drawing a rapid current of air through it for 3 hours, is mixed with ammonium chloride (150 grams) and evaporated to a thick paste Concentrated hydrochloric acid is added with vigorous stirring until no more carbon dioxide is evolved The solution is neutralised with reagent ammonia, treated with 10 c c of 0 88 ammonia, and diluted to 400 c c This solution is warmed for 1 hour on the water bath, and then 300 c c of concentrated hydrochloric acid are added The warming is continued for a further hour, when most of the chloropentammine compound crystallises out and is washed on a filter with dilute hydrochloric acid and finally alcohol

EXPT 48 **Preparation of sodium cobaltinitrite,** $Na_3Co(NO_2)_6$

Cobalt nitrate (50 grams) and sodium nitrite (150 grams) are dissolved in warm water (150 c c ) and cooled to 40°, 50 c c of 50% acetic acid are then added a little at a time with frequent shaking, and the solution is oxidised by drawing a current of air through it for half an hour The precipitate (which consists of sodium cobaltinitrite with a little potassium cobaltinitrite) is drained, stirred with 50 c c of water at 70° to 80°, and after ten minutes filtered off The total filtrate is then precipitated by the addition of 350 grams of 96% alcohol After two hours the precipitate is drained, washed twice with 25 c c of alcohol and dried in a desiccator The product should dissolve in 1½ times its weight of water, and give a precipitate with fairly dilute solutions of potassium salts

**Separation of nickel and cobalt** —The qualitative reactions of nickel and cobalt are very similar to one another, but they can be separated by taking advantage of the greater readiness of cobalt to form tervalent and coordination compounds Thus (i) Bromine water precipitates $Co_2O_3$ aq from neutral solutions of cobalt, whilst nickel remains in solution (ii) When precipitated and redissolved by excess of potassium cyanide, cobalt forms a stable cobalticyanide, $K_3CoC_6N_6$, which is not decomposed by sodium hypochlorite, whilst the double cyanide of nickel, $K_2NiC_4N_4$, gives a precipitate of the peroxide (iii) They can also be separated by precipitation in the form of coordination compounds with complex organic compounds , these can sometimes be weighed directly, but nickel is often weighed after igniting to NiO, and cobalt as $Co_3O_4$ , or the *metals* can be weighed after electro deposition

# CHAPTER XXVI

## IRON

### 26 IRON Fe = 55 84

**Classification.**—Iron has all the characteristic properties of a transition-element Thus it is a heavy steel-forming metal of high melting-point, forms coloured salts and readily develops magnetic properties, both as a metal and in its salts It exhibits in a particularly well-balanced way the phenomenon of variable valency, since the FERROUS and FERRIC SALTS, in which it has a positive electrovalence of 2 or 3, are readily converted into one another Moreover in the FERRATES, such as $K_2FeO_4$ and $BaFeO_4$, it forms part of an oxidised anion, comparable with those formed by chromium and manganese in the chromates and manganates, in which a higher valency is developed, as already recorded in a lesser degree for cobalt and nickel in compounds such as $BaCoO_3$, $BaCo_2O_5$ and $BaNi_2O_5$

In addition to its relation to the other elements of the transition-series, iron is linked rather unexpectedly to *magnesium* and to *aluminium*. Thus in the large group of " ferromagnesian " minerals, ferrous iron is constantly associated with magnesium in isomorphous mixtures of silicates such as olivine, $[Mg,Fe]_2SiO_4$, whilst in the " aluminosilicate " minerals ferric iron is associated with isomorphous aluminium in silicates such as felspar, $K[Al,Fe]Si_3O_8$ These similarities are not confined to mineral chemistry Thus ferrous sulphate, $FeSO_4,7H_2O$, is isomorphous with Epsom salts, $MgSO_4,7H_2O$, and forms double sulphates of the Schonite type, $K_2Mg(SO_4)_26H_2O$, whilst ferric chloride and sulphate are remarkably similar to their aluminium analogues, p 133 These unforeseen associations can now be attributed to similarity of ionic radii

$$\overset{++}{Mg} = 0\ 78, \quad \overset{++}{Fe} = 0\ 83, \quad \overset{+++}{Al} = 0\ 57, \quad \overset{+++}{Fe} = 0\ 67 \text{ A U}$$

**History.**—Although native iron is rarely found, except in meteorites, and the metal is difficult to prepare from its ores, it has been known since about 2000 B C Thus, in the Old Testament, Og, King of Bashan (*circa* 1200 B C ) is stated (Deut , 3, 11) to have had an iron bedstead , and 100,000 talents (2500 tons) of iron were used in the construction of Solomon's Temple (*circa* 1000 B C.) Its value in the ancient world is indicated by Homer (B C 880), who refers to an iron ball given to Achilles for his athletic prowess A famous iron pillar at Delhi, which was possibly made about 300 A D , is 23 feet 8 inches high, with a diameter of

12½ to 10½ inches, it is remarkable both for its size and for its freedom from rust

**Occurrence.**—The most notable deposit of native iron is in Disko Island, West Greenland Meteorites also contain free iron, together with variable amounts of nickel The most important iron ores are HAEMATITE, $Fe_2O_3$, MAGNETITE, $Fe_3O_4$, LIMONITE, $2Fe_2O_3, 3H_2O$, and SIDERITE, $FeCO_3$ IRON PYRITES, $FeS_2$, is important as a source of sulphur, and iron is also present in the sulphide ores of copper, nickel and cobalt

**Manufacture of pig iron.**—Crude iron is manufactured by reducing the oxide and carbonate ores with carbon The ore is often roasted in order to drive off water and to convert any carbonate or sulphide into the oxide Incidentally, ferrous oxide is oxidised to ferric oxide The roasted ore is mixed with limestone and hard coke (about 2 tons of coke and 1 ton of limestone to 5 tons of ore), and fed into the top of a blast furnace (Fig 93) This consists of a vertical shaft, narrowed at the top and bottom and about 80 feet in height The outside is made of sheets of steel and the inside is lined with fire-resisting brick A blast of air, preheated to 800°, is sent in at the bottom of the furnace by means of pipes called TUYERES The coke burns to carbon monoxide, which reduces the ferric oxide to ferrous oxide and then to metallic iron

$$Fe_2O_3 + CO = 2FeO + CO_2, \quad FeO + CO = Fe + CO_2$$

The reduction takes place mainly in the upper and central portions of the furnace, but it is not complete until near the bottom, where the temperature rises to about 1400° and the metal is melted The molten metal sinks to the bottom of the furnace and is tapped off into sand moulds to give PIG IRON, a product which contains from 3 to 4% of carbon (partly in the form of **carbide**, as CEMENTITE, $Fe_3C$), and smaller quantities of silicon, sulphur, phosphorus and manganese

The earthy silicates in the ore are removed with the help of limestone as a fusible SLAG of calcium and aluminium silicates, which floats on the surface of the iron and is tapped off at intervals,

$$CaCO_3 + SiO_2 = CaSiO_3 + CO_2$$

The slag contains under 0 5% of iron as ferrous silicate, and is used as "road metal" in combination with the tar derived from the coke-ovens Since all the materials which are added to the furnace are removed, either as gases or liquids, the process is continuous and is not stopped until the furnace requires relining

The reduction of iron oxide by carbon monoxide is reversible,

$$FeO + CO \rightleftharpoons Fe + CO_2,$$

since metallic iron is oxidised by carbon dioxide The *gases* which leave the blast furnace therefore contain a large amount of unburnt carbon monoxide and small amounts of hydrogen, methane, etc, the average composition including about 60% $N_2$, 24% CO, 12% $CO_2$

The gases are passed through special contrivances (Fig 93) for removing the dust, which often contains appreciable quantities of useful

potassium salts The purified gas is then used (i) for the production of power in gas-engines to operate the blowers, rolling mills, etc, and (ii) for preheating the air-blast For this purpose the purified gas is mixed with air and burnt in a Cowper Stove, consisting of an iron cylinder lined with fire bricks and packed, chequer fashion, with bricks When the temperature of the stove has been raised sufficiently, the gas is switched into a second similar stove This is then heated while the hot stove heats an incoming blast of air to about 800°, and so prevents the chilling of the furnace, which would result from the use of a cold blast A similar economy of heat and improved regularity of working are also effected sometimes by drying the air (by cooling) before it enters the stoves (see water-gas reaction, p 151)

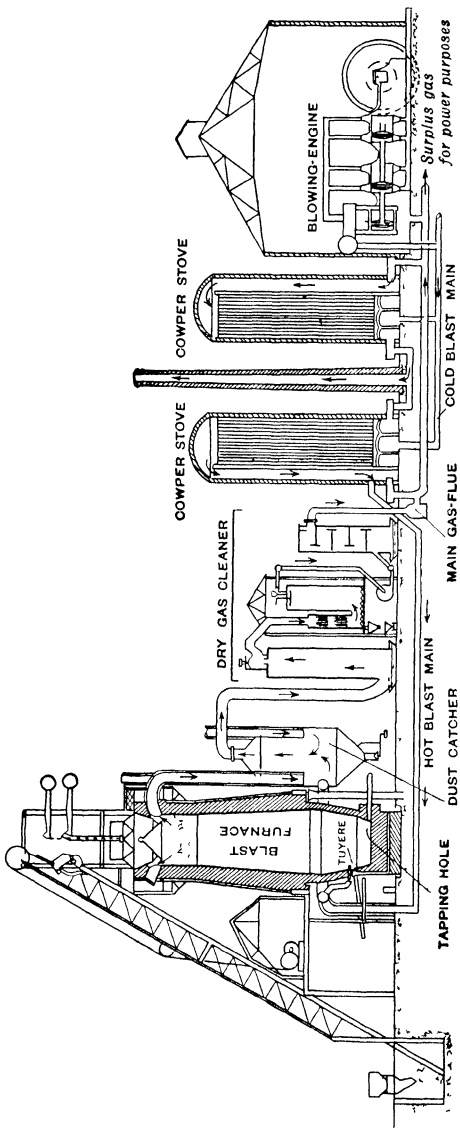



FIG 93 BLAST FURNACE AND PLANT

Pig iron is the crude product from which almost all other forms of iron are manufactured It is brittle, and is not sufficiently malleable to be worked with a hammer, even when hot It is, however, more easily melted (*circa* 1200°) than either wrought iron or steel As it also expands on solidification, it is used under the name of CAST IRON in the manufacture of iron bedsteads, gutter pipes, machine beds, etc, which are not subjected to great strain

**Manufacture of wrought iron.**—MALLEABLE or WROUGHT IRON is very nearly pure iron which has been prepared by burning out the carbon and other impurities in pig iron by melting the latter on the hearth of a

reverberatory furnace, lined with haematite (Fig 94) The silicon and manganese are oxidised and removed as a slag, which also carries with it most of the phosphorus The liberation of carbon monoxide by interaction of the carbon of the metal with the oxygen of the lining then causes the metal to " boil "

$$Fe_2O_3 + 3C = 2Fe + 3CO$$

The removal of the impurities from the iron raises its melting-point and it begins to go pasty It is then collected in lumps which are beaten with steam hammers to squeeze out the slag, and is forged into bars

Wrought iron or malleable iron contains only 0 12 to 0 25% of carbon It is tough and has a high tensile strength and was therefore used for building bridges, ships, etc , but has now been replaced by steel Its most

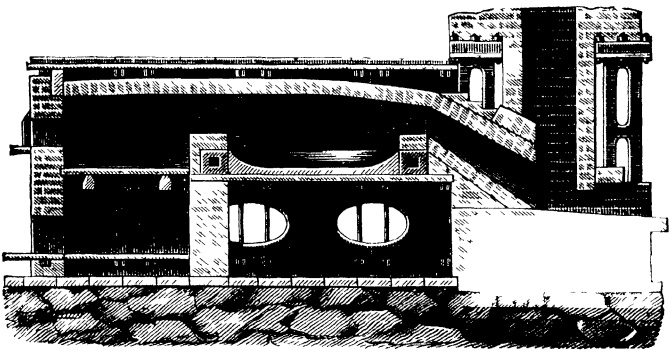


FIG 94 FURNACE FOR MAKING MALLEABLE IRON

valuable property arises from the fact that when heated to 1000° (well below the melting-point at about 1450°) it can be welded together by hammering , it is therefore largely used by blacksmiths

**Manufacture of steel** —The term STEEL was originally applied to alloys containing from 0 5 to 1 5% of carbon, which could be hardened and tempered by heat treatment (see below) , but the term has now been extended to include MILD STEEL, containing 0 1 to 0 5% of carbon, which differs from wrought iron only in having been made by melting instead of by working in a plastic condition

The manufacture of steel demands not only a reduction in the amount of carbon and the removal of most of the silicon in pig iron, but also a very thorough purification from sulphur and phosphorus, which make the metal brittle Sulphur can be removed or neutralised in part by a preliminary addition to molten iron of manganese, which forms a sulphide, MnS, of high melting-point, and only sparingly soluble in the metal , but phosphorus, if present in the pig iron, must usually be eliminated by using a special process of manufacture

(*a*) *The cementation process* —In this process, which was one of the earliest methods for manufacturing steel, bars of wrought iron are heated

with charcoal at 1000° for about eleven days Carbon is absorbed and the wrought iron is converted into a product known as BLISTER STEEL on account of its appearance This is usually converted into SHEAR STEEL by forging it under a steam hammer, and is used for cutlery CRUCIBLE STEEL, made by melting the blister steel in graphite crucibles, is used for high-grade tools

(*b*) *The Bessemer process* —In the Bessemer process, cast iron is converted into steel by blowing air through it until practically all the silicon and carbon has been burnt out The product is then converted into steel by the addition of SPIEGELEISEN, *i e* iron containing a high proportion of manganese and carbon

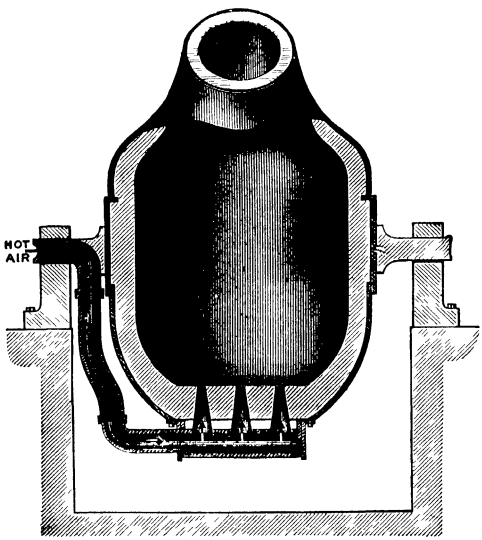



FIG. 95. BESSEMER CONVERTER

The BESSEMER CONVERTER (Fig 95) is a domed vessel with a fixed hood, mounted on trunnions so that it can be tilted, and provided with an air-chamber in the base from which preheated air can be blown through holes in the lining Molten metal is poured into the converter, whilst tilted into a horizontal position, with the mouth directed upwards, so as to keep the air-holes clear The air-blast is then turned on, and the converter brought back to the vertical position, when the air burns out first the silicon and then the carbon, the combustion of the silicon producing so much heat that the iron becomes hotter during the process, and remains molten in spite of its higher freezing-point

The Bessemer converter was at first provided with an acid lining consisting mainly of silica, and the process could only be applied successfully for making ACID STEEL from iron that contained but little phosphorus This difficulty was overcome in the THOMAS AND GILCHRIST PROCESS by making use of a BASIC LINING of lime and magnesia (prepared by calcining dolomite, $CaCO_3,MgCO_3$), which absorbs the phosphorus in the form of calcium phosphate The BASIC SLAG thus produced is a very valuable fertiliser for poor pasture land, giving rise to a strong growth of clover and a great improvement in the food value of the herbage

(*c*) *The Siemens-Martin process* —For making high-grade steels, the Bessemer converter has been superseded by an OPEN-HEARTH FURNACE (Fig 96), heated regeneratively by producer gas to a temperature above the melting-point of wrought iron Pig iron, steel scrap, and iron ore are

melted together in the hearth in such proportions as to eliminate the greater part of the carbon in combination with the oxygen of the ore

$$Fe_2O_3 + 3C = 2Fe + 3CO$$

The process can be used either with an acid lining, if the iron is free from phosphorus, or with a basic lining of calcined dolomite when phosphorus is present

**The properties of steel.**—The properties of steel depend upon the amount of carbon which it contains and on the heat treatment to which it has been submitted Steels containing a little carbon are comparatively soft, like wrought iron, but the hardness increases with the carbon content If steel is heated to redness and then plunged into cold water it becomes

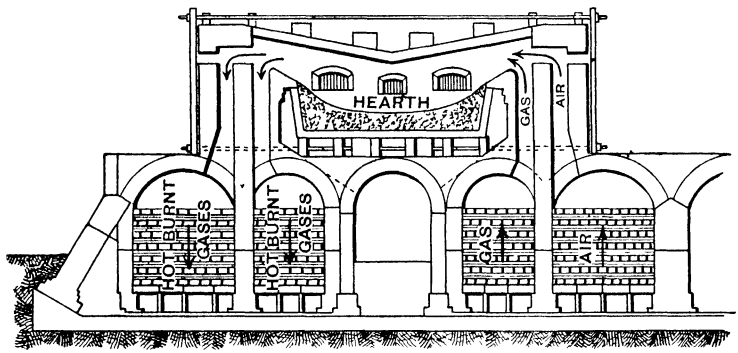



FIG 96 OPEN-HEARTH FURNACE

extremely hard and brittle, and is known as QUENCHED STEEL If this is then heated at a lower temperature, it becomes less hard but tougher The diminution in hardness depends upon the duration and temperature of heating and the process is known as TEMPERING It can be followed by watching the slow oxidation of the surface when the metal is tempered in contact with air , this produces a film of oxide, the colour of which changes from yellow to blue as its thickness increases Thus the pale yellow colour produced by heating to 230° is suitable for tempering razor blades, whilst the dark blue produced by heating to 300° is used in tempering springs

**The allotropy of iron.**—The effects of quenching and tempering on the properties of steel are attributed to the polymorphism of the metal, which exists in four forms, but only three, viz $\alpha$, $\gamma$ and $\delta$ are regarded as allotropic modifications

(i) $\alpha$-Iron, stable up to 766°, is soft and magnetic
(ii) $\beta$-Iron, stable from 766° to 895°, is like $\alpha$-iron but non-magnetic
(iii) $\gamma$-Iron, stable from 895° to 1400°, is miscible with carbon and other steel-forming elements, and forms hard isomorphous mixtures or " solid solutions " with these elements
(iv) $\delta$-Iron, stable above 1400°, resembles $\beta$-iron in its structure and properties,

Quenched steel consists of a solid solution of carbon in $\gamma$-iron, the transition to $\alpha$-iron having been prevented by rapid cooling On slow cooling, the carbon (which is not isomorphous with $\alpha$-iron) separates from the solid solution, usually in hard crystals of CEMENTITE, $Fe_3C$, but sometimes in the form of graphite, together with tough $\alpha$-iron in the form of FERRITE, giving rise to tempered steel The product has a banded structure, made up of alternative films of hard cementite and soft ferrite, and is known as PEARLITE on account of its pearly lustre

**Properties of iron.**—(*a*) *Physical properties*—Pure iron is a grey metal of density 7 8 , it melts at 1530°, and boils in an electric furnace at 2450°

(*b*) *Chemical properties*—Iron is oxidised to "smithy scale," $Fe_3O_4$, when heated in air or steam, as in Lavoisier's experiment with an iron gun-barrel

$$4H_2O + 3Fe \rightleftharpoons Fe_3O_4 + 4H_2$$

This action is reversible, since the oxides of iron are reduced by hydrogen

Iron does not combine directly with nitrogen or hydrogen, although it is permeable to the latter , but it unites with carbon to form a **carbide**, $Fe_3C$, which is held responsible for the production of hydrocarbons when cast iron is dissolved in acids It combines with chlorine to form **ferric chloride**, $FeCl_3$, and with sulphur when heated, to give **ferrous sulphide**, FeS Dilute hydrochloric and sulphuric acids dissolve iron to give hydrogen and a pale green FERROUS SALT, while dilute nitric acid gives **ferrous nitrate** and ammonium nitrate

$$4Fe + 10HNO_3 = 4Fe(NO_3)_2 + NH_4NO_3 + 3H_2O$$

Tervalent yellow FERRIC SALTS are readily formed by oxidising the corresponding ferrous salts with *oxidising agents*, such as boiling dilute nitric acid, hydrogen peroxide, potassium permanganate, potassium dichromate, chlorine, etc

$$6Fe(NO_3)_2 + 8HNO_3 = 6Fe(NO_3)_3 + 2NO + 4H_2O,$$
$$2FeSO_4 + H_2SO_4 + H_2O_2 = Fe_2(SO_4)_3 + 2H_2O, \text{ etc}$$

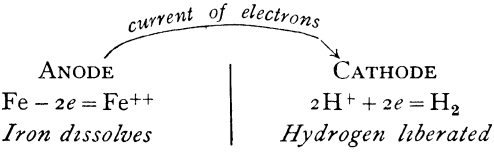
The converse process of reducing a ferric to a ferrous salt is brought about by *reducing agents*, *e g* sulphurous acid, stannous chloride, zinc amalgam (p 427), etc ·

$$Fe_2(SO_4)_3 + H_2SO_3 + H_2O = 2FeSO_4 + 2H_2SO_4,$$
$$2FeCl_3 + SnCl_2 = 2FeCl_2 + SnCl_4, \text{ etc}$$

(*c*) *Passive iron*—Concentrated nitric acid does not dissolve iron, but renders it "passive" or inert Thus PASSIVE IRON does not dissolve in dilute acids, does not displace copper from copper sulphate solution, and on exposure to moist air does not rust like ordinary iron , but the passivity is destroyed by scratching the metal, and disappears gradually on exposure to air Chromium also is rendered passive by concentrated nitric acid, and by oxidising agents, such as chromic and iodic acids The phenomenon has therefore been attributed to the formation of a very thin

but coherent film of oxide, which protects the metal from further action The correctness of this theory has been established by separating the oxide film by dissolving away the metal with electrolytic chlorine, the passive metal being made the anode in a solution of sodium chloride

**Rusting of iron.** When iron is wetted in contact with air it rusts and the product consists mainly of hydrated ferric oxide, $Fe_2O_3xH_2O$, where $x$ is variable but always less than three The initial step in rusting is an electrolytic process at the anode iron atoms shed electrons and pass into solution as ferrous ions, $Fe^{++}$, whilst at the cathode hydrogen ions (from the water) take up electrons and are discharged, as indicated in the scheme




For rusting to occur, liquid water and oxygen are essential,* since the former provides the hydrogen ions whilst the latter acts as a depolariser, oxidising the nascent hydrogen at the cathode to water The cathode may be a less electropositive element than iron, such as tin (p 166) or carbon, but it can equally well be iron, if the metal has been strained (the strained region acting as the anode) or if the supply of oxygen is not uniform at the surface of the metal This latter effect, which is known as *differential aeration*, is probably responsible for much of the rusting of iron and is certainly the cause of rust "pits" Depolarisation, *i e* oxidation of the hydrogen, takes place more readily where there is most oxygen, and such a spot on the surface of the iron can then act as cathode to another spot where there is less oxygen , in other words, rusting takes place where there is least oxygen This explains why iron rusts preferentially under areas covered by wet rust and why "pits" are formed

The ferrous ions, which pass into solution as the initial step in rusting, probably combine with hydroxyl ions (from the water) to form ferrous hydroxide, which is then oxidised by the air and precipitated as hydrated ferric oxide,

$$2Fe^{++} + 4OH^- \rightarrow 2Fe(OH)_2 \xrightarrow{O_2} Fe_2O_3xH_2O.$$

**Expt. 49. The rusting of iron.**

Place some bright iron nails (*a*) in a desiccator, (*b*) in a test tube full of boiled distilled water, then seal the top with a cork, (*c*) in a test tube half full of distilled water, (*d*) in a test tube half full of a normal solution of NaOH, (*e*) in a test tube half full of a 10% solution of sodium chloride Examine the nails every two or three days for ten days or so and comment on your observations

* In addition many electrolytes, such as sodium chloride, accelerate rusting by improving the conductivity of the water, but some electrolytes, *e g* caustic soda, retard it by lowering the concentration of the hydrogen ions as well as by causing the deposit of a film of ferrous hydroxide on the anode

## Ferrous Compounds

**Ferrous oxide**, FeO, is obtained as a black powder when ferric oxide is reduced by hydrogen at 300° When exposed to the air it takes fire, burning with incandescence, to give ferric oxide It dissolves in dilute acids to give solutions of ferrous salts

**Ferrous hydroxide**, $Fe(OH)_2$, is precipitated from ferrous solutions by the addition of an alkali

$$FeSO_4 + 2NaOH = Fe(OH)_2 + Na_2SO_4$$

It is colourless when pure, but on exposure to the air it turns green, and then brown as it is oxidised to ferric hydroxide It is a much stronger base than ferric hydroxide, since it forms a **carbonate,** $FeCO_3$, a **bicarbonate,** $Fe(CO_3H)_2$, and a very stable **sulphide,** FeS , moreover, unlike ferric hydroxide, it is not precipitated completely from solutions of its salts by the addition of ammonia and ammonium chloride in Group 3 of the tables of qualitative analysis (p 381), the solution is therefore boiled with a few drops of nitric acid to oxidise to the ferric state any ferrous iron that may be present

**Ferrous carbonate**, $FeCO_3$, is precipitated by the addition of an air-free solution of sodium carbonate to an air-free solution of a ferrous salt It is colourless, but on exposure to the air it turns brown owing to oxidation When carbon dioxide is passed into a suspension of the carbonate in water, soluble **ferrous bicarbonate,** $Fe(CO_3H)_2$, is formed This is only known in solution and is readily oxidised to ferric hydroxide

**Ferrous chloride**, $FeCl_2$, sublimes in colourless crystals when iron is heated in a current of dry hydrogen chloride Determinations of vapour density show that at 1500° the molecule is $FeCl_2$, but that, as the temperature is lowered, polymerisation to double molecules, $Fe_2Cl_4$, takes place

$$2FeCl_2 \rightleftharpoons Fe_2Cl_4$$

The pale green **hydrate,** $FeCl_2,4H_2O$, crystallises on evaporating a solution of iron in dilute hydrochloric acid

**Ferrous nitrate**, $Fe(NO_3)_2,6H_2O$, is best prepared by double decomposition from ferrous sulphate and barium nitrate, since it is difficult to avoid oxidation of the ferrous salt when iron is dissolved in dilute nitric acid The green crystals of the **hexahydrate,** $Fe(NO_3)_2,6H_2O$, which separate on cautious evaporation, are very soluble and readily yield a basic ferric nitrate

**Ferrous sulphide**, FeS, is formed by heating iron with excess of sulphur, and is precipitated from solutions of ferrous salts by the addition of an alkaline sulphide

$$Na_2S + FeSO_4 = FeS + Na_2SO_4$$

It melts readily and can be cast into sticks or rods, which are black in colour and have a semi-metallic lustre It is used in Kipp's apparatus (Fig. 12, p 70), with moderately dilute hydrochloric acid, for the production of hydrogen sulphide

**Ferrous disulphide**, $FeS_2$, occurs naturally as IRON PYRITES in cubic crystals which contain ferrous and disulphide ions, *viz.* $Fe^{++}S_2^{--}$ It often occurs in coal as a golden metallic-looking substance, and is the principal source of sulphur dioxide in the gases which are produced on the combustion of this fuel Pyrites is stable in air, and is unattacked by dilute acids, but it dissolves in hot concentrated nitric acid giving ferric nitrate and sulphuric acid

**Ferrous sulphate**, $FeSO_4,7H_2O$, has been known for many centuries as GREEN VITRIOL It is prepared in the laboratory by dissolving iron in dilute sulphuric acid and evaporating to crystallisation

$$Fe + H_2SO_4 = H_2 + FeSO_4$$

The **heptahydrate** is isomorphous with Epsom salts, $MgSO_4,7H_2O$, whilst the less stable **pentahydrate**, $FeSO_4,5H_2O$, is isomorphous with copper sulphate, $CuSO_4,5H_2O$, and is a common impurity in the latter When strongly heated, ferrous sulphate decomposes into ferric oxide, steam, sulphur dioxide and sulphur trioxide

$$2(FeSO_4,7H_2O) = Fe_2O_3 + SO_2 + SO_3 + 14H_2O$$

When condensed in a receiver, the gaseous products form NORDHAUSEN OIL OF VITRIOL, and it was by this method (or by heating alum in the same way) that sulphuric acid was first prepared

If nitric oxide is passed into a solution of ferrous sulphate, a brown **nitroso compound**, probably $FeSO_4,NO$, is formed, as in the brown ring test for nitrates (p 395)

Ordinary writing ink is made from ferrous sulphate, tannin (an organic substance obtained from bark) and gum The solution, which contains ferrous tannate, has a very pale colour, so a blue dye is added to make it clearly visible On exposure to the air, the ferrous tannate is oxidised to black ferric tannate, and the blue ink therefore gradually turns black

In the laboratory, ferrous sulphate is often used in the form of **ferrous ammonium sulphate**, $(NH_4)_2Fe(SO_4)_2,6H_2O$, since this double salt is less soluble and therefore more easily purified, and in solution is not so readily oxidised by the air

EXPT 50 **Preparation of ferrous ammonium sulphate.**

Warm 75 c c of dilute (2N) sulphuric acid with an excess of iron filings in a conical flask Whilst the action is taking place find by titration what volume of bench dilute ammonia will be needed to neutralise 75 c c of the dilute sulphuric acid. For this purpose place 25 c c of the acid in a flask with a few drops of methyl orange and add ammonia from a burette until the neutral point is reached Take the mean of two concordant titrations and then mix 75 c c of the dilute acid with the requisite quantity of ammonia for neutrality When the reaction between the iron and acid has subsided, filter the product, and, after adding to the filtrate a further 5 c c. of dilute sulphuric acid (to minimise hydrolysis), mix it with the solution of ammonium sulphate and evaporate to crystallisation (Final volume should be about 100 c c )

In solution, ferrous ammonium sulphate gives all the reactions of its constituent salts It is therefore classified as a DOUBLE SALT, whereas potassium ferrocyanide, $K_4Fe(CN)_6$, which does not give the reactions of the ferrous and cyanide radicals, is classified as a COMPLEX SALT, but the two classes are not very well-defined, since many complex salts dissociate in solution, and therefore give some or all of the reactions of the component ions, as well as those of the complex ion

Ferrous ammonium sulphate contains *one-seventh* of its weight of metallic iron and is used for the preparation of standard solutions of oxidising and reducing agents as described on p 426

## FERRIC COMPOUNDS

**Ferric oxide**, $Fe_2O_3$, occurs naturally in the anhydrous state as HAEMATITE and as the hydrate LIMONITE, $2Fe_2O_3,3H_2O$ It may be prepared by igniting ferric hydroxide or ferrous sulphate The red product obtained from the sulphate is known as COLCOTHAR or ROUGE, and is used as a polishing powder and as a pigment

**Ferroso-ferric oxide**, or MAGNETIC OXIDE OF IRON, $Fe_3O_4$, is the most stable oxide of iron It is formed when iron is heated in air or steam, and (as its name implies) is strongly magnetic It has a slight metallic conductivity and is used as an electrode for arc lights, and in electrolysis as an anode which is not attacked by chlorine or oxygen It appears to be a compound of ferrous and ferric oxides, FeO, $Fe_2O_3$, in which ferrous oxide acts as the base and ferric oxide as the acid, compare $MgAl_2O_4$

**Ferric hydroxide**, $Fe(OH)_3$, is a very weak base and is formed as a brown precipitate by the addition of ammonia, caustic alkalis or carbonates to solutions of its salts

$$2FeCl_3 + 3Na_2CO_3 + 3H_2O = 2Fe(OH)_3 + 6NaCl + 3CO_2$$

It differs from aluminium hydroxide in that it will not dissolve in excess of alkali

**Ferric chloride**, $FeCl_3$, sublimes in black scales when chlorine is passed over red-hot iron It melts at 300° and vaporises readily, its vapour density at 448° corresponds with the formula $Fe_2Cl_6$ (compare $Al_2Cl_6$, p 133), but it diminishes at higher temperatures, perhaps as a result of dissociation, into ferrous chloride and chlorine

$$Fe_2Cl_6 \rightleftharpoons 2FeCl_2 + Cl_2$$

Ferric chloride dissolves readily in water and forms a series of hydrates, which contain from 2 to $6H_2O$ Like other salts derived from a strong acid and a weak base it is hydrolysed by water,

$$FeCl_3 + 3H_2O \rightleftharpoons Fe(OH)_3 + 3HCl,$$

but it does not always give a precipitate, since the ferric hydroxide may be retained as a colloidal suspension.

EXPT 51 **Hydrolysis of ferric chloride.**

A 100 c c measuring cylinder is filled two-thirds full with a 10% solution of gelatin, which has been rendered pink with faintly alkaline phenol-

phthalein When this has set, a 10% solution of ferric chloride is added After a time, three different coloured bands of gelatin will be visible, viz a lower unchanged pink band, a middle colourless band due to the speedier diffusion of the acid, and an upper brown band due to ferric hydroxide

**Ferric sulphate**, $Fe_2(SO_4)_3$, may be prepared in the anhydrous state by boiling ferrous sulphate with fifteen times its own weight of concentrated sulphuric acid for about an hour

$$2FeSO_4 + 2H_2SO_4 = Fe_2(SO_4)_3 + SO_2 + 2H_2O$$

The mixture is allowed to cool, and the concentrated acid poured from the crystals of ferric sulphate, which are then washed with alcohol, and finally with anhydrous ether to remove the adhering acid The crystals are placed in a steam oven and dried to constant weight When ferric sulphate is heated strongly, sulphur trioxide is evolved and ferric oxide left (compare $Al_2(SO_4)_3$, p 134)

$$Fe_2(SO_4)_3 = Fe_2O_3 + 3SO_3$$

**Ferric alum**, $(NH_4)Fe(SO_4)_2,12H_2O$, is much less soluble and is readily prepared on a large scale , it has a pale violet tint, which has been attributed to traces of tervalent manganese

## Cyanogen Compounds

**Potassium ferrocyanide and its derivatives** —The FERROCYANIDES are an important series of double salts formed by the combination of ferrous cyanide with four equivalents of another cyanide, *e g*

$$FeC_2N_2 + 4KCN = K_4FeC_6N_6,$$

but they are so stable that they are conveniently regarded as metallic salts of hydroferrocyanic acid, $H_4FeC_6N_6$ (see below)

(*a*) *Preparation from nitrogenous waste* —Cyanides were formerly prepared by heating charred nitrogenous organic matter (horns, hoofs, blood, etc ), in a reverberatory furnace with molten potash and iron turnings , after solidification, the product was digested and finally extracted with hot water, from which on evaporation crystals of the ferrocyanide were deposited This method is now obsolete owing to the fact that only 20% of the " organic " nitrogen was converted into ferrocyanide

(*b*) *Preparation from spent iron oxide* —In the manufacture of coal gas a considerable proportion of the volatile nitrogen of coal is liberated as prussic acid or hydrogen cyanide, HCN (p 150), and is absorbed (with sulphuretted hydrogen) by oxide of iron in the " purifiers," where it is fixed as **ferric ferrocyanide** or Prussian blue

$$Fe(OH)_2 + 2HCN = FeC_2N_2 + 2H_2O$$
$$Fe(OH)_3 + 3HCN = FeC_3N_3 + 3H_2O$$
$$3FeC_2N_2 + 4FeC_3N_3 = Fe_7C_{18}N_{18}$$

| Ferrous cyanide | Ferric cyanide | Prussian blue |
|---|---|---|

The spent oxide is washed to remove soluble ammonium salts, and then mixed with lime in order to convert the Prussian blue into **calcium ferrocyanide**, $Ca_2Fe(CN)_6$, this compound is dissolved in cold water and converted into **potassium ferrocyanide** by the action of potassium carbonate

$$Ca_2Fe(CN)_6 + 2K_2CO_3 = 2CaCO_3 + K_4Fe(CN)_6$$

(*c*) *Properties of potassium ferrocyanide*.—Potassium ferrocyanide separates from water in yellow crystals of the **trihydrate**, $K_4FeC_6N_6,3H_2O$, which are described in commerce as "yellow prussiate of potash." They lose their water at 100°, leaving the anhydrous salt as a colourless powder which ignites readily when heated in air

Potassium ferrocyanide is one of the most stable COMPLEX SALTS that is known, since it gives none of the ordinary reactions of iron, the presence of which can usually be detected only when the cyanogen has been destroyed, *e g* by ignition to carbide of iron and nitrogen

$$K_4FeC_6N_6 = 4KCN + FeC_2 + N_2$$

When boiled with dilute sulphuric acid, hydrogen cyanide is evolved and **potassium ferrous ferrocyanide**, $K_2Fe_2C_6N_6$, is left

$$2K_4Fe(CN)_6 + 3H_2SO_4 = 3K_2SO_4 + K_2Fe_2(CN)_6 + 6HCN$$

Hot concentrated sulphuric acid gives a mixture of potassium sulphate, ferrous sulphate and ammonium sulphate, and carbon monoxide is evolved

$$K_4Fe(CN)_6 + 6H_2SO_4 + 6H_2O = 2K_2SO_4 + FeSO_4 + 3(NH_4)_2SO_4 + 6CO$$

The formation of carbon monoxide may be attributed to the hydrolysis of the prussic acid to ammonium sulphate and formic acid (p 716), and simultaneous dehydration of formic acid

$$2HCN + H_2SO_4 + 4H_2O = (NH_4)_2SO_4 + 2H\ CO\ OH,$$
$$H\ CO\ OH = CO + H_2O$$

If hydrochloric acid is added to a cold saturated solution of potassium ferrocyanide, **hydroferrocyanic acid**, $H_4Fe(CN)_6$, is set free and can be precipitated by the addition of ether This acid crystallises in colourless scales, which are quite stable in dry air, but turn blue in moist air owing to oxidation, probably to Prussian blue

**Potassium ferricyanide**, $K_3FeC_6N_6$, is prepared by the action of chlorine on potassium ferrocyanide

$$2K_4Fe(CN)_6 + Cl_2 = 2K_3Fe(CN)_6 + 2KCl$$

It separates from water in anhydrous deep red crystals and is known commercially as "red prussiate of potash" It is less stable than the ferrocyanide and can therefore be used as an oxidising agent, since the conversion of the ferricyanide into the ferrocyanide ion involves an acquisition of electrons, and is equivalent to the conversion of a ferric into the corresponding ferrous compound

$$FeC_6N_6^{---} \rightarrow FeC_6N_6^{----}$$

**Prussian blue.**—Complex compounds of iron and cyanogen are formed by precipitating ferrous and ferric salts with ferro- and ferri-cyanides Thus INSOLUBLE PRUSSIAN BLUE or **ferric ferrocyanide,** $Fe_4(FeC_6N_6)_3$ or $Fe_7C_{18}N_{18}$, is precipitated when a ferric salt is added in excess to a ferrocyanide

$$4FeCl_3 + 3K_4Fe(CN)_6 = Fe_4(FeC_6N_6)_3 + 12KCl.$$

It is used as " blue " in laundry work, and is also a valuable pigment, *e g* 1 lb of it will colour 500 lbs of white lead TURNBULL'S BLUE, obtained by adding excess of a ferrous salt to a ferricyanide, appears to be identical with the above compound, although it would be expected to be ferrous ferricyanide, $Fe_3(FeC_6N_6)_2$ When a ferric salt is added to an excess of a ferrocyanide, or a ferrous salt to an excess of ferricyanide, the precipitate is soluble in plenty of water and is called SOLUBLE PRUSSIAN BLUE, $KFe_2C_6N_6$ or $KFe(FeC_6N_6)$ With a soluble ferrocyanide, ferrous salts give a white precipitate of **ferrous ferrocyanide,** $Fe_2(FeC_6N_6)$, which is rapidly oxidised by air to Prussian blue, so that the laboratory reagents always give a pale blue precipitate Finally **ferric ferricyanide,** which is brown, is soluble in water, so that a precipitate is not obtained when a ferric salt is added to a dilute solution of a ferricyanide

**Estimation of iron.**—(*a*) Iron is estimated gravimetrically by boiling a ferric solution with excess of ammonia , ferrous compounds must be oxidised first by heating with a little nitric acid The precipitate of ferric hydroxide is ignited in a platinum crucible and weighed as $Fe_2O_3$ (p 439)

(*b*) The volumetric estimation of iron usually depends on oxidising ferrous to ferric iron by means of standard permanganate or dichromate, as described on pp 427 and 429

# CHAPTER XXVII

## CHROMIUM AND MANGANESE

24 CHROMIUM Cr = 52 01
25 MANGANESE. Mn = 54 93

**Classification.**—The two elements, chromium and manganese, which precede iron in the periodic table, have the characteristic properties of transition-elements They are hard, white or grey, steel-forming metals of high melting-point and of similar density to iron They form the usual series of bivalent and tervalent salts, which are isomorphous with those of the other transition-elements The bivalent CHROMOUS SALTS are difficult to prepare and are oxidised to tervalent CHROMIC SALTS even more readily than in the case of iron, but the bivalent MANGANOUS SALTS are stable in air, like the bivalent cobaltous salts, and are almost equally difficult to oxidise to the tervalent MANGANIC SALTS

A novel characteristic of these elements is the definite acidity of their higher oxides, which provides the only valid excuse for their classification with the non-metals, sulphur and chlorine Thus, although salts derived from $NiO_2$, $CoO_2$, and $FeO_2$ can be prepared by fusion with a base in an electric furnace, these salts cannot usually be handled in solution, and the oxides are neutral and insoluble On the other hand, **chromium trioxide**, $CrO_3$, or CHROMIC ACID gives acid solutions in water, and yields two series of salts, the CHROMATES and DICHROMATES, *e g* $K_2CrO_4$ and $K_2Cr_2O_7$, which are isomorphous with the corresponding sulphates and pyrosulphates, and are quite stable in the absence of reducing agents

Unlike chromium, manganese yields an amphoteric dioxide, $MnO_2$, and a series of MANGANITES, *e g* $CaMnO_3$, $FeMnO_3$, corresponding with the compounds of nickel and cobalt which have been cited above The higher oxides of manganese are much more difficult to prepare than chromic acid, but there are two well-known series of salts, the green MANGANATES, which resemble the sulphates, since $Na_2MnO_4,10H_2O$ is isomorphous with $Na_2SO_4,10H_2O$, and the purple PERMANGANATES, which resemble the perchlorates, since $KMnO_4$ is isomorphous with $KClO_4$ Manganese, therefore, exhibits the phenomenon of variable valency in a maximum degree since it exists in the following stages of oxidation

| $MnO$ $Mn_2O_3$ | $MnO_2$ | $MnO_3$ $Mn_2O_7$ |
|---|---|---|
| basic | amphoteric | acidic |

## 24 CHROMIUM Cr = 52·01

**Occurrence of chromium.**—Chromium has never been found in the free state, but occurs as **ferrous chromite**, under the name of CHROMITE or CHROME IRONSTONE, $FeO,Cr_2O_3$ or $FeCr_2O_4$ Other minerals are CHROMITITE, $Fe_2O_3,2Cr_2O_3$, **lead chromate** or CROCOITE, $PbCrO_4$, and the **oxide**, $Cr_2O_3$

**Preparation of chromium.**—On account of its high melting-point (1615°) chromium cannot be prepared in the blast furnace The most convenient method of preparing it is by the THERMITE PROCESS (p 131), in which the oxide is reduced with aluminium

$$Cr_2O_3 + 2Al = 2Cr + Al_2O_3 + 112{,}000 \text{ calories}$$

As in the reduction of iron by aluminium, the reduction is not easy to start, but proceeds with great evolution of heat

EXPT 52 **Preparation of chromium**

Mix 3 parts by weight of chromium sesquioxide, $Cr_2O_3$, with 1 part of coarse aluminium powder Press the mixture firmly into a Battersea crucible and place on the top a little magnesium powder mixed cautiously with potassium chlorate to act as an igniter The bottom of the crucible is heated strongly in the blow-pipe flame, it is then placed in a tin box filled with sand, and the reaction is started by igniting the magnesium with a Bunsen burner The reaction is very violent and the experiment should be carried out in a fume chamber If the above instructions are carefully followed, a button of metallic chromium will be obtained at the bottom of the crucible

On a larger scale, chromic oxide may be reduced by carbon in an electric furnace

$$Cr_2O_3 + 3C = 2Cr + 3CO$$

The product is freed from carbide (as in the case of iron) by remelting the crude metal with the oxide Alloys of iron and chromium, known as FERRO-CHROME, are also prepared by reducing chrome-ironstone with carbon in an electric furnace

$$FeCr_2O_4 + 4C = Fe + 2Cr + 4CO$$

**Properties of chromium.**—(*a*) *Physical properties* —Chromium is a silver-white metal with a melting-point of 1615°, and a density of 7 1 It is very hard, and when alloyed with carbon is only less hard than diamond

(*b*) *Chemical properties* —Chromium is stable in moist air, but burns brightly to the sesquioxide when heated in the oxy-hydrogen flame It dissolves rapidly in dilute hydrochloric and sulphuric acids, liberating hydrogen and forming bivalent CHROMOUS SALTS Dilute nitric acid attacks the metal, giving a tervalent CHROMIC SALT and oxides of nitrogen, but concentrated nitric acid renders the metal passive

(*c*) *Uses of chromium* —The most important use of chromium is in the manufacture of STAINLESS STEEL (12% Cr, 0 3% C, and up to 0·7% Ni)

Chromium and tungsten are also essential constituents of HIGH SPEED TOOL STEELS, which have the property of retaining their hardness even at a red heat, so that a cutting tool of this material can do something like one hundred times as much work as ordinary steel without softening and losing its edge NICHROME (Ni 60%, Fe 25%, Cr 15%), which has a high melting-point and high resistance and is not oxidised when heated in air, is used in the form of wire for winding the resistances of electric furnaces Chromium has also displaced nickel in electroplating, since it gives a hard deposit which retains its bright polish instead of " fogging " like nickel-plating on exposure to the atmosphere

## CHROMOUS COMPOUNDS

**Chromous oxide**, CrO, is black in colour and like ferrous oxide is readily oxidised It is produced when chromium amalgam is exposed to the air

**Chromous hydroxide**, $Cr(OH)_2$, can be obtained as a yellow powder by adding caustic soda to a solution of a chromous salt It is unstable and on exposure to the air is oxidised to chromic hydroxide, $Cr(OH)_3$ On heating, chromic oxide and hydrogen are produced and not chromous oxide .

$$2Cr(OH)_2 = Cr_2O_3 + H_2O + H_2$$

With acids it gives solutions of chromous salts, which are blue in colour and are far more powerful reducing agents than the ferrous salts

**Chromous chloride**, $CrCl_2$, is prepared in the anhydrous state by passing hydrogen chloride over the heated metal (cf $FeCl_2$ and $SnCl_2$) or hydrogen over chromic chloride A solution of chromous chloride can be prepared by reducing a chromate or a chromic salt by means of zinc and hydrochloric acid By pouring the crude product into a saturated solution of sodium acetate, red **chromous acetate**, $Cr(C_2H_3O_2)_2$, can be precipitated , on redissolving the acetate in hydrochloric acid and crystallising in the absence of air, the **tetrahydrate** of chromous chloride, $CrCl_2,4H_2O$, separates in blue needles

**Chromous sulphate**, $CrSO_4$, prepared by dissolving metallic chromium or chromous acetate in dilute sulphuric acid, separates from water in blue crystals as the **heptahydrate**, $CrSO_4,7H_2O$, isomorphous with ferrous sulphate , it forms a blue **double sulphate**, $K_2Cr(SO_4)_2,6H_2O$, corresponding with the double sulphates of copper, zinc, manganese, etc

## CHROMIC COMPOUNDS

**Chromic oxide**, $Cr_2O_3$, is the most stable oxide of chromium and is always produced when the other oxides are heated strongly in air It may be prepared by igniting the hydroxide, or ammonium dichromate, or a mixture of ammonium chloride and potassium dichromate

$$2NH_4Cl + K_2Cr_2O_7 = (NH_4)_2Cr_2O_7 + 2KCl,$$
$$(NH_4)_2Cr_2O_7 = Cr_2O_3 + N_2 + 4H_2O$$

It is green in colour, and is so stable that it cannot be reduced, like ferric oxide, by heating in hydrogen or carbon monoxide.

EXPT 53 **Preparation of chromic oxide**

An intimate mixture of potassium dichromate (20 grams) and ammonium chloride (9 grams) is heated in a large crucible until fumes of ammonium chloride are no longer evolved The crude product is heated with water (100 c c ) in a beaker, filtered on a Buchner funnel, washed with hot water and dried in an oven

**Chromic hydroxide**, $Cr(OH)_3$, is a very weak base, since it is precipitated (with ferric and aluminium hydroxides) by ammonia in presence of ammonium chloride

$$CrCl_3 + 3NH_4OH = Cr(OH)_3 + 3NH_4Cl$$

Moreover, the **sesquisulphide**, $Cr_2S_3$, which can be prepared by direct combination of chromium with sulphur, or by igniting the oxide in sulphuretted hydrogen, is decomposed by water , ammonium sulphide therefore precipitates the hydroxide and not the sulphide from solution

$$2CrCl_3 + 3(NH_4)_2S + 6H_2O = 2Cr(OH)_3 + 6NH_4Cl + 3H_2S$$

The hydroxide also shows weak acid properties, since it dissolves in an excess of caustic alkali, forming a CHROMITE, $KCrO_2$, which is unstable and is decomposed by boiling.

**Chromic chloride**, $CrCl_3$, may be prepared by heating the metal, or a mixture of chromic oxide and carbon, in a stream of chlorine It forms a **hydrate**, $CrCl_3,6H_2O$, which can exist in three different forms, two of which are green and one violet Silver nitrate precipitates the three chlorine atoms of the blue form, but only two atoms and one atom, respectively, of the green forms, unless several hours are allowed for the double decomposition The three isomers are therefore formulated as follows

| | |
|---|---|
| Blue form, | $[Cr\ 6H_2O]Cl_3$ |
| First green form, | $[Cr\ 5H_2O\ Cl]Cl_2,H_2O$ |
| Second green form, | $[Cr\ 4H_2O\ 2Cl]Cl,2H_2O$ |

**Chromic sulphate**, $Cr_2(SO_4)_3,18H_2O$, can be prepared in violet crystals by covering chromium hydroxide with cold concentrated sulphuric acid, dissolving in water the crude crystals which separate from the acid solution, and reprecipitating them by the addition of alcohol The sulphate is more commonly prepared in the form of CHROME ALUM or **potassium chromium sulphate**, $KCr(SO_4)_2,12H_2O$, by reducing potassium dichromate with sulphur dioxide or alcohol in the presence of sulphuric acid

EXPT 54 **Preparation of chrome alum.**

Pour 100 c c of water on to 20 grams of finely-powdered potassium dichromate in a beaker, then stir and cautiously add 15 c c of concentrated sulphuric acid Slowly add 15 c c of alcohol to this product, stirring vigorously and keeping it below 60° C by immersion in cold water, otherwise a complex salt will be formed Warm the product to about 50° C and stir until all solid material is dissolved, then set aside to crystallise.

Chrome alum crystallises in purple octahedra, and is isomorphous with the corresponding aluminium salt It is used in the tanning of leather, the hides being steeped in a solution of the salt to produce a chrome-tanned leather, for which superior wear has been claimed

## Chromic Acid and its Derivatives.

**Chromium trioxide** or **chromic anhydride**, $CrO_3$, crystallises in crimson needles, when concentrated sulphuric acid is added to a concentrated solution of potassium dichromate

$$K_2Cr_2O_7 + H_2SO_4 = K_2SO_4 + 2CrO_3 + H_2O.$$

Expt 55 **Preparation of chromic acid.**

Potassium dichromate (3 grams) is dissolved in hot water (25 c c ) in a boiling tube, and concentrated sulphuric acid (25 c c ) is then cautiously added with stirring The mixture is allowed to cool slowly by placing it in a beaker of boiling water, so that large crystals are obtained, which can be separated from the mother-liquid by decanting on to a Buchner funnel, without using a filter-paper

Chromium trioxide is very soluble in water and has an exceptionally small temperature-coefficient (a saturated solution contains 57% $CrO_3$ at $-105°$ and 71% $CrO_3$ at the boiling-point of 127°), in striking contrast to sulphur trioxide, however, no hydrate has yet been isolated from the solutions The aqueous solutions are strongly acidic, and measurements of freezing-point and conductivity suggest that they contain **dichromic acid**, $H_2Cr_2O_7$, in equilibrium perhaps with much smaller amounts of **chromic acid**, $H_2CrO_4$

$$H_2Cr_2O_7 + H_2O \rightleftharpoons 2H_2CrO_4$$

Chromium trioxide melts without decomposition at 196°, but decomposes into chromic oxide, $Cr_2O_3$, and oxygen when heated more strongly It is a very powerful oxidising agent, *e g* absolute alcohol ignites when dropped on it; but, when diluted, it oxidises the alcohol to aldehyde (p 689)·

$$2C_2H_6O + O_2 = 2C_2H_4O + 2H_2O$$

**Chromates.**—Although chromic acid, $H_2CrO_4$, has not been isolated, a series of yellow CHROMATES exist, which are often isomorphous with the corresponding sulphates, *e g*

| | | | | |
|---|---|---|---|---|
| | $Na_2CrO_4,10H_2O$, | $K_2CrO_4$, | $BaCrO_4$, | $PbCrO_4$, |
| compare | $Na_2SO_4,10H_2O$, | $K_2SO_4$, | $BaSO_4$, | $PbSO_4$ |

**Potassium chromate**, $K_2CrO_4$, which is used in the laboratory as an oxidising agent and indicator, can be prepared directly from chromite, but even carbon dioxide converts it into the dichromate, and a caustic alkali must be used to make it from the dichromate

$$2K_2CrO_4 + CO_2 = K_2Cr_2O_7 + K_2CO_3,$$
$$K_2Cr_2O_7 + 2KOH = 2K_2CrO_4 + H_2O.$$

**Barium chromate**, $BaCrO_4$, and **lead chromate**, $PbCrO_4$, which are well known as confirmatory tests for barium and lead in qualitative analysis, are used as pigments under the names of LEMON YELLOW and CHROME YELLOW, a **basic lead chromate**, $PbO,PbCrO_4$, is used as CHROME RED for painting letter-boxes

**Dichromates**.—Chromic acid also forms a series of DICHROMATES, corresponding with the pyrosulphates **Sodium dichromate**, $Na_2Cr_2O_7$, is manufactured from chromite by heating the powdered mineral to bright redness in a reverberatory furnace with lime (and a little sodium carbonate) with free access of air In this operation the chromite is oxidised to calcium chromate

$$4FeCr_2O_4 + 8CaO + 7O_2 = 8CaCrO_4 + 2Fe_2O_3$$

On digesting the residue with hot sodium carbonate, calcium carbonate is precipitated and sodium chromate goes into solution This solution is concentrated and acidified with sulphuric acid, when sodium sulphate crystallises out, leaving a solution of sodium dichromate, from which deliquescent crystals of the **dihydrate**, $Na_2Cr_2O_7,2H_2O$, are deposited after further evaporation

$$2Na_2CrO_4 + H_2SO_4 = Na_2SO_4 + Na_2Cr_2O_7 + H_2O$$

**Potassium dichromate** is easily prepared from the above solution by adding potassium chloride, since the potassium salt is only sparingly soluble and separates in anhydrous orange-red crystals

$$2KCl + Na_2Cr_2O_7 = 2NaCl + K_2Cr_2O_7$$

The dichromates are used extensively as oxidising agents in presence of sulphuric acid, when chromic acid is reduced to chromic sulphate Thus dichromates liberate iodine quantitatively from iodides, and oxidise ferrous salts to ferric salts, sulphurous acid to sulphuric acid, and alcohol to aldehyde (p 689), etc

$$K_2Cr_2O_7 + 7H_2SO_4 + 6KI = 4K_2SO_4 + Cr_2(SO_4)_3 + 3I_2 + 7H_2O,$$
$$K_2Cr_2O_7 + 7H_2SO_4 + 6FeSO_4 = 3Fe_2(SO_4)_3 + Cr_2(SO_4)_3 + K_2SO_4 + 7H_2O$$
$$K_2Cr_2O_7 + H_2SO_4 + 3SO_2 = K_2SO_4 + Cr_2(SO_4)_3 + H_2O,$$
$$K_2Cr_2O_7 + 4H_2SO_4 + 3C_2H_6O = K_2SO_4 + Cr_2(SO_4)_3 + 3C_2H_4O + 7H_2O$$

Standard solutions for the volumetric analysis of iron, etc (p 429) are prepared by weighing out potassium dichromate, which, unlike the corresponding sodium compound, is not deliquescent, and can be prepared in a very high state of purity Sodium dichromate is used in preference to the potassium salt for organic oxidations, since it is cheaper and much more soluble in water

**Chromyl chloride**, $CrO_2Cl_2$, compare sulphuryl chloride, $SO_2Cl_2$, is prepared by distilling potassium dichromate with salt and excess of concentrated sulphuric acid The sulphuric acid liberates anhydrous hydrogen chloride from the salt, and this reacts with the dichromate to give chromyl chloride

$$4NaCl + 6H_2SO_4 + K_2Cr_2O_7 = 2KHSO_4 + 4NaHSO_4 + 2CrO_2Cl_2 + 3H_2O$$

An excess of sulphuric acid is used to prevent the hydrolysis of the acid chloride by the water which is formed in the above reaction

$$CrO_3 + 2HCl \rightleftharpoons CrO_2Cl_2 + H_2O$$

EXPT 56 **Preparation of chromyl chloride**

An intimate mixture of finely-ground potassium dichromate (50 grams) and sodium chloride (43 grams) is placed in a 500 c c distilling flask fitted with a thermometer, dropping funnel and water-cooled condenser (Fig 99). Concentrated sulphuric acid (150 c c ) is gradually added and the mixture heated carefully on a sand bath to distil off the chromyl chloride

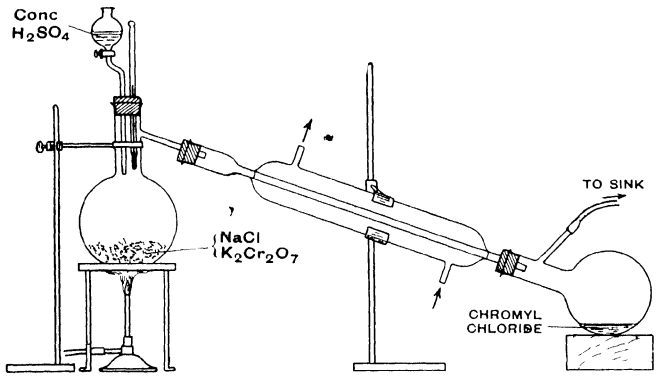



FIG 99 PREPARATION OF CHROMYL CHLORIDE

Chromyl chloride is a heavy blood-red liquid, resembling bromine It has a density of about 2, boils at 117°, and its vapour density corresponds with the formula $CrO_2Cl_2$ It is hydrolysed slowly by water and has the chemical and physical properties of an acid chloride (p 711), Cl $CrO_2$ Cl, and not of a salt When added to a saturated solution of potassium chloride it gives red crystals of **potassium chlorochromate,** Cl $CrO_2$ OK

$$CrO_2Cl_2 + KCl + H_2O = KCrO_3Cl + 2HCl$$

This compound, which is both a salt and an acid chloride, can also be prepared by adding powdered potassium dichromate to warm concentrated hydrochloric acid, and cooling the mixture until the chlorochromate begins to crystallise

**Perchromic acid.**—When hydrogen peroxide is added to a solution of chromic acid, a dark solution is produced from which ether extracts a blue product , this serves as a sensitive test both for hydrogen peroxide and for chromium The solution contains a **perchromic acid,** which can be isolated as a **pyridine salt,** $(C_5H_6N)CrO_5$, and is therefore formulated as $HCrO_5$ , but it is probable that other perchromic acids are also present, since a variety of salts has been prepared

## 25 MANGANESE Mn = 54 93

**Occurrence of manganese.**—Manganese is never found in the free state The **dioxide**, $MnO_2$, as PYROLUSITE (Greek, *πύρ*, fire, and *λύω*, I dissolve), has been known since the time of Pliny, as an agent for decolorising glass (see below) Other minerals are HAUSMANITE, $Mn_3O_4$, MANGANITE, $Mn_2O_3,H_2O$, and the **sulphides**, MnS and $MnS_2$

**Preparation and properties of manganese.**—(*a*) *Preparation* —Although metallic manganese has a lower melting-point than iron, it cannot be prepared readily by reducing the oxide in the blast furnace, since its melting-point is raised instead of being lowered by the presence of carbon Pig iron, however, usually contains manganese ; and large quantities of FERRO-MANGANESE are made by reducing mixed ores of iron and manganese in the blast furnace Pure manganese is prepared, like metallic chromium, by reducing the oxide with aluminium (Goldschmidt process)

(*b*) *Physical properties* —Manganese is a soft grey metal like iron It melts at 1230° and has a density of 7 4 It is isomorphous with $\gamma$-iron and is used to make MANGANESE STEELS , these are used for steel helmets and for tramway points and cross-overs on account of their extreme toughness and resistance to wear

(*c*) *Chemical properties* —Manganese does not readily oxidise in the air, but when heated it combines directly with oxygen, nitrogen, chlorine, boron, carbon, etc It decomposes water even in the cold, and dissolves in dilute acids to give hydrogen and bivalent MANGANOUS SALTS (cf iron) These are pale pink in colour, and isomorphous with the ferrous salts, whilst the tervalent MANGANIC SALTS are violet and isomorphous with ferric salts Unlike the ferric salts, however, the manganic salts decompose readily in solution, giving a soluble manganous salt and a precipitate of manganese dioxide As in the case of iron, there is no tendency to develop a higher electrovalence than *three*, but a valency of *four* is developed in the oxide, and still higher valencies are developed in the anions of salts such as $K_2MnF_6$, where the metal has a covalence of *six* whilst the complex anion has a negative electrovalence of *two*, and $K_2MnO_4$ and $KMnO_4$, where a covalence of *four* is associated with positive electrovalences of *two* and *three* on the central metallic atom of the anion (see p 306)

### MANGANOUS COMPOUNDS

**Manganous oxide**, MnO, is formed as a green powder by igniting the higher oxides in a stream of hydrogen (compare FeO and CoO) It is a basic oxide and dissolves in dilute acids to give manganous salts

**Manganous hydroxide**, $Mn(OH)_2$, is prepared as a white precipitate by adding an alkali to a solution of a manganous salt, but it rapidly turns brown on exposure to air, owing to oxidation It is a fairly strong base, since it forms a normal carbonate and is not precipitated by dilute ammonia and ammonium chloride

**Manganous carbonate**, $MnCO_3$, separates as a buff-coloured precipitate when sodium carbonate is added to a solution of a manganous salt Like calcium and magnesium carbonates, it dissolves in water containing carbon dioxide, forming the bicarbonate This, like ferrous bicarbonate, is oxidised by moist air liberating carbon dioxide and depositing manganic hydroxide, $Mn(OH)_3$, which is therefore associated with ferric hydroxide in sedimentary deposits

**Manganous chloride**, $MnCl_2,4H_2O$, and **manganous sulphate**, $MnSO_4,7H_2O$, separate from the solutions obtained by dissolving the metal, oxide, hydroxide, or carbonate in dilute hydrochloric and sulphuric acids, but above 8° the sulphate is deposited as a **pentahydrate**, $MnSO_4,5H_2O$, isomorphous with " blue vitriol " Double sulphates, *e g*

$$(NH_4)_2Mn(SO_4)_2,\ 6H_2O,$$

isomorphous with ferrous ammonium sulphate, can also be prepared

**Manganous sulphide,** MnS, is formed as a buff-coloured precipitate when ammonium sulphide is added to a neutral solution of a manganous salt It is readily dissolved by dilute acids, even by acetic acid , since zinc sulphide is insoluble in this acid, a mixture of the sulphides may be separated by this method

## Manganic Compounds

**Mangano-manganic oxide**, $Mn_3O_4$, is formed when any other oxide of manganese is heated strongly in the air It dissolves in cold concentrated sulphuric acid, giving a solution of manganous and manganic sulphates

$$Mn_3O_4 + 4H_2SO_4 = MnSO_4 + Mn_2(SO_4)_3 + 4H_2O$$

It is therefore regarded as a compound of MnO and $Mn_2O_3$ (compare $Fe_3O_4$)

**Manganic oxide**, $Mn_2O_3$, is prepared by heating manganese dioxide in a current of ammonia

$$6MnO_2 + 2NH_3 = 3Mn_2O_3 + N_2 + 3H_2O$$

It is a weakly basic oxide, which forms a series of tervalent MANGANIC SALTS These are much more difficult to prepare than manganous salts, since the relative stability of the bivalent and tervalent salts is reversed completely on passing from chromium to manganese A cold solution of manganese dioxide in concentrated hydrochloric acid is deep green in colour, and yields the **double salt**, $2KCl,MnCl_3$, or $K_2MnCl_5$, on addition of potassium chloride In the same way **manganic sulphate**, $Mn_2(SO_4)_3$, is formed as a dark green powder by the action of concentrated sulphuric acid on manganese dioxide at 140°, but even the alums derived from it are unstable in presence of water

## Compounds of Higher Valency

**Manganese dioxide**, $MnO_2$, occurs as PYROLUSITE, usually mixed with ferric oxide, since both oxides are deposited by atmospheric oxidation of the bicarbonate It is amphoteric, since it forms salts with bases,

*e.g.* **calcium manganite,** $CaMnO_3$ (p 276), but also yields **manganese tetrachloride,** $MnCl_4$, with ethereal hydrogen chloride at low temperatures When heated strongly, it loses oxygen, forming **mangano-manganic oxide,** $Mn_3O_4$, but in the preparation of oxygen it is generally used as a mere catalyst to promote the separation of oxygen from potassium chlorate With hot concentrated hydrochloric acid it gives chlorine and manganous chloride

$$MnO_2 + 4HCl = MnCl_4 + 2H_2O = MnCl_2 + Cl_2 + 2H_2O$$

Similarly, when heated with sulphuric acid it gives manganic sulphate and oxygen at 140°, but at higher temperatures manganous sulphate is left

$$2MnO_2 + 3H_2SO_4 = Mn_2(SO_4)_3 + 3H_2O + \tfrac{1}{2}O_2,$$
$$2MnO_2 + 2H_2SO_4 = 2MnSO_4 + O_2 + 2H_2O$$

In addition to serving as an ore in the preparation of manganese and manganese steels, manganese dioxide is used in the paint and varnish industry as a catalyst to promote the oxidation of " drying oils " to resins It is used to decolorise glass, since, when added to the melt, it oxidises green ferrous silicate to ferric silicate, the pale yellow colour of which is " neutralised " by the violet tint of manganic silicate On account of its oxidising properties, manganese dioxide is also used as a depolariser in the Leclanché cell, since it is cheap and possesses some electrical conductivity

The percentage of available oxygen in a specimen of manganese dioxide may be estimated by heating a known weight of it with dilute sulphuric acid and excess of oxalic acid, which it oxidises to carbon dioxide and water, the excess of oxalic acid is then determined with standard permanganate

$$MnO_2 + H_2SO_4 + (COOH)_2 = 2CO_2 + MnSO_4 + 2H_2O$$

The available oxygen may also be determined by heating a known quantity of the oxide with concentrated hydrochloric acid, passing the evolved chlorine through potassium iodide solution in Liebig bulbs, and titrating the iodine with thiosulphate (p 424)

**Manganates and permanganates.**—When manganese dioxide is fused with an alkali in presence of air, or of an oxidising agent such as potassium chlorate or nitrate, a green mass containing a MANGANATE is produced, *e g*

$$4KOH + 2MnO_2 + O_2 = 2K_2MnO_4 + 2H_2O$$

When the fused mass is extracted with water a green solution is obtained, which turns purple on heating or on further dilution, owing to the formation of a PERMANGANATE

$$3K_2MnO_4 + 2H_2O = 4KOH + 2KMnO_4 + MnO_2$$

This change is assisted by passing carbon dioxide into the boiling solution of the manganate, since the manganates are only stable in presence of free alkali

$$3K_2MnO_4 + 4CO_2 + 2H_2O = 2KMnO_4 + 4KHCO_3 + MnO_2.$$

The same oxidation can also be effected by the action of chlorine

$$2K_2MnO_4 + Cl_2 = 2KCl + 2KMnO_4,$$

compare $2K_4Fe(CN)_6 + Cl_2 = 2KCl + 2K_3Fe(CN)_6$

EXPT 57 **Preparation of potassium permanganate.**

A mixture of caustic potash (60 grams) and potassium chlorate (30 grams) is melted in an iron dish which is clamped securely on a tripod stand Finely powdered manganese dioxide (60 grams) is then added in small quantities at a time (say 4 grams every 30 sec ), the mixture being stirred vigorously with an iron rod and heated to maintain it in a molten condition The heating must be as moderate as possible at the start, otherwise the chlorate will give up much of its oxygen to the air, but stronger heating will be necessary when most of the manganese dioxide has been added, since the mixture stiffens

The above product is heated strongly for 40 minutes and stirred more or less continuously It is then allowed to cool, and after being powdered up in a mortar, is boiled gently (to avoid excessive evaporation) for about 1½ hours with 700 c c of water in a large beaker A stream of carbon dioxide is passed into the liquid during the whole of this period to speed up the conversion of the manganate into permanganate, and the transformation is judged to be complete when a drop of the liquid no longer gives a green tint to filter paper The solid matter (consisting mainly of manganese dioxide) is allowed to settle for a few minutes, and the clear upper liquid is then filtered through a thick plug of glass wool (why not filter paper ?) in a funnel The solution is evaporated in a basin until a drop of it deposits a good crop of crystals when rubbed on a watch-glass , it is then filtered once again and left to crystallise If the yield of crystals is small, the mother liquid should be evaporated to half its bulk and left to crystallise again

Potassium permanganate crystallises from water in anhydrous purple prisms which are isomorphous with potassium perchlorate It is only moderately soluble in water (5·3 parts in 100 parts of water at 15°) When heated alone or boiled with a strong alkali, oxygen is evolved and a manganate is formed

$$2KMnO_4 = K_2MnO_4 + MnO_2 + O_2,$$
$$4KMnO_4 + 4KOH = 4K_2MnO_4 + 2H_2O + O_2$$

When dissolved in cold concentrated sulphuric acid, potassium permanganate gives a green solution which appears to contain a **permanganic sulphate,** $(MnO_3)_2SO_4$ If this solution is diluted with ice-cold water, **manganese heptoxide,** $Mn_2O_7$, separates out as an unstable reddish-brown liquid With much water this liquid forms a violet solution which possibly contains **permanganic acid,** $HMnO_4$, an unstable compound which can be prepared by adding dilute sulphuric acid to a solution of barium permanganate

**Oxidation by permanganates.**—The most striking property of permanganates is their power of oxidising substances. Thus in acid solution

permanganates oxidise ferrous salts to ferric salts, oxalic acid to carbon dioxide (at 70°), nitrites to nitrates and hydriodic acid to iodine, as represented by the equations

$$10FeSO_4 + 2KMnO_4 + 8H_2SO_4 = 5Fe_2(SO_4)_3 + K_2SO_4 + 2MnSO_4 + 8H_2O,$$
$$5(COOH)_2 + 2KMnO_4 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 10CO_2 + 8H_2O,$$
$$5KNO_2 + 2KMnO_4 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 5KNO_3 + 3H_2O,$$
$$10KI + 2KMnO_4 + 8H_2SO_4 = 6K_2SO_4 + 2MnSO_4 + 5I_2 + 8H_2O$$

In alkaline solution, however, iodides are oxidised to iodates, *e g*

$$KI + 2KMnO_4 + H_2O = KIO_3 + 2KOH + 2MnO_2$$

On the other hand hydrogen peroxide is reduced by permanganates, *e g*

$$5H_2O_2 + 2KMnO_4 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 8H_2O + 5O_2$$

Under suitable conditions all of the above reactions take place quantitatively, they are therefore discussed in greater detail in Chapter XXX

It should be noted that the above reactions take place mainly between ions and not unionised molecules, since with the exception of oxalic acid, water and hydrogen peroxide, all the substances on the left-hand side of the equations are strong electrolytes (p 622) The molecular equations have been given because it is easier for the inexperienced student to learn these and then deduce the ionic equations Thus writing ions for the molecules in the first equation at the top of the page gives,

$$10Fe^{++} + 2K^+ + 2MnO_4^- + 16H^+ + 18SO_4^{--} = 10Fe^{+++} + 2K^+ + 2Mn^{++} + 18SO_4^{--} + 18H_2O,$$

which simplifies to :

$$5Fe^{++} + MnO_4^- + 8H^+ = 5Fe^{+++} + Mn^{++} + 4H_2O$$

Similarly, the other reactions may be represented as follows

$$5(COOH)_2 + 2MnO_4^- + 6H^+ = 2Mn^{++} + 10CO_2 + 8H_2O,$$
$$5NO_2^- + 2MnO_4^- + 6H^+ = 2Mn^{++} + 5NO_3^- + 3H_2O,$$
$$10I^- + 2MnO_4^- + 16H^+ = 2Mn^{++} + 5I_2 + 8H_2O,$$
$$I^- + 2MnO_4^- + H_2O = 2MnO_2 + IO_3^- + 2OH^-,$$
$$5H_2O_2 + 2MnO_4^- + 6H^+ = 2Mn^{++} + 5O_2 + 8H_2O$$

**Estimation of Manganese.**—Manganese is estimated gravimetrically as the oxide, $Mn_3O_4$, by ignition after precipitating the metal as carbonate, sulphide or peroxide Manganous salts may also be estimated by precipitating as the double phosphate, $NH_4MnPO_4$, and igniting this to give the pyrophosphate, $Mn_2P_2O_7$, as in the case of magnesium

$$2NH_4MnPO_4 = Mn_2P_2O_7 + 2NH_3 + H_2O$$

# *PART IV*

# ANALYSIS

## CHAPTER XXVIII

## QUALITATIVE ANALYSIS OF A PURE SUBSTANCE

**General considerations.**—Qualitative analysis in inorganic chemistry is concerned chiefly with the identification of the radicals of which an unknown salt is composed Some of the tests depend on reduction to the metal, or burning to an oxide, or the like , but, since salts either are electrolytes, or are similar in composition to electrolytes, the majority of the tests depend on IONIC REACTIONS, *i e* on an interchange of ions, whereby insoluble or coloured products are formed, *e g*

$$\overset{+}{\mathrm{Ag}}\overset{-}{\mathrm{NO_3}} + \overset{+}{\mathrm{K}}\overset{-}{\mathrm{I}} = \overset{+}{\mathrm{Ag}}\overset{-}{\mathrm{I}} + \overset{+}{\mathrm{K}}\overset{-}{\mathrm{NO_3}}$$

| Silver nitrate (solution) | Potassium iodide (solution) | Silver iodide (yellow solid) | Potassium nitrate (solution) |
|---|---|---|---|

In addition to serving as a means of identification of the acid and basic radicals of a salt, these reactions should be studied as illustrations of the physico-chemical principles on which they depend, *e g* the laws of mass action (p 555) and of solubility-products (p 636) , they are also of value as a practical introduction to the chemistry of the metals and of the acid radicals, and for this reason the groups into which the elements are sorted out in analysis should be compared with the grouping of the elements in the Periodic Classification, when many similarities will be observed

It is also significant that, with the exception of silver and magnesium, the metals are precipitated as compounds which are of considerable importance in mineralogy Thus the metals of Groups 2 and 4 are found principally as *sulphides*, the metals of Group 3 as *oxides*, and those of Group 5 as *carbonates*

In the scheme given below, the analysis of the metallic radicals is considered before that of the acid radicals, because (i) it is generally easier to identify the metal than the acid, (ii) some of the wet tests for acid radicals require a previous knowledge of the metals which are present (p 393), and (iii) the identification of the metal often helps in the recognition of the acid, *e g* a soluble calcium salt cannot be the carbonate, oxalate,

tartrate, citrate, fluoride or phosphate, but might be the chloride, bromide, iodide or nitrate, etc

The tests used in analysis can be divided into two classes, viz (i) dry tests, and (ii) wet tests Dry tests are carried out on the solid direct, *e g* the ignition of the substance in a test tube or on a charcoal block, whilst wet tests depend on reactions in solution. In this chapter the wet tests for metals are described first, because they are generally quicker to perform, and usually give more definite information, but the more important dry tests have been summarised on page 395, as they provide useful confirmatory evidence, particularly for substances which can only be got into solution by special methods

**Preparation of the solution.**—A dilute solution of the substance is obtained in the first of the following solvents in which the substance can be dissolved, if necessary by heating (i) distilled water, (ii) dilute hydrochloric acid, (iii) concentrated hydrochloric acid, (iv) dilute nitric acid, (v) concentrated nitric acid, (vi) aqua regia When concentrated acids are used, the resulting solution must be diluted, otherwise the test in Group 2 may fail

It is important to realise that substances which dissolve in acids, but not in water, do so because an ionic change has taken place Thus calcium oxalate dissolves to a slight extent in water to give oxalate ions as indicated by the equation

$$\underset{\text{(solid)}}{CaC_2O_4} \rightleftharpoons \underset{\text{(solution)}}{Ca^{++} + C_2O_4^{--}} \qquad (i)$$

The addition of an acid converts some of the oxalate ions into oxalic acid

$$C_2O_4^{--} + 2H^+ \rightleftharpoons H_2C_2O_4 \qquad (ii)$$

It therefore displaces the equilibrium (i) from left to right, with the result that more calcium oxalate dissolves The same considerations may be applied to other substances which dissolve in dilute acids In the case of carbonates, however, a further change takes place, since carbonic acid is unstable and breaks down into carbon dioxide, which escapes as a gas

If a substance will not dissolve in any of the above solvents,* it should be examined in the dry way as explained on page 395, whilst a portion of it is fused for a few minutes in a crucible with four times its weight of FUSION MIXTURE, containing equal amounts of sodium and potassium carbonates Insoluble salts, such as barium and lead sulphates, are thus converted into the carbonate or oxide, which can then be dissolved in dilute nitric or hydrochloric acid

$$Na_2CO_3 + BaSO_4 = Na_2SO_4 + BaCO_3,$$
$$Na_2CO_3 + PbSO_4 = PbO + CO_2 + Na_2SO_4$$

The fused mass is digested with boiling water and filtered The filtrate

* Common substances insoluble in acids are silica, silicates, sulphates of lead, barium and strontium, halides of silver, and finally stannic, ferric, chromic and aluminium oxides, which are rendered soluble by fusion with potassium bisulphate and not with fusion mixture

is kept for the identification of the acid radical, whilst the insoluble residue is washed free of alkali salts before being dissolved in dilute acid However, metals such as tin, aluminium, chromium, manganese and zinc, which have amphoteric oxides, may pass into the filtrate as soluble alkali salts. The filtrate may have to be tested therefore for the metal as well as for the acid radical If the solid is unaffected by fusion with the alkali carbonates, it should be heated with potassium bisulphate (see footnote, p 378).

If the original substance is a metal, it is generally convenient to dissolve it in rather strong nitric acid, and to evaporate off the surplus acid before diluting with water Dilute nitric acid, or concentrated hydrochloric acid, are sometimes better solvents Thus lead dissolves more readily in dilute than in concentrated nitric acid, whilst aluminium is nearly insoluble in nitric acid, but easily soluble in concentrated hydrochloric acid

## Detection of Metals

**Identification of the metal** --In the scheme outlined below, the common metals have been divided into six main groups according to their behaviour towards certain reagents Separate portions of the solution of the unknown substance, prepared as recommended above, are treated with successive group reagents until a positive result is obtained Special tests are then applied to decide which member of the ascertained group is present

### Group 1. Dilute hydrochloric acid.

*Silver, mercurous mercury and lead are precipitated as chlorides by the addition of dilute hydrochloric acid*

(i) $AgNO_3 + HCl = AgCl + HNO_3$ or $\overset{+}{Ag} + \overset{-}{Cl} = \overset{+}{Ag}\overset{-}{Cl}$,

(ii) $Hg_2(NO_3)_2 + 2HCl = Hg_2Cl_2 + 2HNO_3$ or $\overset{++}{Hg_2} + 2\overset{-}{Cl} = Hg_2Cl_2$,

(iii) $Pb(NO_3)_2 + 2HCl = PbCl_2 + 2HNO_3$ or $\overset{++}{Pb} + 2\overset{-}{Cl} = \overset{++}{Pb}\overset{--}{Cl_2}$

The precipitate is decanted and heated with excess of ammonia which (i) dissolves silver chloride as a soluble complex salt or "ammine" (p 324), (ii) blackens mercurous chloride, but (iii) is without effect on lead chloride The blackening of mercurous chloride is due to the separation of finely-divided mercury, which masks the white colour of the ammino-mercuric chloride

$$Hg_2Cl_2 + 2NH_3 = Hg + NH_2{\cdot}Hg{\cdot}Cl + NH_4Cl$$

Lead chloride is also distinguished by the fact that it is moderately soluble in hot water, its solubility even in cold water is sufficient to prevent its precipitation from very dilute solutions, but in such cases it is precipitated and identified in the next group

Confirmatory tests for these metals are given in the "Summarised Tables for the Identification of One Metal" (Table 31, p 384).

**Group 2. Hydrogen sulphide in acid solution.**

*The sulphides of arsenic (yellow), antimony (orange), tin (brown stannous and yellow stannic), lead (black), mercury (black mercuric), copper (brownish black), bismuth (brownish black), and cadmium (yellow) are precipitated when hydrogen sulphide is passed into solutions of these metals made slightly acid with hydrochloric acid*

(i) $HgCl_2 + H_2S = HgS + 2HCl$ (so also Pb, Cu, Cd),

(ii) $SnCl_2 + H_2S = SnS + 2HCl$,

$SnCl_4 + 2H_2S = SnS_2 + 4HCl$,

(iii) $As_2O_3 + 3H_2S = As_2S_3 + 3H_2O$,
$As_2O_5 + 5H_2S = As_2S_3 + 2S + 5H_2O$ } (so also Sb),

(iv) $2BiCl_3 + 3H_2S = Bi_2S_3 + 6HCl$

Iron, cobalt, nickel, zinc and manganese, which also form insoluble sulphides, are not precipitated in this group, because the acid represses the ionisation of the hydrogen sulphide to such an extent that the solubility-products (p 636) of their sulphides are not reached

In equations (iii) the formulae of the oxides are used because quinquevalent arsenic and antimony are always, and the tervalent elements are sometimes, present in solution in the acid radical, *e g* sodium arsenate, $Na_2HAsO_4$, and sodium arsenite, $NaAsO_2$ The separation of sulphur can be attributed to the oxidising action of arsenic acid, other oxidising agents may also precipitate sulphur in this group, but it can be easily distinguished from a sulphide precipitate by its milky appearance

The sulphide precipitate is coagulated by heating, washed with water and then digested with hot yellow ammonium sulphide (a mixture of ammonium polysulphides, thiosulphate, etc, p 185), which dissolves the sulphides of arsenic, antimony and tin, but not the other sulphides, although copper sulphide is slightly soluble The solubility of the above sulphides is due to the formation of THIOSALTS

$$As_2S_3 + (NH_4)_2S = 2(NH_4)AsS_2 \quad \text{(Ammonium thioarsenite)}$$
$$\text{cf } (NH_4)NO_2$$
$$As_2S_3 + 3(NH_4)_2S + 2S = 2(NH_4)_3AsS_4 \quad \text{(Ammonium thioarsenate)}$$
$$\text{cf } (NH_4)_3PO_4$$
$$As_2S_5 + 3(NH_4)_2S = 2(NH_4)_3AsS_4 \quad \text{(Ammonium thioarsenate)}$$

Antimony behaves in the same way as arsenic, but tin only forms a thiostannate, with the result that stannous sulphide is only dissolved when polysulphides are present in the ammonium sulphide

$$SnS + (NH_4)_2S_2 = (NH_4)_2SnS_3, \quad \text{cf } (NH_4)_2CO_3$$
$$SnS_2 + (NH_4)_2S = (NH_4)_2SnS_3, \quad \text{cf } (NH_4)_2CO_3$$

Arsenic, antimony, and tin differ in the colour of their sulphides, although stannic and arsenic sulphides are somewhat similar, but may be distinguished by MARSH'S TEST (p 222) This depends upon the fact that "nascent hydrogen" will reduce arsenic and antimony, but not tin, to their gaseous hydrides, arsine, $AsH_3$, and stibine, $SbH_3$ If the gaseous mixture of hydrogen and hydrides is then ignited, the heat of the flame

decomposes the arsine or stibine, and the metals can be condensed on a cold surface as a black stain A suspension of bleaching powder, or a solution of a hypochlorite, oxidises and dissolves the arsenic stain, but is without action on antimony, whilst tin of course gives no stain The test can be carried out by placing the original substance with arsenic-free zinc and hydrochloric acid in a test tube fitted with a delivery tube (Fig 100) The jet of crude hydrogen issuing from the delivery tube is ignited, and allowed to impinge on the inside of a cold evaporating basin Further tests are given in Table 31, not only for the confirmation of these metals, but also for deciding the valency of the metal in the compound

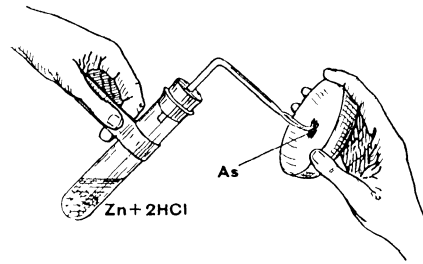



FIG 100 MARSH'S TEST FOR ARSENIC

The remaining metals of the group, with the exception of cadmium, form black or brown-black sulphides They may be distinguished from one another by the behaviour of their iodides Potassium iodide is added to a neutral, or nearly neutral, solution of the substance, when

(i) *Lead* gives a yellow precipitate of lead iodide, $PbI_2$, which is insoluble in potassium iodide unless a *large* excess is used

(ii) *Mercury* gives a red precipitate of mercuric iodide, $HgI_2$, which dissolves in excess of potassium iodide to give a colourless solution of potassium mercuric iodide, $K_2HgI_4$

(iii) *Bismuth* gives a brown precipitate of bismuth iodide, $BiI_3$, which dissolves in excess of iodide to give a yellow solution of the complex salt, $KBiI_4$, as well as in acids

(iv) *Cupric copper* liberates iodine and gives a cream precipitate of cuprous iodide, $Cu_2I_2$, insoluble in excess of iodide

$$2CuSO_4 + 4KI = Cu_2I_2 + 2K_2SO_4 + I_2$$

Copper in any case is easy to identify because dilute cupric solutions are always blue or green, and cuprous solutions, although colourless, rapidly turn blue or green owing to oxidation by the atmosphere It is for this reason that no special tests have been given for cuprous copper

(v) *Cadmium* gives no precipitate because the iodide is soluble in water

**Group 3. Ammonium hydroxide and ammonium chloride.**

*The tervalent metals, aluminium, chromic chromium, and ferric iron are precipitated as hydroxides by the addition of ammonium chloride and ammonia to their solutions, e g*

$$FeCl_3 + 3NH_4OH = Fe(OH)_3 + 3NH_4Cl$$

The ammonium chloride provides a large concentration of ammonium ions, which represses the ionisation of ammonium hydroxide to such an extent that the sparingly soluble hydroxides of cobalt, nickel, zinc, and manganese are not precipitated, since their solubility-products are not

exceeded (p 636) Ferrous iron is a border-line metal, in that it is only partially precipitated under these conditions The original solution is therefore boiled with a little concentrated nitric acid, before the addition of ammonium chloride and ammonia, in order to oxidise ferrous iron to the ferric state It is important to remember that manganese will be precipitated in this group unless plenty of ammonium chloride is added first, and then only just sufficient ammonia to render the solution alkaline to litmus In order to confirm the identification of these three metals, the original solution is heated with caustic soda, when

(i) *Aluminium* gives a white precipitate of aluminium hydroxide, soluble in excess of alkali

$$AlCl_3 + 3NaOH = Al(OH)_3 + 3NaCl,$$
$$Al(OH)_3 + NaOH = NaAlO_2 + 2H_2O$$

(ii) *Ferrous iron* and *ferric iron* give respectively a green precipitate of ferrous hydroxide, $Fe(OH)_2$, and a red-brown precipitate of ferric hydroxide, $Fe(OH)_3$, both of which are insoluble in excess of alkali

(iii) *Chromic chromium* gives a green precipitate of the hydroxide, $Cr(OH)_3$, which is soluble in excess of alkali, but is reprecipitated by boiling Chromium is not precipitated here when it is present as a stable anion, *e g* in a chromate such as $K_2CrO_4$, and must therefore be reduced by boiling with alcohol and dilute sulphuric acid before adding the group reagents The presence of a chromate will have been indicated already by the fact that the yellow or orange-red acid solution turned green on adding hydrogen sulphide in Group 2

$$\underset{\text{yellow}}{2K_2CrO_4} + 2HCl = \underset{\text{orange-red}}{K_2Cr_2O_7} + 2KCl + H_2O,$$

$$\underset{\text{orange-red}}{K_2Cr_2O_7} + 8HCl + 3H_2S = 2KCl + \underset{\text{green}}{2CrCl_3} + 3S + 7H_2O$$

The analysis of these metals is complicated by the fact that certain salts of the metals of succeeding groups are insoluble in neutral or alkaline solutions, and therefore are also precipitated in this group, *e g*

(i) The *phosphates* of calcium, strontium, barium and magnesium, cobalt, nickel, manganese and zinc phosphates may also be partially precipitated

(ii) The *oxalates*, *tartrates*, *fluorides*, etc , of calcium, strontium and barium

The salts enumerated above are white, with the exception of cobalt and nickel phosphates, but are easily distinguished from aluminium hydroxide because they are insoluble in excess of caustic soda Their presence will also have been indicated by the fact that the original substance would not dissolve in water There is therefore little likelihood of their being confused with aluminium, chromium or iron (see Table 31 for their conversion into soluble salts)

**Group 4. Hydrogen sulphide in alkaline solution.**

*The sulphides of nickel (black), cobalt (black), manganese (buff) and zinc (white) are precipitated when hydrogen sulphide is passed into solu-*

*tions of these metals, made alkaline with ammonium chloride and ammonia*

$$MSO_4 + H_2S + 2NH_4OH = MS + (NH_4)_2SO_4 + 2H_2O,$$

where M = Ni, Co, Mn, or Zn

These sulphides are not usually precipitated by the mere addition of hydrogen sulphide to neutral solutions of the metals, because the acid liberated by the double decomposition tends to reverse the action

$$NiSO_4 + H_2S \rightleftharpoons NiS + H_2SO_4$$

Zinc sulphide, however, is precipitated in the presence of weak acids such as acetic acid, since its solubility is little greater than that of a sulphide of Group 2, *e g*

$$(CH_3\ CO{\cdot}O)_2Zn + H_2S \rightleftharpoons ZnS + 2CH_3\ CO\ OH\ \text{(Acetic acid)}$$

A solution of ammonium sulphide can be used in place of hydrogen sulphide , but it must be freshly prepared, as it is readily oxidised by air to the sulphate, which would precipitate barium and strontium, metals of the next group

The above metals are distinguished from one another by adding caustic soda to the solution of the unknown salt, when

(i) *Nickel* (green) and *cobalt* (blue or pink, p 346) are precipitated as hydroxides, which do not dissolve in excess of alkali

$$CoSO_4 + 2NaOH = Co(OH)_2 + Na_2SO_4$$

(ii) *Manganese* gives a whitish precipitate of manganous hydroxide, $Mn(OH)_2$, which, when shaken with air, rapidly oxidises to a brown mass of variable composition, *e g* $xMnO, yMnO_2, zH_2O$

(iii) *Zinc* gives a white precipitate of zinc hydroxide, $Zn(OH)_2$, which is converted into soluble sodium zincate by excess of alkali

$$Zn(OH)_2 + 2NaOH = Na_2ZnO_2 + 2H_2O$$

Table 31 (p 387) contains additional tests for these metals.

**Group 5. Ammonium carbonate with ammonium chloride and ammonia.**

*The carbonates of calcium, strontium and barium are thrown down as white precipitates when ammonium carbonate solution is added to solutions of their salts already containing ammonium chloride and ammonia*

The ammonium chloride prevents the precipitation of magnesium in this group, by forming a soluble double salt, $(NH_4)_2Mg(CO_3)_2$, whilst the presence of a little ammonia ensures that the solution is not acid The metals are distinguished from one another by making use of the different solubilities of their sulphates Thus, the addition of a saturated solution of calcium sulphate to the original solution immediately precipitates barium sulphate, whilst strontium sulphate is only thrown down on boiling the solution, or leaving it to stand

$$BaCl_2 + CaSO_4 = BaSO_4 + CaCl_2$$

The metals are also easily identified by the characteristic colours which they impart to the flame of a Bunsen burner (p 397)

**Group 6. No special group reagent.**

The remaining metals, magnesium, sodium and potassium, together with the ammonium radical, are placed for convenience in one group, although there is no group reagent The original solution is boiled with caustic soda, when

(i) *Magnesium* gives a white precipitate of magnesium hydroxide, $Mg(OH)_2$, insoluble in excess of alkali (see note 12, page 389)
(ii) *Ammonium* salts give ammonia gas
(iii) *Sodium* and *potassium* give no reaction.

The latter metals may be distinguished by the characteristic yellow and violet colours which they impart to a flame, and by the fact that moderately dilute solutions of potassium salts give a yellow precipitate with sodium cobaltinitrite

$$3KCl + Na_3Co(NO_2)_6 = K_3Co(NO_2)_6 + 3NaCl.$$

Magnesium is confirmed by boiling the solution with ammonium chloride, ammonia and ammonium phosphate, when a white precipitate of magnesium ammonium phosphate, $Mg(NH_4)PO_4$, is formed.

TABLE 31 SUMMARISED TABLES FOR THE IDENTIFICATION OF ONE METAL

See also notes (1) to (12), pp 388-389

Portions of the solution of the unknown substance, prepared as recommended on page 378, are tested as follows

**Group 1.**

| Add dilute HCl, a white precipitate indicates the chloride of | Decant liquid and shake precipitate with excess of $NH_3$ | Confirmatory tests with original solution unless stated otherwise |
|---|---|---|
| SILVER | Dissolves (1) | (i) Brown precipitate of $Ag_2O$ with NaOH, insoluble in excess<br>(ii) In neutral solution, crimson precipitate with $K_2CrO_4$ |
| MERCUROUS MERCURY | Blackens | (i) Black precipitate of $Hg_2O$ with NaOH, insoluble in excess<br>(ii) Heat solid in ignition tube with solid $Na_2CO_3$, grey sublimate of Hg at cold end (2) |
| LEAD | Unaffected | (i) White precipitate of $Pb(OH)_2$ with NaOH, soluble in excess<br>(ii) Yellow precipitate with $K_2CrO_4$, soluble in NaOH |

**Group 2.**

| Add excess of $H_2S$ to a solution just acid with HCl, heat (3) A precipitate (4) indicates a sulphide of | Wash, and digest sulphide precipitate with hot yellow ammonium sulphide | Confirmatory tests with original solution unless stated otherwise |
|---|---|---|
| ARSENIC (yellow). | Soluble. | (i) Marsh's test (p 380)<br>(ii) Gutzeit's test (5)<br>(iii) Arsenites give a yellow precipitate, arsenates a red precipitate with neutral silver nitrate (6) |
| ANTIMONY (orange) | Soluble | (i) and (ii) as above<br>(iii) Distinguish $Sb^{III}$ from $Sb^{V}$ by $Ag_2O$ test (7) |
| STANNOUS TIN (brown) | Soluble | (i) No stain in Marsh's test |
| STANNIC TIN (dirty yellow) | Soluble | (ii) $Sn^{II}$, but not $Sn^{IV}$, reduces mercuric chloride to insoluble mercurous chloride |
| LEAD (8) (black) | Insoluble | (i) Yellow precipitate of $PbI_2$ with KI, which only dissolves in a *large* excess of KI<br>(ii) See Group 1 |
| MERCURY (black) | Insoluble | (i) Red precipitate of $HgI_2$ with KI, soluble in excess<br>(ii) NaOH gives yellow precipitate, HgO, insoluble in excess<br>(iii) Dry test as mercurous (ii) in Group 1 |
| BISMUTH (brownish black) | Insoluble | (i) Brown precipitate of $BiI_3$ with KI, but yellow solution with excess KI or HCl (p 381)<br>(ii) White precipitate of $Bi(OH)_3$ with ammonia, insoluble in excess<br>(iii) BiOCl test (9). |
| COPPER (brownish black). | Almost insoluble | (i) Cream precipitate of CuI and brown soln of iodine with KI<br>(ii) Addition of $NH_3$ gives first a light blue precipitate of $Cu(OH)_2$ and then a deep blue solution of $Cu(NH_3)_4(OH)_2$ |
| CADMIUM (yellow). | Insoluble. | (i) Nothing with KI<br>(ii) White precipitate of $Cd(OH)_2$ with $NH_3$, soluble in excess |

**Group 3.**

| Boil original* solution with 1 c c conc $HNO_3$, add $NH_4Cl$, then $NH_3$, drop by drop until just alkaline, boil, a ppt indicates | Test original solution with NaOH | Confirmatory tests with original solution unless stated otherwise |
|---|---|---|
| ALUMINIUM (white) | White gelatinous precipitate, $Al(OH)_3$, easily soluble in excess NaOH | Hydroxide (or solid salt + $Na_2CO_3$) heated on charcoal block gives white infusible residue, which is turned blue by adding $Co(NO_3)_2$ solution and reheating |
| FERRIC IRON (red-brown) | Dirty green, $Fe(OH)_2$, insoluble in excess NaOH, or red-brown, $Fe(OH)_3$, insoluble in excess NaOH | (i) $K_4Fe(CN)_6$ gives { light blue precipitate (ferrous), dark blue precipitate (ferric)<br>(ii) $K_3Fe(CN)_6$ gives { dark blue (ferrous), no precipitate (ferric)<br>(iii) KCNS gives blood-red colour with ferric, nothing with pure ferrous |
| CHROMIUM (blue-green) | Green precipitate, $Cr(OH)_3$, soluble in excess NaOH, reprecipitated by boiling | (i) Fuse hydroxide precipitate with $Na_2O_2$ to give yellow mass of chromate, confirm chromate by lead test (ii)<br>(ii) Red or yellow, $Cr^{VI}$, reduced to green, $Cr^{III}$, by $SO_2$ solution |
| PHOSPHATES of Ca, Sr, Ba, sometimes also Mn and Zn (white) | White precipitate, insoluble in excess NaOH | Confirm phosphate by molybdate test (p 393) The phosphate is removed as ferric phosphate or $FePO_4$ (10), as follows dissolve ammonia precipitate in least possible dilute HCl, add excess $NH_4Ac$ and a few drops of acetic acid, followed by ferric chloride solution The latter is added drop by drop until the red colour of ferric acetate is produced The mixture is boiled to precipitate surplus ferric chloride as basic acetate, and then filtered, filtrate to Groups 4 and 5 |

* See p 382 for treatment of chromates

**Group 3**—*Cont*

| Boil original solution with 1 c c conc $HNO_3$, add $NH_4Cl$, then $NH_3$, drop by drop until just alkaline, boil, a ppt indicates | Test original solution with NaOH | Confirmatory tests with original solution unless stated otherwise |
|---|---|---|
| OXALATE, FLUORIDE, BORATE, etc of Ca, Sr, Ba (white) | White precipitate, insoluble in excess NaOH | (i) Oxalate is ignited to give carbonate (ii)<br>(ii) Borates, fluorides, etc are converted into the carbonate by fusion mixture and the residue washed free from alkali salts<br>The carbonate from (i) and (ii) is dissolved in dilute HCl and the solution tested for metals of Group 5 |
| SILICA (white) | Add concentrated HCl to original solid and evaporate to dryness A white residue insoluble in concentrated HCl indicates silica | |

**Group 4**

| Pass $H_2S$ into solution made alkaline with $NH_4Cl + NH_3$, a ppt indicates | Add NaOH to original solution | Confirmatory tests with original solid or solution |
|---|---|---|
| NICKEL (black) | Green precipitate, $Ni(OH)_2$, insoluble in excess | (i) A solution made alkaline with ammonium chloride and ammonia gives a red precipitate with dimethylglyoxime (p 708)<br>(ii) Violet-brown and grey borax beads (p 396) |
| COBALT (black) | Blue precipitate, turning pink when boiled | (i) Nothing with dimethylglyoxime in presence of excess of ammonia<br>(ii) Blue borax bead in both flames |
| MANGANESE (buff) | Dirty white precipitate, $Mn(OH)_2$, insoluble in excess, rapidly oxidised to brown $Mn_2O_3$ by air | (i) Fuse solid on porcelain with $Na_2CO_3 + NaClO_3$ to give purple-green mass of manganate<br>(ii) $Mn^{III}$, $Mn^{IV}$, $Mn^{VI}$ give $Cl_2$ with hot concentrated HCl<br>(iii) Violet and colourless borax beads |
| ZINC (white) | White precipitate, $Zn(OH)_2$, soluble in excess | Heat solid with $Na_2CO_3$ on charcoal block, yellow infusible mass turns white on cooling Reheating with a drop of $Co(NO_3)_2$ solution gives a bright green mass |

**Group 5**

| Add $NH_4Cl,NH_3$ and $(NH_4)_2CO_3$ A white precipitate indicates a carbonate of | Add saturated $CaSO_4$ solution to original solution | Confirmatory tests with original solid or solution |
|---|---|---|
| BARIUM | Immediate white precipitate | (i) Flame test, green (p 397)<br>(ii) Yellow precipitate with $K_2CrO_4$, insoluble in acetic acid |
| STRONTIUM | White precipitate on boiling | (i) Flame test, crimson<br>(ii) No precipitate with $K_2CrO_4$ if dilute, or if acetic acid is present |
| CALCIUM | Nothing | (i) Flame test, orange-red<br>(ii) No precipitate with $K_2CrO_4$<br>(iii) White precipitate with ammonium oxalate, insoluble in acetic acid |

**Group 6.**

| | Boil original solution with NaOH(12) | Confirmatory tests |
|---|---|---|
| MAGNESIUM | White precipitate insoluble in excess | Boil solution with $NH_4Cl,NH_3$ and $(NH_4)_2HPO_4$ to give white precipitate of $Mg(NH_4)PO_4$ |
| AMMONIUM | Ammonia evolved | Ammonia detected by smell and yellow coloration with Nessler's solution, p 340 |
| SODIUM | — | Flame test, yellow |
| POTASSIUM | — | (i) Flame test, violet<br>(ii) Yellow precipitate with sodium cobaltinitrite |

(1) The solubility of silver chloride in ammonia is due to the removal of silver ions as complex ammines, $[Ag\ 2NH_3]^+$, so that the solubility-product is not reached

$$\underset{\text{(solid)}}{AgCl} \rightleftharpoons \underset{\text{(solution)}}{Ag^+ + Cl^-} \rightleftharpoons [Ag\ 2NH_3]^+ + Cl^-$$

(2) Mercuric carbonate is formed by double decomposition, and then decomposes into mercury, oxygen and carbon dioxide

$$2HgCO_3 = 2Hg + O_2 + 2CO_2$$

(3) Arsenates yield $As_2S_3$ and S on heating, precipitation is slow

(4) Sulphur is liberated when an oxidising agent is present, *e g* a dichromate

$$K_2Cr_2O_7 + 8HCl + 3H_2S = 2KCl + 2CrCl_3 + 3S + 7H_2O$$

The semi-colloidal product is easily distinguished from a sulphide precipitate

(5) Hydrogen containing arsine, as in Marsh's test, immediately blackens filter paper soaked in silver nitrate

$$6AgNO_3 + AsH_3 + 3H_2O = 6Ag + H_3AsO_3 + 6HNO_3$$
(black)

On the other hand stibine, $SbH_3$, only blackens the filter paper very slowly

$$3AgNO_3 + SbH_3 = Ag_3Sb + 3HNO_3$$

(6) These reactions may be represented by the following equations

$Na_3AsO_3 + 3AgNO_3 = 3NaNO_3 + Ag_3AsO_3$ (yellow silver arsenite),
$Na_3AsO_4 + 3AgNO_3 = 3NaNO_3 + Ag_3AsO_4$ (red silver arsenate)

(7) This test depends upon the fact that tervalent, but not quinquevalent, antimony reduces silver oxide to silver The solution is therefore shaken with a mixture of silver nitrate and sodium hydroxide, and then treated with ammonia, which dissolves silver oxide but not silver

$$2AgNO_3 + 2NaOH = Ag_2O + 2NaNO_3 + H_2O,$$
$$Sb_2O_3 + 2Ag_2O = Sb_2O_5 + 4Ag$$

(8) In the presence of HCl a red precipitate of $PbCl_2$, PbS, is first formed but this is blackened by more $H_2S$

(9) The precipitate obtained with ammonia ((11) p 385) is dissolved in the minimum of dilute hydrochloric acid The addition of much water to this solution should then cause the precipitation of the oxy-chloride

$$BiCl_3 + H_2O \rightleftharpoons BiOCl + 2HCl$$

(10) The phosphates of the iron group, unlike those of manganese, calcium, etc , are insoluble in a weakly acidic solution, such as that given by acetic acid in the presence of an excess of ammonium acetate The phosphate can therefore be removed as ferric phosphate by the addition of ferric chloride to the above solution Phosphoric acid is a weak acid (except the first hydrogen), so that a small increase in the hydrogen ion concentration of its solution decreases the concentration of the $PO_4^{---}$ ions to such an extent that only the solubility-products of the more sparingly soluble phosphates are exceeded

$$PO_4^{---} + H^+ \rightleftharpoons HPO_4^{--}$$

$$[Fe^{+++}][PO_4^{---}] > S \quad [Ca^{++}]^3[PO_4^{---}]^2 < S,$$

where S is the " solubility-product " of the phosphate in question

(11) $CaC_2O_4 = CaCO_3 + CO$

(12) The precipitate of magnesium hydroxide is almost colourless and may remain undetected for this reason it is always advisable to confirm the absence of magnesium by performing the ammonium phosphate test, since this is much more sensitive

## Detection of Acids

**Detection of one acid radical.**—A good deal of information about the nature of an acid can be obtained by heating the unknown substance either alone, as a " dry " test (p 395), or with hydrochloric or sulphuric acids, when easily recognisable gases, such as oxygen, carbon dioxide, etc , are often set free A summary of the commoner reactions is given below, together with characteristic tests for the gases evolved , further tests for gases are given in Table 34 (p 398)

1 **Heat the solid in a hard glass test tube,** when the following gases may be set free

(*a*) *Oxygen*, from silver and mercury oxides, from peroxides and higher oxides, and from oxy-salts, such as chlorates (p 288), bromates, potassium and sodium nitrates (p 201) Test for oxygen with a glowing splinter

(*b*) *Oxygen* and *oxides of nitrogen*, from the nitrites and nitrates of heavy metals (p 201) Oxides of nitrogen are detected by the liberation of iodine from acidified solutions of potassium iodide (p 203)

(*c*) *Nitrous oxide*, from ammonium nitrate

$$NH_4NO_3 = N_2O + 2H_2O$$

Nitrous oxide will relight a strongly glowing splinter and is easily soluble in water

(*d*) *Nitrogen*, from ammonium nitrite and ammonium dichromate , the latter gives a green residue of chromic oxide

$$(NH_4)_2Cr_2O_7 = Cr_2O_3 + N_2 + 4H_2O$$

Nitrogen is inert to most tests, but does not extinguish burning magnesium

(*e*) *Carbon monoxide*, from oxalates, *e g* calcium oxalate,

$$CaC_2O_4 = CaCO_3 + CO$$

Carbon monoxide burns with a characteristic blue flame

(*f*) *Carbon dioxide*, from bicarbonates, and all carbonates except those of sodium, potassium and barium Carbon dioxide turns lime water milky

(*g*) *Sulphur dioxide*, from acid sulphites, certain sulphites and sulphates, whilst thiosulphates give in addition a yellow sublimate of sulphur Sulphur dioxide is recognised by its smell and reducing action on dichromate, etc

(*h*) *Iodine*, from certain iodides and iodates , the latter give oxygen in addition

$$2PbI_2 + O_2(\text{from air}) = 2PbO + 2I_2$$

Iodine is recognised by its violet vapour and action on starch

Other changes may take place and should be recorded Thus, the oxides of arsenic and antimony, the chlorides and bromides of mercury, ammonium salts, etc , sublime when heated and are deposited as white sublimates in the cold end of the tube Mercuric iodide gives a yellow sublimate which turns red on rubbing Hydrated copper sulphate loses its water of crystallisation and becomes white, whilst ferrous sulphate decomposes into red ferric oxide, sulphur dioxide, and sulphur trioxide

$$2FeSO_4 = Fe_2O_3 + SO_2 + SO_3.$$

The ignition of the original solid, therefore, may provide valuable evidence as to the nature not only of the acid radical, but also of the metallic constituent For this reason many people prefer to ignite the solid *before* carrying out the wet tests for metals

The residue left after ignition should be kept and tested with hydrochloric and concentrated sulphuric acids Thus a perchlorate would give oxygen in Test 1, but no positive result with any of the other tests, 2 to 7 The residue after ignition, however, would give fumes of hydrogen chloride with concentrated sulphuric acid, thereby showing that it was a chloride and that the original salt was a perchlorate

2 **Dilute hydrochloric acid (cold and hot)** —Add dilute hydrochloric acid to the solid, in a test tube fitted with a delivery tube , heat, if there is no reaction in the cold, and test for

(*a*) *Carbon dioxide*,* from bicarbonates and carbonates, *e g* sodium carbonate

$$Na_2CO_3 + 2HCl = 2NaCl + CO_2 + H_2O$$

(*b*) *Hydrogen sulphide*, from some sulphides, *e g* ferrous sulphide

$$FeS + 2HCl = FeCl_2 + H_2S$$

Lead nitrate paper is blackened by hydrogen sulphide

(*c*) *Sulphur dioxide*, from sulphites and thiosulphates , the latter give in addition a precipitate of sulphur

$$Na_2SO_3 + 2HCl = 2NaCl + SO_2 + H_2O,$$
$$Na_2S_2O_3 + 2HCl = 2NaCl + SO_2 + S + H_2O$$

(*d*) *Oxides of nitrogen*, from nitrites

$$2NaNO_2 + 2HCl = 2NaCl + NO_2 + NO + H_2O$$

(*e*) *Chlorine*, from hypochlorites and bleaching powder

$$NaOCl + 2HCl = NaCl + Cl_2 + H_2O$$

Bromates give in addition free bromine

$$2NaBrO_3 + 12HCl = 2NaCl + Br_2 + 5Cl_2 + 6H_2O$$

Chlorine is a greenish gas with a choking smell , it reddens and then bleaches moist blue litmus paper (p 279)

(*f*) *Hydrogen cyanide*, HCN, from many cyanides, such as sodium cyanide , concentrated hydrochloric acid is sometimes required

$$NaCN + HCl = NaCl + HCN$$

The vapour has a sickly almond-like odour and is dangerously poisonous

3 **Hot concentrated hydrochloric acid.**—Results similar to the above are obtained, and in addition

(*a*) *Chlorine* is liberated by oxidising agents such as peroxides, permanganates, etc

$$MnO_2 + 4HCl = MnCl_2 + Cl_2 + 2H_2O,$$
$$2KMnO_4 + 16HCl = 2KCl + 2MnCl_2 + 5Cl_2 + 8H_2O$$

* Carbon dioxide is also evolved by cyanates, *e g*

$$KCNO + 2HCl + H_2O = KCl + NH_4Cl + CO_2,$$

but a little HCNO escapes and can be recognised by its unpleasant odour

Chlorates give chlorine and chlorine dioxide, $ClO_2$, a yellow explosive gas

$$8KClO_3 + 24HCl = 8KCl + 9Cl_2 + 6ClO_2 + 12H_2O$$

(*b*) *Hydrogen sulphide*, from most sulphides which are insoluble in dilute hydrochloric acid, *e g* antimony sulphide

$$Sb_2S_3 + 6HCl = 2SbCl_3 + 3H_2S$$

(*c*) *Hydrogen cyanide*, from some cyanides which are not decomposed by dilute hydrochloric acid Sulphocyanides, *e g* KCNS, give in addition carbon dioxide and hydrogen sulphide

4 **Concentrated sulphuric acid (cold and hot)**.—This test need not be carried out if hydrochloric acid has liberated carbon dioxide, sulphur dioxide, or hydrogen sulphide, since these gases prove respectively the presence of a carbonate, sulphite or thiosulphate, and sulphide Concentrated sulphuric acid is added *cautiously* to a small quantity of the solid in a test tube , the mixture is heated if there is no reaction in the cold The following gases may be evolved

(*a*) *Hydrogen fluoride*, from fluorides , recognised by its corrosive action on glass Silicifluorides give *silicon fluoride*, $SiF_4$, in addition to HF (see Test 5)

(*b*) *Hydrogen chloride*, from chlorides , add manganese dioxide and heat to give free chlorine

(*c*) *Bromine* and *sulphur dioxide*, from bromides, *e g* potassium bromide

$$2KBr + 3H_2SO_4 = 2KHSO_4 + Br_2 + SO_2 + 2H_2O$$

Bromine is recognised by its deep red-brown vapour, which condenses at the cool end of the test tube to a dark red-brown liquid

(*d*) *Iodine*, *sulphur dioxide* and traces of *hydrogen sulphide*, from iodides (p 298) Iodine gives a mauve colour to the vapour , sulphur dioxide and hydrogen sulphide are recognised by the chromate, baryta and lead acetate tests (p 251)

(*e*) *Chlorine dioxide*, from chlorates, *e g* potassium chlorate

$$3KClO_3 + 3H_2SO_4 = 3KHSO_4 + 2ClO_2 + HClO_4 + H_2O$$

(*f*) *Carbon monoxide*, from formates, cyanides and ferrocyanides The liquid does not blacken

$$HCO{\cdot}ONa + H_2SO_4 = NaHSO_4 + CO + H_2O,$$
$$2NaCN + 3H_2SO_4 + 2H_2O = 2NaHSO_4 + 2CO + (NH_4)_2SO_4$$

See Tests 7 and 8 below

(*g*) *Carbon monoxide* and *carbon dioxide*, from oxalates (no blackening of liquid), tartrates (immediate blackening) and citrates (very slow blackening)

$$Na_2C_2O_4 + 2H_2SO_4 = 2NaHSO_4 + CO_2 + CO + H_2O.$$
Sodium oxalate

The reactions with tartrates and citrates are too complex to be represented by simple equations.

(*h*) *Nitric acid*, from nitrates, the vapour is coloured brown by nitrogen peroxide (see Test 9 (*a*))

(*i*) *Acetic acid*, from acetates, the addition of alcohol, $C_2H_5OH$, gives the " fruity " odour of ethyl acetate, $CH_3CO\,OC_2H_5$

$$CH_3CO{\cdot}ONa + H_2SO_4 = NaHSO_4 + CH_3CO\,OH,$$
$$CH_3{\cdot}CO\,OH + C_2H_5OH = CH_3CO\,OC_2H_5 + H_2O$$

See also Test 9 (*c*)

All the common acid radicals except phosphates, borates and some sulphates will have been recognised or roughly indicated by the above tests on the original solid The following additional tests require *a solution of the acid radical from which all the metals of Groups* 1 *to* 5 *and magnesium have been removed*, so that the solution contains only *ammonium*, *potassium* and *sodium* salts If the unknown salt contains other metals, it should be converted into the corresponding sodium salt by boiling with excess of sodium carbonate, when heavy metals and alkaline earths are precipitated and removed as carbonates or basic carbonates The reason for this procedure is that heavy metals may interfere with the ensuing tests, *e g* lead salts would give a precipitate of lead chloride in Tests 5 and 6 below The main bulk of the filtrate from the carbonate treatment is boiled with a slight excess of dilute nitric acid to expel all carbon dioxide (otherwise calcium carbonate will be precipitated in Test 7), and portions of it are then tested as follows

5 **Barium chloride acidified with hydrochloric acid** *—Sulphates and silicifluorides give a white precipitate of barium sulphate, $BaSO_4$, or barium silicifluoride, $BaSiF_6$ The latter is distinguished by the action of concentrated sulphuric acid, which liberates hydrogen fluoride and silicon fluoride, Test 4

$$Na_2SiF_6 + H_2SO_4 = Na_2SO_4 + SiF_4 + 2HF$$

6 **Calcium chloride acidified with acetic acid** —A white precipitate indicates an oxalate or fluoride Oxalates and fluorides are distinguished by their behaviour towards concentrated sulphuric acid, Test 4

7 **Calcium chloride made alkaline with ammonia.**—A white precipitate indicates citrate, tartrate, arsenate, phosphate, borate or silicate The citrate and tartrate will have been identified by Test 4, the arsenate in Group 2, whilst the remaining salts may be identified thus

(*a*) Phosphates give a yellow colour or precipitate when heated with *excess* of ammonium molybdate acidified with dilute nitric acid The three classes of phosphates are distinguished as follows

(i) *Ortho-phosphates* give a yellow precipitate, *meta-* and *pyro-phosphates* a white precipitate with neutral silver nitrate

(ii) *Meta-phosphates* coagulate egg albumen

(*b*) *Borates*, when mixed with alcohol and concentrated sulphuric acid, give a green edge to the flame of the burning alcohol

* Note italicised instructions in preceding paragraph.

(*c*) *Silicates* are confirmed by evaporating the precipitate to dryness with hydrochloric acid, when a residue is obtained which is insoluble in dilute hydrochloric acid

8 **Silver nitrate acidified with dilute nitric acid.**—Table 32 below shows the colour and behaviour towards ammonia of silver salts which are insoluble in nitric acid In addition, some confirmatory tests have been added in the last column, although in most cases sufficient evidence to identify the salt will have been obtained from the previous tests Thus, the halides are easily distinguished by their behaviour to concentrated sulphuric acid, Test 4

TABLE 32 —ACTION OF SILVER NITRATE

| A solution of the alkali salt is added to excess of silver nitrate acidified with dilute nitric acid, when a precipitate indicates | Shake precipitate with ammonia | Additional tests with original solution |
|---|---|---|
| CYANIDE (white) | Soluble | (i) Silver cyanide is soluble in excess of cyanide<br>(ii) Blue colour with a mixture of ferrous and ferric salts |
| SULPHOCYANIDE (white) | Soluble | (i) Silver sulphocyanide is soluble in excess of sulphocyanide<br>(ii) Blood-red colour with ferric chloride, bleached by $HgCl_2$, but not by HCl |
| FERRICYANIDE (orange) | Soluble | (i) Dark blue precipitate with ferrous solutions, nothing with ferric solutions |
| CHLORIDE (white) | Soluble | Test 4 (*b*) (p 392) |
| BROMIDE (cream) | Sparingly soluble | Chlorine liberates free bromine, shake with carbon disulphide, when bromine dissolves to give a yellow or brown layer of carbon disulphide |
| IODIDE (yellow) | Insoluble | Iodine liberated by chlorine, violet solution with carbon disulphide (see bromine) |
| FERROCYANIDE (white) | Insoluble | (i) Light blue precipitate with ferrous solutions<br>(ii) Dark blue precipitate with ferric solutions |

9 **Additional tests.**—(*a*) *Nitrites* and *nitrates* A " brown ring " of $FeSO_4,NO$ is obtained at the junction of the two liquids when concentrated sulphuric acid is poured carefully down the side of a test tube containing a solution of ferrous sulphate and a nitrate or nitrite This test is not conclusive because certain other salts behave similarly, *e g* iodides give a brown ring of free iodine A good confirmatory test is to warm the original solid with aluminium turnings and caustic soda, when nitrites and nitrates are reduced to ammonia, which is identified by its smell, action on litmus, etc If the original solid contains an ammonium salt it must be heated with caustic soda alone, until all the free ammonia has been driven off, the aluminium turnings can then be added

Nitrites, unlike nitrates, decolorise acidified permanganate and liberate iodine immediately from acidified potassium iodide (p 203), they are also distinguished from nitrates by their reaction with warm dilute acids, Test 2 (*d*)

(*b*) *Formates* and *tartrates* (but not *citrates*) give a " silver mirror " when a neutral solution is heated in a test tube with an ammoniacal solution of silver hydroxide The latter is obtained by adding dilute ammonia drop by drop to silver nitrate until the precipitate of silver hydroxide is just redissolved

(*c*) *Acetates* and *formates* give a red coloration with ferric chloride, bleached by hydrochloric acid, but not by mercuric chloride (converse behaviour to sulphocyanide)

(*d*) *Oxides* If none of the acid radicals given in the previous sections appears to be present, it is probable that the substance is an oxide Oxides should be classified by noting their behaviour towards water, dilute acids, caustic soda and concentrated hydrochloric acid (p 232)

## Dry Tests

**Examination of a simple substance in the dry way.**—The following is a summary of the commoner " dry tests " which can be used in the identification of a substance

1 *Heat the substance in a hard glass test tube* —This test is of value mainly in the detection of the acid radical, and has already been considered under this heading (p 390)

2 *Heat the substance with dry sodium carbonate in an ignition tube* — Mercury salts give a grey ring of mercury in the cold upper portion of the tube, mercurous (or mercuric) carbonate is formed by double decomposition, and then decomposes as indicated by the equations

$$HgCO_3 = HgO + CO_2, \quad 2HgO = 2Hg + O_2$$

Ammonium salts give the odour of free ammonia

3 *Heat the substance with sodium carbonate on a charcoal block* —The substance is mixed with twice its bulk of dry sodium carbonate and heated in a cavity in a charcoal block by means of the reducing flame * from a

* The air-hole of the Bunsen burner is closed, and the tip of the blowpipe is placed just inside at the bottom of the luminous flame, which should be about

blowpipe The metal carbonate, formed by double decomposition with the alkali carbonate, decomposes into the oxide, which is either left in the form of a crust or is reduced to the metal Thus

(i) *Mercury* salts yield the liquid metal, which volatilises

(ii) *Copper* salts yield a red malleable bead of the metal

(iii) *Silver* salts yield a silvery malleable bead of the metal

(iv) *Tin* salts yield a silvery malleable bead of the metal, with a white crust of oxide which is yellow when hot

(v) *Lead* salts yield a silvery malleable bead of the metal, with a yellow crust of oxide

(vi) *Antimony* salts yield a grey brittle bead of the metal, with a white crust of oxide

(vii) *Bismuth* salts yield a grey brittle bead of the metal, with a yellow crust of oxide

(viii) *Iron*, *cobalt* and *nickel* salts yield a fine brittle powder of the metal.

(ix) *Arsenic* salts give an odour of garlic due to $As_4O_6$ vapour

(x) *Ammonium* salts give an odour of ammonia

(xi) *Aluminium* salts give a white infusible residue of oxide, which becomes blue,* yellow when hot, when reheated after addition of a drop of cobalt chloride solution

(xii) *Magnesium* salts give a white infusible residue of oxide, which becomes pink, yellow when hot, when reheated after addition of a drop of cobalt chloride solution

(xiii) *Zinc* salts give a white infusible residue of oxide, which becomes green, yellow when hot, when reheated after addition of a drop of cobalt chloride solution

(xiv) *Calcium* and *strontium* salts give a white infusible residue of oxide

This list shows that contiguous elements in the periodic table usually behave alike as regards reduction The formation of an oxide crust round the metallic beads of tin, lead, antimony and bismuth is due to the volatility of the metal, the vapour of which is reoxidised by the air and condensed as oxide Owing to the high melting-points of the metals, compounds of iron, cobalt and nickel are reduced to metallic powders and do not give metallic beads



FIG 101
BUNSEN FLAME

4 *Heat the substance in a borax bead*—This test depends upon the fact that the compounds of some metals (notably the transition elements) react with fused borax, $Na_2B_4O_7$, to give borates, which usually have the characteristic colours of the metallic ions A small speck of the substance is added to a fused bead of borax on a clean platinum wire, and the bead is then reheated

an inch in height, on blowing gently, a reducing flame is obtained, containing unburnt gases in the tip An oxidising flame, containing excess of hot oxygen in the tip, is produced by placing the end of the blowpipe well inside the Bunsen flame and blowing hard

* Certain other salts behave similarly, *e g* calcium phosphate

either in the oxidising part of the Bunsen flame, *i e* on the edge of the outer cone 3, or in the reducing part of the flame, *i e* in the bright blue inner cone 2 In the latter case the bead is allowed to cool in the cold unburnt gases, 1, before removal, otherwise it will be reoxidised by the air The reason for using both the oxidising and reducing parts of the Bunsen flame is that some metals form two borates, one derived from the higher oxide and the other from a lower oxide Thus, iron gives yellow and green beads, containing ferric and ferrous borate respectively, whilst cobalt gives a blue bead in both flames The more important of these tests are given in Table 33 The student should observe that the table is composed of six adjacent transition metals (p 302), and therefore illustrates in a striking way the formation of coloured ions, which is a characteristic feature of the transition elements

TABLE 33.—COLOURS OF BORAX BEADS

| Metal | Oxidising flame | Reducing flame |
|---|---|---|
| Chromium - - | Green | Green |
| Manganese - - | Violet | Colourless |
| Iron - - - - | Yellow | Green |
| Cobalt - - - | Blue | Blue |
| Nickel - - - | Violet-brown | Grey (finely divided nickel) |
| Copper - - - | Blue (green when hot) | Red (metallic copper) |

5 *Heat the substance, moistened with concentrated hydrochloric acid, on a platinum wire in a Bunsen flame*

A platinum wire, moistened with concentrated hydrochloric acid and smeared with a little of the substance, is held in a Bunsen flame, when certain metals (more particularly those of the alkalis and alkaline earths) volatilise and impart characteristic colours to the flame Hydrochloric acid is used in order to form the chloride, as this is usually more volatile than other salts Characteristic flames of particular value in analysis are given by sodium (yellow), potassium (lilac), calcium (orange-red), strontium (crimson), barium (green) It should be observed that these metals occur together in the first and second groups of the periodic classification

**The identification of gases.**—The various gases, which are set free in dry or wet tests, are identified by noting their physical properties, such as colour and smell, and by observing their behaviour towards certain reagents Table 34 summarises the chief characteristics of the commoner gases In the case of mixtures of gases, it is sometimes necessary to remove one or more of the constituents before the recognition of the others is possible, *e g* when carbon dioxide is mixed with much chlorine, it is necessary to remove the latter by washing with a solution of potassium iodide before applying the lime-water test.

| | Colour | Smell | Lighted splint | Litmus paper | Potassium iodide solution | Very dilute permanganate | Special tests |
|---|---|---|---|---|---|---|---|
| Hydrogen | — | — | Gas burns with non-luminous flame | — | — | — | Squeaks when mixed with air in a test tube and ignited |
| Oxygen | — | — | Splint burns more vigorously | — | — | — | Glowing splint easily relighted |
| Ozone | Blue in bulk | Odour of electrical machines | Splint burns more vigorously | — | Liberates iodine | — | Makes mercury "tail," p 337 |
| Nitrogen | — | — | Extinguished | — | — | — | Burning magnesium continues to burn |
| Ammonia | — | Pungent | ,, | Alkaline | — | — | Brown colour or precipitate with Nessler's solution |
| Nitrous oxide | — | — | Splint burns vigorously | — | — | Decolorised | Relights strongly glowing splint |
| Nitric oxide | — | — | Extinguished | — | — | ,, | Turns brown in air, and forms brown-black compound with $FeSO_4$, p 395 |
| Nitrogen peroxide | Brown | Choking | ,, | Acidic | Liberates iodine | ,, | Brown-black compound with $FeSO_4$ |
| Carbon monoxide | — | — | Gas burns with blue flame | — | — | — | Burn and test for $CO_2$ by lime-water |
| Carbon dioxide | — | — | Extinguished | Weakly acidic | — | — | Lime-water turned milky |
| Hydrogen sulphide | — | Bad eggs | Gas burns with blue flame | Acidic | — | Decolorised | Lead acetate paper blackened |
| Sulphur dioxide | — | Pungent | Extinguished | ,, | — | ,, | Warm aqueous solution with $H_2O_2$ and test for sulphate |
| Chlorine | Greenish yellow | ,, | ,, | Bleaches | Liberates iodine | — | Bleaches writing ink, white fumes with $NH_3$ |
| Hydrogen chloride | Fumes in moist air | ,, | ,, | Acidic | — | Chlorine liberated | White fumes with $NH_3$ |
| Hydrogen bromide | Fumes in moist air | ,, | ,, | ,, | — | Bromine liberated | Test solution in water for chloride, bromide and iodide by $AgNO_3$ |
| Hydrogen iodide | Fumes in moist air | ,, | ,, | ,, | — | Iodine liberated | |

# CHAPTER XXIX

## QUALITATIVE ANALYSIS OF MIXTURES

**General considerations.**—The identification of the components of a mixture is necessarily more complicated than that of a pure substance Thus, when two metals belonging to the same analytical group are present, it is necessary to separate them before they can be recognised with certainty The identification of the acid radicals in a mixture is even more difficult, because they cannot be separated in a systematic way like the metals, and their behaviour towards a particular reagent is often profoundly modified by the presence of other acid radicals In the scheme outlined below, the metals are isolated and identified before the acid radicals, and, to avoid repetition, a detailed explanation is given only of those reactions which have not been discussed in the previous chapter The dry tests described on page 395 should generally only be applied when the constituents of the mixture have been separated in the wet way For this reason they are not discussed again in this chapter

**The separation and identification of metals.**—A solution of the mixture is first prepared in exactly the same way as was recommended for a pure substance In general, it is more convenient to find some solvent which will dissolve all the constituents of the mixture, since there is no certain means of knowing whether partial solubility in a given solvent is due to the complete insolubility of one of the components, *i e* the separation may only be partial and therefore worthless However, if the mixture is not completely soluble in concentrated acids, it is probable that at least one of the constituents is insoluble in water, so that this solvent (or dilute HCl) may be used to effect an initial separation of the mixture The solution can then be tested in the usual way, and the insoluble portion examined in the dry way before an attempt is made to get it into solution by means of fusion mixture

The solution of the mixture is heated in turn with the five group reagents which were used for the analysis of a pure substance If a precipitate forms it is removed by filtration before passing to the next group

**Group 1. Silver, mercurous mercury and lead** are precipitated as chlorides by the addition of cold dilute hydrochloric acid The precipitate is filtered off, and the filtrate is passed to Group 2 The precipitate is washed with cold water to remove traces of metals belonging to succeeding groups, and then boiled with much water to dissolve lead chloride The solution is filtered from the insoluble residue (if any), and the presence of lead is confirmed by the chromate test The residue, which does not dissolve in boiling water, is treated with ammonia, when silver chloride

dissolves and mercurous chloride is converted into a black mass of mercury and ammino-mercuric chloride The presence of silver is proved either by acidifying the ammoniacal filtrate to reprecipitate silver chloride, or by adding potassium iodide, when yellow silver iodide is precipitated, since this salt is insoluble in ammonia

**Group 2. Arsenic, antimony, tin, mercury, lead, copper, cadmium and bismuth** are precipitated as sulphides by passing hydrogen sulphide into the filtrate from Group 1 The mixture is warmed to coagulate the sulphides and filtered, the filtrate being treated with more hydrogen sulphide to ensure that it is free from the metals of Group 2 before being tested for metals of Group 3 The sulphide precipitate is washed with water and warmed with yellow ammonium sulphide, when arsenic, antimony, and tin sulphides are dissolved as thiosalts (p 380), and separated from the other sulphides by filtration The former are identified in Group 2A, and the latter in Group 2B

**Group 2A. Arsenic, antimony and tin.**—The sulphides, which are soluble in yellow ammonium sulphide, are reprecipitated by the addition of dilute hydrochloric acid Some sulphur is also liberated from the polysulphides, but is easily recognised by its pale yellow colour and milky appearance Arsenic is separated from the other sulphides by boiling with a solution of ammonium carbonate and filtering , the filtrate contains arsenic as ammonium arsenite and thioarsenite, whilst tin and antimony sulphides are left unchanged

$$2(NH_4)_2CO_3 + 2As_2S_3 = NH_4AsO_2 + 3NH_4AsS_2 + 2CO_2$$

Arsenic sulphide is again deposited on the addition of a dilute acid, and can be confirmed by Marsh's test, etc

$$NH_4AsO_2 + 3NH_4AsS_2 + 4HCl = 4NH_4Cl + 2As_2S_3 + 2H_2O$$

The antimony and tin are separated by boiling with milk of lime, when antimony sulphide passes into solution as calcium antimonite and thioantimonite, and can be separated by filtration from the insoluble sludge of calcium stannate

$$4Ca(OH)_2 + 4Sb_2S_3 = Ca(SbO_2)_2 + 3Ca(SbS_2)_2 + 4H_2O,$$
$$3Ca(OH)_2 + SnS_2 = CaSnO_3 + 2CaS + 3H_2O$$

The addition of hydrochloric acid to the filtrate reprecipitates orange antimony sulphide The sludge is dissolved in hot dilute acid and boiled with ammonium chloride and ammonia, when, if tin is present, a white floating precipitate of stannic hydroxide is produced

$$CaSnO_3 + 6HCl = CaCl_2 + SnCl_4 + 3H_2O$$

**Group 2B. Mercury, lead, bismuth, copper, cadmium.**—The sulphides, which are insoluble in yellow ammonium sulphide, are boiled with dilute (twice normal) nitric acid Mercuric sulphide remains undissolved, and can be confirmed by heating with sodium carbonate in an ignition tube (p 395). A portion of the nitric acid solution is tested for lead by adding dilute sulphuric acid and alcohol, since lead sulphate is insoluble in aqueous alcohol If lead is present, the main portion of the solution is

then treated in this way and filtered from the precipitate of lead sulphate The filtrate is boiled free of alcohol (this step is, of course, unnecessary if lead is absent) and treated with *excess* of ammonia, which precipitates bismuth as the hydroxide, $Bi(OH)_3$, but converts copper and cadmium into soluble ammino-complexes, which are respectively deep blue and colourless

$$CuSO_4 + 6NH_3 + 2H_2O = (NH_4)_2SO_4 + \underset{\text{blue}}{[Cu\ 4NH_3](OH)_2},$$

$$CdSO_4 + 6NH_3 + 2H_2O = (NH_4)_2SO_4 + \underset{\text{colourless}}{[Cd\ 4NH_3](OH)_2}$$

If the ammoniacal filtrate is blue, it must be decolorised with excess of potassium cyanide before it is treated with hydrogen sulphide Copper and cadmium both form anionic complexes with potassium cyanide, as represented by the equations

$$\begin{cases} 2CuSO_4 + 4KCN = 2CuCN + C_2N_2 + 2K_2SO_4, \\ CuCN + 3KCN = K_3[CuC_4N_4], \\ CdSO_4 + 4KCN = K_2[CdC_4N_4] + K_2SO_4 \end{cases}$$

The copper complex is formulated as a cuprous compound because cupric cyanide undergoes rapid decomposition even at room temperature The addition of hydrogen sulphide to the above cyanide solution precipitates cadmium as sulphide, but not copper, because the anion, $[CuC_4N_4]^{---}$, is so stable that the solubility-product of cuprous sulphide is not exceeded, in spite of the fact that the concentration of sulphide ions has been increased enormously by the reaction

$$2NH_3 + H_2S = 2NH_4^+ + S^{--}$$

The dissociation of the complex cyanide anions may be represented, therefore, by the equations

$$[CuC_4N_4]^{---} \rightleftharpoons \overset{+}{Cu} + 4\overset{-}{CN},$$

$$[CdC_4N_4]^{--} \rightleftharpoons \overset{++}{Cd} + 4\overset{-}{CN}$$

**Group 3 Aluminium, chromium and iron.**—The filtrate from Group 2 is boiled to expel hydrogen sulphide and then oxidised by boiling with a few drops of concentrated nitric acid (p 382) The hydroxides of aluminium, ferric iron, and chromium are precipitated by boiling this solution with excess of ammonium chloride and just sufficient ammonia to render it alkaline to litmus The separation of the above metals is complicated, however, because manganese and zinc hydroxides may be partially precipitated here, as well as certain salts of the metals in subsequent groups, notably the phosphates, oxalates and fluorides of calcium, strontium and barium The precipitate is well washed with hot water and small portions of it are tested as follows

(*a*) *Aluminium* and *chromium* are detected by boiling with water and sodium peroxide until no further change takes place, when chromium

hydroxide is oxidised and dissolved as chromate, $Na_2CrO_4$, whilst aluminium hydroxide is dissolved as aluminate, $NaAlO_2$

$$2Cr(OH)_3 + 3Na_2O_2 = 2Na_2CrO_4 + 2NaOH + 2H_2O,$$
$$2Na_2O_2 + 2H_2O = 4NaOH + O_2,$$
$$Al(OH)_3 + NaOH = NaAlO_2 + 2H_2O$$

Ferric hydroxide and any manganese contamination are left undissolved and may be separated by filtration The filtrate is boiled with excess of ammonium chloride to reprecipitate aluminium hydroxide

$$NaAlO_2 + NH_4Cl + H_2O = NaCl + Al(OH)_3 + NH_3$$

The presence of chromium as chromate is shown by the yellow colour of the filtrate and can be confirmed by the hydrogen peroxide or lead tests (Table 31, p 384)

When the original precipitate with ammonia and ammonium chloride is white, iron and chromium cannot be present, since their hydroxides are brown and green respectively In this case the precipitate is heated with aqueous caustic soda in place of the peroxide, and (after filtering if necessary) the resulting solution is boiled with ammonium chloride to reprecipitate aluminium hydroxide If the above precipitate is completely soluble in caustic soda, there is no need to look for the salts mentioned in 4 and 5 below This, however, does not exclude the presence of the phosphate radical, because aluminium phosphate behaves like the hydroxide towards caustic soda

(*b*) *Iron* is detected by dissolving the precipitate in dilute hydrochloric acid and adding potassium ferrocyanide, when a deep blue coloration or precipitate is formed

(*c*) *Manganese* only occurs as an impurity, since it belongs properly to the next group Its presence is best detected by fusing the residue, which was insoluble in peroxide, with potassium carbonate and nitrate on a piece of porcelain Manganese (if any) is converted into a green mass of potassium manganate, $K_2MnO_4$, which dissolves in dilute acids to give a purple solution of potassium permanganate, $KMnO_4$ Even if manganese is detected here it will probably be found again when the filtrate from Group 3 is treated for the Group 4 metals

(*d*) *Phosphates* are detected by dissolving the precipitate in dilute nitric acid and boiling with a large excess of ammonium molybdate, when a yellow coloration or precipitate proves the presence of a phosphate

(*e*) *Fluorides*, *oxalates*, *tartrates* and *citrates* are best identified by testing the original substance as recommended in 1 to 6, pages 390 to 393 because they are not easily identified in a small quantity of material like that of the hydroxide precipitate

If any of the acids mentioned in (*d*) and (*e*) are present, it is now necessary to remove them from the main portion of the precipitate Organic acids are best destroyed by ignition, when a carbonate or oxide is left, whilst a fluoride may be converted into chloride by evaporating to dryness twice with concentrated hydrochloric acid The residue is dissolved in dilute hydrochloric acid and passed to

Group 4,* after treatment with ammonium chloride and ammonia, followed if necessary by filtration

If a phosphate has been found in the ammonia precipitate, it is necessary to remove it in the manner indicated in Table 31 (p 386) It may happen that more iron is already present than is required to precipitate the phosphate as ferric phosphate In this case ammonium phosphate, and not ferric chloride, must be added drop by drop to the acetic acid solution in order to remove all the iron, because ferric phosphate is partially dissolved by ferric acetate The filtrate from the phosphate separation is boiled with ammonium chloride and ammonia to reprecipitate any aluminium or chromium still present The filtrate from this mixture is added to the main filtrate (obtained originally with ammonium chloride and ammonia) and tested for Group 4 metals as indicated below

**Group 4 Nickel, cobalt, zinc and manganese** —The ammoniacal filtrate from Group 3 is treated with a little more ammonia and saturated with hydrogen sulphide, when the sulphides of nickel (black), cobalt (black), zinc (white) and manganese (buff) are precipitated If the precipitate is blackish, it is boiled for a few minutes to convert nickel and cobalt sulphides into forms which are insoluble in dilute hydrochloric acid It is then collected on a filter-paper (the filtrate being kept for Group 5), washed well with water and digested with cold dilute hydrochloric acid (1 vol conc HCl to 8 vols water) Zinc and manganese sulphides dissolve as chlorides and are separated by filtration from the insoluble sulphides of cobalt and nickel The " hydrochloric acid filtrate " is boiled to expel hydrogen sulphide and then treated with a large excess of cold caustic soda, which precipitates manganese as hydrated oxide, but converts zinc into soluble sodium zincate The large excess of caustic soda is necessary to prevent the manganese hydroxide from bringing down most, if not all, of the zinc The " caustic soda filtrate " is treated with hydrogen sulphide, when zinc sulphide is precipitated

$$Na_2ZnO_2 + 2H_2S = Na_2S + ZnS + 2H_2O$$

The sulphides of cobalt and nickel (if any) are transferred to an evaporating dish and converted into chlorides by evaporating to dryness with aqua regia Most of this residue is dissolved in water and portions of the solution are tested as follows

(*a*) *Cobalt* is detected by adding a strong solution of ammonium sulphocyanide, $(NH_4)CNS$, when the pink colour (green if much nickel is present) of the solute changes to blue owing to the conversion of cobaltous cations, $Co^{++}$, into complex anions, $[Co\,4CNS]^{--}$ The pink colour returns on dilution with water, owing to the dissociation of the complex

$$CoCl_2 + 4NH_4CNS = (NH_4)_2[Co\,4CNS] + 2NH_4Cl,$$

$$[Co\,4CNS]^{--} \rightleftharpoons Co^{++} + 4CNS^-$$

If a mixture of ether and amyl alcohol is now added, the complex, which is still present in the pink aqueous solution, is preferentially dissolved and a blue ethereal layer results Nickel does not interfere with this test, but

* If a phosphate is present in addition to fluoride, oxalate, etc , it must be removed at this point

iron must not be present, since the blood-red colour of ferric sulphocyanid would mask the blue colour of the cobalt complex Iron should have bee removed in Group 3, but, if its presence is suspected here, it should b precipitated from the sulphocyanide solution by the addition of a fe drops of sodium carbonate solution

(*b*) *Nickel* is detected by boiling with ammonium chloride, ammonia an dimethylglyoxime (p 708), when a scarlet precipitate of nickel dimethyl glyoxime is thrown down

$$2(CH_3)_2C_2(NOH)_2 + NiCl_2 + 2NH_3 = Ni[(CH_3)_2C_2(NOH)NO]_2 + 2NH_4Cl$$

Cobalt gives a dark coloration with the glyoxime, but no precipitate i dilute solution, so that its presence can be ignored

Cobalt and nickel are often separated from one another by making us of the fact that cobalt, but not nickel, forms a stable cobalticyanide, corre sponding to a ferricyanide, $K_3FeC_6N_6$ A solution of potassium cyanid is added drop by drop to a solution of the metals, until the precipitates o (green) nickel cyanide, $Ni(CN)_2$, and (brown) cobalt cyanide redissolv as the complexes, $K_2Ni(CN)_4$ and $K_4Co(CN)_6$ This solution is boile with sodium hypochlorite, when nickel is precipitated as a hydrated oxide $Ni(OH)_3$, whilst cobalt remains in solution as a cobalticyanide

$$2K_4CoC_6N_6 + H_2O + NaOCl = 2K_3CoC_6N_6 + 2KOH + NaCl$$

The cobalticyanide is filtered from the nickel oxide and converted int cobalt chloride by evaporating to a small bulk and heating to drynes with aqua regia This procedure is necessitated by the fact that th cyanide complex is so stable that it does not give any of the ionic reaction of cobalt

**Group 5. Calcium, strontium and barium.**—The filtrate from Group is warmed with ammonium carbonate and filtered from the precipitate c calcium, strontium and barium carbonates The filtrate is kept for Grou 6, whilst the carbonate precipitate is dissolved in the least possible quar tity of dilute hydrochloric acid *

A small portion of this solution is treated with an equal volume of saturated solution of calcium sulphate, when an immediate precipitatio shows the presence of at least barium, whilst if the mixture has to b warmed before any cloudiness is produced, then strontium, but not barium is indicated When barium is present, it is precipitated as chromate b adding potassium chromate, ammonium acetate (to remove free HCl) an acetic acid to the main portion of the above solution The chromates c strontium and calcium are soluble in acetic acid and therefore remain i solution A hot concentrated solution of ammonium sulphate is the added in excess to the " chromate filtrate " to precipitate strontium (i any) as sulphate, whilst calcium remains in solution as calcium sulphate The strontium sulphate is removed by filtration, and the filtrate treate with ammonium oxalate (and ammonia, if free HCl is present) to precipitat calcium as oxalate It is advisable to add the ammonium sulphate eve when calcium sulphate has given no precipitate, in case strontium ha

* If mesh acid has been used, it is advisable to neutralise with ammon

been missed accidentally The three metals in this group can be confirmed by the flame test

**Group 6. Magnesium, ammonium, potassium and sodium.**—The filtrate from Group 5 is evaporated to dryness and the residue ignited to expel the ammonium salts Most of the residue is dissolved in water, and portions tested as follows

(*a*) *Magnesium* is detected by boiling with potassium hydroxide, when magnesium hydroxide is precipitated and can be confirmed by the cobalt charcoal block test (p 396) The filtrate is kept and tested for sodium by adding a solution of potassium pyroantimonate, $K_2H_2Sb_2O_7$, when white sodium pyroantimonate is thrown down

(*b*) *Potassium* is detected by adding a freshly prepared solution of sodium cobaltinitrite, $Na_3Co(NO_2)_6$, when a yellow precipitate of $K_3Co(NO_2)_6$ is formed Magnesium does not interfere with this test

Sodium and potassium can be confirmed by applying the flame test to the ignited residue If both metals are present, the intense yellow colour of sodium may obscure the lilac colour of potassium , the latter, however, can be seen as a red flame by looking through a piece of cobalt glass The sodium flame test is so sensitive that this metal will be indicated even if it is present in quantities which are too minute for ordinary analysis

## TABLE 35.—SUMMARISED TABLES FOR THE IDENTIFICATION OF METALS IN MIXTURES

A solution of the mixture is prepared (pp 378 and 399), and tested thus

**Group 1.** *Add dilute hydrochloric acid to precipitate the chlorides of lead, silver and mercurous mercury , filter and pass filtrate to Group 2*

Wash the precipitate with cold water, then boil it with much water and filter

| *Solution* | *Precipitate* Digest with excess ammonia and filter | |
|---|---|---|
| | *Solution* | *Black residue* |
| Add potassium chromate, when a yellow precipitate, soluble in NaOH, but insoluble in acetic acid, proves | Add (i) dilute nitric acid , white precipitate of AgCl, or (ii) potassium iodide, yellow precipitate of AgI, proves | Heat with powdered sodium carbonate in ignition tube , grey ring in cold part of tube proves |
| LEAD | SILVER | MERCURY |

**Group 2.** *Saturate the filtrate from Group 1 with hydrogen sulphide to precipitate the sulphides of arsenic (yellow), antimony (orange), stannous tin (brown), stannic tin (dirty yellow), mercury (black), lead (black), bismuth (brown), cadmium (yellow), copper (brownish black)*

Heat the mixture to coagulate the sulphides, filter , pass the filtrate to Group 3 after first testing with more $H_2S$ and water Wash the precipitate and digest it with hot yellow ammonium sulphide, filter and test the insoluble residue for metals of Group 2B and the filtrate for 2A

**Group 2A.** Reprecipitate the sulphides of arsenic, antimony, and tin by adding dilute hydrochloric acid to the ammonium sulphide solution. Wash the sulphide precipitate and digest it with hot ammonium carbonate solution, filter

| *Solution* | *Precipitate*<br>Warm with milk of lime until colour of precipitate has disappeared, filter | |
|---|---|---|
| | *Solution* | *Precipitate* |
| Acidify with dilute hydrochloric acid to reprecipitate arsenic sulphide Confirm by Marsh's test, p 380 | Acidify with dilute hydrochloric acid to reprecipitate antimony sulphide Confirm by Marsh's test | Dissolve in hot dilute hydrochloric acid Boil solution with ammonia and ammonium chloride to give white floating precipitate of stannic hydroxide |
| ARSENIC | ANTIMONY | TIN |

**Group 2B.** Boil the sulphides, insoluble in yellow ammonium sulphide, with fairly dilute nitric acid (1 part concentrated acid to 4 parts water), filter

| *Residue* | *Solution*<br>Test portion of solution for lead by adding sulphuric acid and alcohol If a white precipitate forms, treat main bulk of solution with sulphuric acid and alcohol, and filter, otherwise add ammonia as below | | |
|---|---|---|---|
| | *Precipitate* | *Solution*<br>Boil off alcohol and add ammonia until no further change occurs, filter | |
| | | *Precipitate* | *Solution* |
| Mercuric sulphide remains undissolved Heat with dry sodium carbonate in bulb tube to give grey sublimate of mercury | Dissolve precipitate in a strong solution of ammonium acetate, then add potassium chromate when a yellow precipitate proves | Dissolve precipitate, $Bi(OH)_3$, in least possible hydrochloric acid, dilute with much water to give white precipitate of bismuth oxychloride | If blue, add KCN until colourless, then add $H_2S$ Copper remains in solution as a complex anion, whilst (yellow) cadmium sulphide is precipitated |
| MERCURY (IC) | LEAD | BISMUTH | COPPER CADMIUM |

**Group 3.** *Boil the filtrate from Group 2 to expel hydrogen sulphide, and then heat it with a few drops of concentrated nitric acid until no further change takes place, p* 382 *Precipitate the hydroxides of aluminium (white), chromium (green), ferric iron (brown) (possibly also manganese and zinc, and certain salts (p* 382)) *by boiling with excess of ammonium chloride* (5 *c c to every* 25 *c c solution) and just sufficient ammonia to render the solution alkaline to litmus, filter, filtrate to Group* 4

Wash the precipitate with water and test small portions of it as follows

| 1 | 2 | 3 | 4 |
|---|---|---|---|
| Boil with water and sodium peroxide until no further change takes place Filter, discard insoluble residue and boil filtrate with plenty of ammonium chloride, filter | Dissolve in dilute hydrochloric acid and add ferrocyanide A dark blue precipitate or coloration proves | Fuse with potassium carbonate and nitrate on a piece of porcelain (If Test 1 shows chromium, use residue insoluble in peroxide in place of the original precipitate.) A green mass turning purple with acids (p 373) proves | Boil with dilute nitric acid and a large excess of ammonium molybdate A yellow coloration or precipitate proves the presence of a phosphate See pp 393 and 403 for procedure when a phosphate is present See p 402 for oxalates, fluorides, etc |
| | IRON | | |
| *Precipitate* | *Solution* | | |
| A white precipitate indicates aluminium hydroxide, confirm by charcoal block test | If yellow, chromium is present as chromate, confirm by peroxide and ether test | | |
| ALUMINIUM | CHROMIUM | MANGANESE | |

**Group 4.** *Saturate the filtrate from Group 3 with hydrogen sulphide to precipitate the sulphides of nickel (black), cobalt (black), manganese (buff) and zinc (white) If the precipitate is black, indicating cobalt or nickel, boil the mixture for three minutes before filtering Keep the filtrate for Group 5 and examine the precipitate thus*

Wash the precipitate and digest it with cold dilute hydrochloric acid (1 part concentrated acid to 8 parts water) , filter

| *Precipitate* | *Solution* | |
|---|---|---|
| Evaporate to dryness with aqua regia Dissolve portion of residue in water and divide solution into two parts<br>(1) Add a concentrated solution of ammonium sulphocyanide drop by drop If cobalt is present the solution will turn blue The colour reverts to pink on dilution with water, but a blue upper layer forms when this is shaken with a mixture of ether and amyl alcohol<br>COBALT<br>(2) Heat with ammonium chloride, ammonia and dimethylglyoxime A scarlet red precipitate proves the presence of<br>NICKEL | Boil to expel all hydrogen sulphide, cool, and then add a large excess of caustic soda , filter | |
| | *Precipitate* | *Solution* |
| | A white precipitate turning brown on exposure to air indicates manganese hydroxide Confirm by borax bead, violet in oxidising and colourless in reducing flames<br>MANGANESE | Pass in $H_2S$ , a whitish precipitate indicates zinc Roast precipitate on charcoal block, and then heat residue with a drop of cobalt nitrate solution when a green mass proves<br>ZINC |

**Group 5.** *Warm the filtrate from Group 4 with ammonium carbonate to precipitate the carbonates of calcium, strontium and barium Filter, pass the filtrate to Group 6*

Wash the precipitate with water and dissolve it in the least possible quantity of dilute hydrochloric acid Test a portion of this solution for barium and strontium by adding an equal volume of a saturated solution of calcium sulphate An immediate precipitate indicates at least barium, but if the solution only becomes cloudy on heating, then strontium is present, but not barium, so that the chromate separation can be omitted.

If barium is present, add ammonium acetate, acetic acid, and potassium chromate to the main portion of the hydrochloric acid solution, filter

| *Precipitate* | *Solution* | |
|---|---|---|
| Yellow precipitate of barium chromate, insoluble in sodium hydroxide, but soluble in dilute hydrochloric acid Confirm by flame test — apple green | Heat with a strong solution of ammonium sulphate, filter | |
| | *Precipitate* | *Solution* |
| | White precipitate of strontium sulphate Confirm by flame test—crimson | Neutralise with ammonia and add ammonium oxalate to precipitate calcium oxalate (white) Confirm by flame test—orange |
| BARIUM | STRONTIUM | CALCIUM |

**Group 6.** *Evaporate the filtrate from Group 5 and ignite the residue to expel ammonium salts Dissolve part of the residue in water and test portions of the solution thus*

| 1 | | 2 |
|---|---|---|
| Add excess of potassium hydroxide, boil and filter (see note 12, page 380) | | Add a freshly prepared solution of sodium cobaltinitrite, a yellow precipitate indicates potassium Confirm by flame test on ignition residue—lilac (or red if looked at through cobalt glass, p 405) |
| *Precipitate* | *Solution* | |
| A white precipitate indicates magnesium hydroxide Confirm by dissolving in acid and boiling with ammonium chloride, excess of ammonia and ammonium phosphate, a white crystalline precipitate proves | Add potassium pyroantimonate, when a white precipitate indicates sodium Confirm by flame test on ignition residue | |
| MAGNESIUM | SODIUM | POTASSIUM |

Ammonium salts are detected by heating the original solid with sodium hydroxide, when ammonia is evolved

**The identification of acid radicals in mixtures.**—The acid radicals in a mixture are sometimes very difficult to identify, because there is no general systematic method for separating them, as in the case of the metals, and a particular test may be modified or invalidated by the presence of other acid radicals The procedure for their identification is very similar to that recommended for a pure substance Thus the solid is

examined as in Tests 1 to 4 (p 390), due allowance being made for possible complications For example, the ignition of a mixture of lead nitrate and sodium oxalate might give carbon dioxide and nitric oxide, instead of the expected carbon monoxide, nitrogen peroxide and oxygen

$$Pb(NO_3)_2 + 3Na_2C_2O_4 = PbO + 3Na_2CO_3 + 3CO_2 + 2NO$$

Again, concentrated sulphuric acid would react with a mixture of manganese dioxide and a chloride to give chlorine, a product which would not be obtained with either pure dioxide or chloride It is essential when a gas is evolved that it should be subjected to a very careful analysis, since it may easily be a mixture of gases whose identity would provide valuable information Thus both hydrogen sulphide and carbon dioxide are liberated when hydrochloric acid is added to a mixture of calcium carbonate and ferrous sulphide The presence of the hydrogen sulphide would be so obvious that the student might overlook the carbon dioxide In certain cases it is necessary to remove one of the gases before testing for others, *e g* the lime-water test for carbon dioxide does not function in the presence of much sulphur dioxide or chlorine These gases must be removed, therefore, by washing with solutions of chromate or iodide respectively, before the lime-water test is applied

$$2K_2CrO_4 + 3SO_2 + 2H_2SO_4 = 2K_2SO_4 + Cr_2(SO_4)_3 + 2H_2O,$$
$$2KI + Cl_2 = 2KCl + I_2$$

When the preliminary tests, 1 to 4, have been applied, a solution of the mixture is prepared as recommended on p 393 and portions of it are added to the following reagents

5 **Barium chloride acidified with hydrochloric acid.**—Sulphates and silicifluorides give a white precipitate (see p 393)

6 **Calcium chloride** (acid and neutral) —The solution is warmed with calcium chloride acidified with acetic acid, and the resulting mixture is filtered, if necessary

| *Precipitate* | *Solution* |
|---|---|
| A precipitate indicates oxalate, fluoride or possibly sulphate If Test 4 has indicated a fluoride, or Test 5 a sulphate, it is necessary to warm the precipitate with a strong solution of ammonium sulphate, when only the oxalate remains undissolved The oxalate can be confirmed by the fact that it decolorises acidified permanganate | Add ammonia until neutral, when a precipitate indicates a citrate, tartrate, arsenate, phosphate, borate The presence of the first two of these salts will have been shown by the sulphuric acid test The existence of a borate or phosphate is confirmed by the tests given on p 393 If arsenic is present it is necessary to remove it by treatment with hydrogen sulphide *before* applying the ammonium molybdate test, because arsenates behave like phosphates towards this reagent |

7 **Silver nitrate acidified with nitric acid.**—A precipitate indicates cyanide (white), sulphocyanide (white), ferrocyanide (white), ferricyanide (orange), chloride (white), bromide (cream), iodide (yellow) Filter

| *Precipitate* | | *Solution* |
|---|---|---|
| Wash well with water and digest with a large excess of ammonia, filter | | Add dilute ammonia drop by drop until the solution is just neutral, a precipitate indicates<br>Phosphate, arsenite—yellow ppt<br>Arsenate—red ppt<br>Oxalate, formate,* tartrate, citrate—white ppt<br><br>* See Test 9(*b*), p 395 |
| *Residue* | *Solution* | |
| Iodide (yellow) and ferrocyanide (white) Confirm by tests given in last column of table on p 394 The bromide is only sparingly soluble in $NH_3$ and may occur here | Acidify with dilute nitric acid, when cyanide, sulphocyanide, ferricyanide, chloride and bromide are reprecipitated Confirm by tests given in last column of table on p 394 | |

The additional tests given on pp 393 and 395 for radicals such as nitrates, acetates, etc, should be tried Sufficient information should then have been obtained to identify most of the simpler acid radicals

# CHAPTER XXX

## VOLUMETRIC ANALYSIS

**Volumetric and gravimetric analysis.**—Quantitative analysis is carried out by two methods (*a*) VOLUMETRIC ANALYSIS (*b*) GRAVIMETRIC ANALYSIS

Volumetric analysis depends on the use of STANDARD SOLUTIONS, prepared in such a way that a given volume of solution contains a known weight of a reagent, such as an acid or alkali, or an oxidising or reducing agent These solutions are " titrated " by running one solution into another, until the " end-point " of the action is shown by some change in the appearance of the liquid For this purpose an INDICATOR may be added to show, for instance, when the solution changes from an acid to an alkaline reaction

Gravimetric analysis depends upon the separation, collection and weighing of a pure compound of the element or radical which is to be estimated These processes are applicable to a very wide range of analyses, but are relatively slow and tedious

Since volumetric analyses are quick and easy to perform, volumetric methods have been devised for many of the common analyses, *e g* for the estimation of acids and alkalis, and of oxidising and reducing agents These processes usually take place entirely in solution, but another large group of volumetric analyses depends on the precipitation of an insoluble salt Thus, silver salts and halogens are estimated by determining the end-point at which measured volumes of two solutions exactly precipitate one another , and in the same way the hardness of water can be estimated by observing what volume of a standard soap solution must be used to precipitate all the lime and produce a permanent lather

**Preparation of standard solutions** —The calculation of the results of volumetric analysis are greatly simplified if standard solutions are used which contain *equivalent* weights rather than *equal* weights in a given volume Standard solutions are therefore generally prepared in accordance with the following definitions

*A* NORMAL SOLUTION *contains one gram-equivalent* of the solute in each litre of solution*

*A* DECINORMAL SOLUTION *contains one-tenth of a gram-equivalent of the solute in each litre of the solution*

For some purposes " weight-normal " solutions are preferred to " volume-

* A GRAM-EQUIVALENT is the equivalent expressed in grams, *e g* 8 grams of oxygen A GRAM ATOMIC WEIGHT is the atomic weight expressed in grams, *e g* 16 grams of oxygen A GRAM MOLECULAR WEIGHT is the molecular weight expressed

normal " solutions ; they may be prepared in such a way as to contain one gram-equivalent of the solute in 1000 grams of the solvent, or (more commonly) in 1000 grams of solution The equivalents required in volumetric analyses have already been discussed in Chapter VII (p 46)

In a few cases, the materials used in preparing standard solutions are sufficiently pure to be weighed out directly Thus a standard solution of *silver nitrate* can be prepared by weighing out the calculated quantity of the salt. For work of the highest precision, however, *metallic silver* is generally weighed, dissolved in nitric acid, and evaporated to dryness to get rid of acid, before dissolving in a known volume of water to make the standard solution A standard solution of an alkali can be prepared by weighing *sodium carbonate*, prepared by gently igniting *sodium bicarbonate*, since this is more readily purified than the more soluble carbonate A standard acid can be prepared by weighing out crystals of *oxalic acid*, $H_2C_2O_4,2H_2O$

In other cases a solution of approximately the desired strength is prepared from ordinary laboratory materials, and is then " standardised " by titration against a pure material The solution can then be used with a factor, *e g* as 1 065$N$ or 0 997$N$, where $N$ represents a normal solution, or (if too strong) can be diluted in a known ratio to give a solution of exactly the desired strength Thus hydrochloric acid may be standardised (i) by titrating against pure *sodium carbonate* as described above, or (ii) by placing a known excess of pure *calcite*, $CaCO_3$, in a known volume of the acid, and determining what weight of the carbonate is left over. Conversely, a solution of caustic soda or baryta is standardised by titration against a standard acid Amongst oxidising and reducing agents, *potassium dichromate*, $K_2Cr_2O_7$, and *ferrous ammonium sulphate*,

$$(NH_4)_2SO_4,FeSO_4,6H_2O$$

(which contains one-seventh of its weight of iron), may be weighed out directly, but *potassium permanganate*, $KMnO_4$, and *sodium thiosulphate*, $Na_2S_2O_3,5H_2O$, are not pure enough to be weighed out directly, and must always be standardised

**Measurements of volume** —The measuring vessels used in volumetric work must be scrupulously clean and free from grease, otherwise drops of liquid will stick to the glass and the correct volume of liquid will not be delivered Dirty apparatus can be freed from grease by rinsing it for a few minutes with a saturated solution of caustic soda in methylated spirits, followed by distilled water For further cleansing, the apparatus may be filled with a solution of dichromate in concentrated sulphuric acid, and allowed to stand overnight before being washed out with distilled water

Measuring vessels should never be dried by heating, since glass expands when heated and takes several weeks to contract to its former volume They are therefore dried by rinsing with acetone, which can then be removed by blowing dust-free air into the apparatus The air from foot bellows can be freed from dust by passing it through a tube packed with glass wool

Ordinary laboratory apparatus is graduated to within about $\frac{1}{2}$% of the correct volume, and must therefore be recalibrated when great accuracy

is required Pipettes and burettes may be calibrated by delivering a measured volume of water from them into a weighed flask, fitted with a cork to prevent loss by evaporation The water is weighed and its volume is deduced from its known density at the atmospheric temperature In the case of a burette, a graph can be plotted from the results obtained for the delivery of 5 c c , 10 c c , 15 c c , etc , and subsequent readings can be corrected with the help of this graph A flask can be calibrated by weighing it empty and then filled to the mark with water, since (unlike a pipette or burette) it should *contain* and not *deliver* a known volume of water

Instead of applying a correction to the nominal volume of a flask or pipette, it is often convenient to find the true calibration mark This may be done by gumming a thin strip of paper to the stem or neck 2 cms above or below the original mark, according to whether the volume delivered was too small or too great, and finding the new weight of water which is delivered from this point The exact position for the new calibration can then be calculated and etched on the glass by means of hydrofluoric acid

The relative strengths of the solutions that are titrated should be so adjusted that the volumes delivered from the pipette and burette are not less than 10 c c , but larger volumes of the order of 25 c c or more are to be recommended, since the errors of measurement are then relatively less Thus an error of 0 05 c c in reading the volume delivered by a burette involves an error of $\frac{1}{2}\%$ on 10 c c but only 0 2% on 25 c c Errors are also minimised by taking the mean of at least three concordant titrations the results should *never* be based on one titration

## A Neutralisation

**General considerations** —Volumetric methods can be applied very readily to the estimation of acids and bases, by reason of the ease with which the point of neutrality can be detected Acids and bases can be classified as follows

| *Strong acids* | *Weak acids* |
|---|---|
| Hydrochloric acid | Oxalic acid |
| Nitric acid | Acetic acid |
| Sulphuric acid | Carbonic acid |
| *Strong bases* | *Weak bases* |
| Sodium hydroxide | Ammonia |
| Potassium hydroxide | *Sodium carbonate |
| Barium hydroxide | *Sodium bicarbonate |

It is shown in Chapter XLV (p 634) that the choice of an indicator in titrating an acid and a base depends on the strength of the acid and base, thus

| *Acid* | *Base* | *Indicator* |
|---|---|---|
| Strong | Strong | Any indicator |
| Strong | Weak | Methyl orange or methyl red |
| Weak | Strong | Phenolphthalein |
| Weak | Weak | No indicator is satisfactory |

* Sodium carbonate and bicarbonate are really *salts* of carbonic acid , but this acid is so weak that its presence merely serves to convert the strongly basic alkali, sodium hydroxide, into the equivalent of a weak base

The direct titration of a weak acid against a weak base should be avoided, as it is impossible to obtain a sharp end-point with any indicator

**Preparation of standard solutions.**—(*a*) Pure anhydrous *sodium carbonate*, suitable for preparing standard solutions by direct weighing, can be prepared by passing carbon dioxide into a strong solution of washing soda, and collecting, drying and gently igniting the precipitate of sodium bicarbonate

$$2NaHCO_3 \rightleftharpoons Na_2CO_3 + CO_2 + H_2O$$

The whole or a suitable part of the residue of sodium carbonate is weighed out from the crucible, washed into a standard flask and diluted to a known volume with distilled water

(*b*) As an alternative, a piece of freshly-cut *sodium* can be weighed out in a stoppered weighing bottle, taking care to avoid exposure to moist air The sodium is dissolved in alcohol as sodium ethoxide, which is then hydrolysed to *sodium hydroxide* by diluting to a known volume with distilled water

$$2C_2H_5OH + 2Na = 2C_2H_5ONa + H_2,$$
$$C_2H_5ONa + H_2O = NaOH + C_2H_5OH$$

(*c*) A standard solution of *hydrochloric acid* can be prepared by Moody's method by direct absorption and weighing of gaseous hydrogen chloride (Lowry, *Inorganic Chemistry*, Fig 122, p 323), and dilution to a known volume with distilled water In the same way, a standard solution of *sulphuric acid* can be prepared by Marshall's method, which depends on measuring the density, and thence deducing the strength of sulphuric acid which has been diluted to about 75% $H_2SO_4$ by pouring the concentrated acid into half its volume of water This concentration is used because the density of sulphuric acid becomes almost constant as the concentration approaches 100% $H_2SO_4$ The relative density at 18° of this diluted acid is determined with a pyknometer, without making any correction for buoyancy of the air, and its concentration is read off from a table of densities specially prepared for this purpose A calculated amount of acid is then weighed out directly from the pyknometer into a graduated flask to give a standard acid of the required strength

TABLE 36 —RELATIVE DENSITIES OF SULPHURIC ACID AT 18°

| $d_{18}^{18}$ | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 65 | 73 16 | 73 25 | 73 33 | 73 42 | 73 50 | 73 59 | 73 67 | 73 76 | 73 84 | 73 93 |
| 1 66 | 74 01 | 74 10 | 74 18 | 74 27 | 74 35 | 74 44 | 74 52 | 74 61 | 74 69 | 74 78 |
| 1 67 | 74 86 | 74 95 | 75 03 | 75 12 | 75 20 | 75 29 | 75 37 | 75 46 | 75 54 | 75 63 |
| 1 68 | 75 71 | 75 80 | 75 88 | 75 97 | 76 05 | 76 14 | 76 22 | 76 31 | 76 40 | 76 48 |
| 1 69 | 76 57 | 76 65 | 76 74 | 76 82 | 76 91 | 76 99 | 77 08 | 77 17 | 77 25 | 77 34 |
| 1 70 | 77 42 | 77 51 | 77 59 | 77 68 | 77 77 | 77 85 | 77 94 | 78 03 | 78 11 | 78 20 |

Table 36 gives the concentrations for increments of density of 0 001, corresponding with increments of concentration of 0 08 to 0 09% $H_2SO_4$ When using this table, the quantities of acid and water which fill the pyknometer at 18° should be weighed without making any correction for the buoyancy of air or for the absolute density of water at 18° (Marshall, *J Soc Chem Ind*, 1899, **18**, 6)

(*d*) As an alternative, solutions which are definitely above the desire strength can be prepared by assuming that concentrated hydrochlori acid is approximately 10*N*, and must therefore be diluted about 10-fol to give a normal solution Similarly, concentrated sulphuric acid may b weighed out roughly (or measured out in a graduated cylinder) on th assumption that the strong acid contains about 95% $H_2SO_4$, and has density of 1 84 The exact strength of the solution is determined b titration against a standard alkali, prepared as described under (*a*) or (*b* above , a standard solution of the desired strength can then be prepare by dilution with the calculated proportion of pure water

(*e*) A solution of hydrochloric acid can also be standardised by Orm Masson's method, by determining the weight of pure *calcium carbonat* which it will dissolve For this purpose a piece of Iceland spar (abou 3 grams is a convenient weight) is weighed in a beaker, into which 50 c c of approximately *N*/10 HCl are then run The beaker is covered with watch glass, to prevent loss of acid spray, and set aside in a warm plac until effervescence ceases The beaker is then heated to expel carbo dioxide and to ensure completion of the action The residue of spar rinsed with distilled water, dried in the beaker at 110°, and reweighe The strength of the acid is deduced on the assumption that two equiva lents dissolve 100 grams of calcite, according to the equation

$$\underset{\text{100 grams}}{CaCO_3} + \underset{\text{2 equivalents}}{2HCl} = CaCl_2 + CO_2 + H_2O$$

Since the action is completed in a warm solution, in which carbon dioxid is not allowed to accumulate, the carbonate is dissolved exclusively a chloride and the experiment is not vitiated by dissolution as bicarbonate

**Examples of neutralisation.**—It is assumed that the student is alread familiar with the direct titration of an acid against an alkali The est mation of atmospheric carbon dioxide by titration with baryta wate (Pettenkofer's method) has been described in Expt 31 (p 241) Othe estimations may be made as follows

EXPT 58 **Estimation of a mixture of hydroxide and carbonate**

Sodium and potassium bicarbonates behave as alkalis towards meth orange but are neutral towards phenolphthalein The conversion of th hydroxide into chloride can therefore be followed by titrating with hydr chloric acid and noting the end-point at which the pink colour of (alkalin phenolphthalein vanishes,

$$NaOH + HCl = NaCl + H_2O$$

Since sodium and potassium carbonates also behave as alkalis towar phenolphthalein, the conversion of carbonate into bicarbonate is include in this stage of the titration

$$Na_2CO_3 + HCl = NaCl + NaHCO_3$$

Methyl orange can now be added to the colourless solution, and will give a alkaline reaction until the bicarbonate has been converted into chloride

$$NaHCO_3 + HCl = NaCl + CO_2 + H_2O$$

The calculations are carried out as in the following example

20 c c of a solution containing potassium hydroxide and carbonate required 25 c c of $N/10$ acid for neutralisation, using phenolphthalein as the indicator

On the addition of methyl orange, a further 5 c c of $N/10$ acid were required for neutrality, *i e*

$N/10$ acid used to neutralise half the carbonate in 20 c c of solution $= 5$ c c

$N/10$ acid required to neutralise all the carbonate in 20 c c of solution $= 10$ c c

Hence normality of carbonate $= N/10 \times 10/20 = N/20$

But total acid required for neutralisation of carbonate and hydroxide $= 25 + 5 = 30$ c c

$N/10$ acid required to neutralise the hydroxide in 20 c c of solution $= 30 - 10$ c c $= 20$ c c

Hence normality of hydroxide $= N/10 \times 20/20 = N/10$

The estimation of a mixture of bicarbonate and carbonate is carried out in precisely the same way as the above Litmus can be used in place of methyl orange in these titrations, provided that the carbon dioxide is expelled by boiling the solution

EXPT 59 **Estimation of the percentage of ammonium sulphate in lawn sand**

The percentage of ammonium sulphate in " lawn sand " can be estimated by boiling a known weight of the mixture (about 2 5 grams) with 25 c c of normal sodium hydroxide in a beaker flask

$$(NH_4)_2SO_4 + 2NaOH = Na_2SO_4 + 2NH_3 + 2H_2O$$

When all the free ammonia has been expelled, as shown by holding in the vapour some paper soaked in Nessler's solution, the residual liquid is decanted from the sand and made up to 250 c c with the washings from the beaker flask The excess of alkali is then estimated by titrating 25 c c portions against $N/10$ hydrochloric acid, using methyl orange or methyl red as the indicator The calculation is made as in the following example

Two grams of " lawn sand " were boiled with 25 c c of $N/2$NaOH The residual liquor, after expulsion of the ammonia, was decanted and made up to 100 c c with distilled water 25 c c portions of this solution required 15 c c of $N/10$ sulphuric acid for neutralisation

Normality of residual sodium hydroxide $= N/10 \times 15/25 = N \times 3/50$

Sodium hydroxide left in 100 c c $= \frac{100}{1000} \times \frac{3}{50} = \frac{3}{500}$ equivalents

But sodium hydroxide originally added $= \frac{25}{1000} \times \frac{1}{2} = \frac{1}{80}$ equivalents

Sodium hydroxide used up by the sulphate $= \frac{1}{80} - \frac{3}{500} = \frac{13}{2000}$ equivalents

One equivalent weight of ammonium sulphate, $\frac{1}{2}(NH_4)_2SO_4 = 66$ grams, neutralises one equivalent weight of sodium hydroxide

Weight of ammonium sulphate $= 66 \times \frac{13}{2000} = 0\ 429$ gram

Hence ammonium sulphate in lawn sand $= \frac{0\ 429 \times 100}{2} = 21\ 5\%$

EXPT 60 **Estimation of nitrogen in potassium nitrate by reduction to ammonia**

In alkaline solutions, nitrates and nitrites are reduced quantitatively by Devarda's alloy (Cu 50%, Al 45%, Zn 5%) to ammonia, which can be estimated by means of standard acid

$$KNO_3 + 4H_2 = KOH + NH_3 + 2H_2O$$

About one gram of accurately weighed potassium nitrate, together with 50 c c of water and 2 to 3 grams of powdered Devarda's alloy, are placed in a 500 c c flask fitted with a rubber stopper carrying a funnel and delivery tube (Fig 102) The delivery tube is fitted with a trap, *B*, to prevent

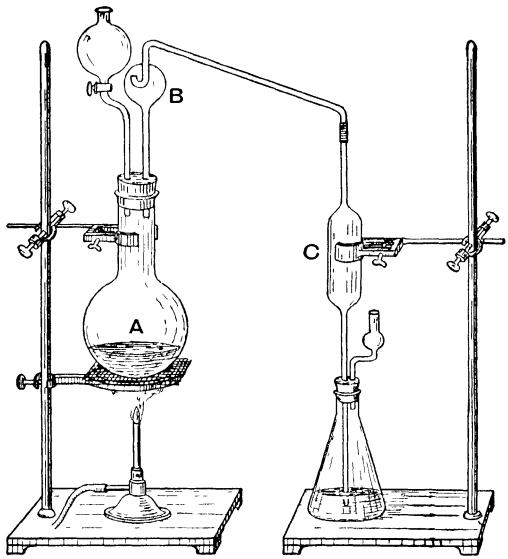



FIG 102 ESTIMATION OF AMMONIA

alkaline spray being carried over in the subsequent distillation, and is connected by a rubber joint to a 50 c c pipette, which dips into 50 c c of $N/2$ sulphuric acid in a conical flask The conical flask is fitted with an absorption tube, containing pieces of broken glass which have been moistened with acid by running the sulphuric acid through it The object of this tube is to avoid loss of ammonia during the distillation 100 c c of 30% caustic soda are then added gradually from the tap-funnel and the mixture is left for about an hour before about half of it is cautiously distilled over into the sulphuric acid The distillation must be continued until a drop of the residual liquor no longer responds to Nessler's reagent The excess of sulphuric acid is then estimated by washing out the contents of the conical flask and absorption tube into a 250 c c flask, making up to the mark, and titrating 25 c c portions of it with $N/10$ caustic soda, using methyl red as the indicator.

## B. Oxidation and Reduction

**General considerations.**—A large number of oxidations and reductions can be carried out by volumetric methods, and these can be used *inter alia* for the estimation of metals, such as iron, which can exist in solution in two states of oxidation The principal agents used in these titrations are as follows

| *Oxidising agents* | *Reducing agents* |
|---|---|
| Iodine | Ferrous sulphate |
| Potassium permanganate | Sodium thiosulphate |
| Potassium dichromate | Arsenious oxide |

**Determinations by means of iodine and sodium thiosulphate.**—The fundamental reaction is represented by the equation

$$2Na_2S_2O_3 + I_2 = Na_2S_4O_6 + 2NaI$$

As an example, *iodine* can be estimated by adding a standard solution of sodium thiosulphate from a burette, until the yellow colour of the iodine just disappears Since the last traces of yellow colour are easily disguised, *e g* by impurities in the solution, a few drops of starch solution are generally added when most of the iodine has been removed , this unites with the residue of free iodine to form an intensely blue complex, which is decolorised when enough thiosulphate is added to eliminate the residual iodine according to the equation set out above The end-point of the titration is then marked by the disappearance of the blue colour of the starch-iodine complex

*Sodium thiosulphate*, $Na_2S_2O_3,5H_2O$, is not sufficiently pure to be weighed out directly for the preparation of standard solutions Free *iodine* can be used, if previously resublimed from potassium iodide, but it is not easily soluble in water and is therefore generally dissolved with the help of potassium iodide, as $KI_3$, which can be titrated in exactly the same way as iodine

$$KI_3 + 2Na_2S_2O_3 = KI + 2NaI + Na_2S_4O_6$$

As an alternative, an approximately decinormal solution of sodium thiosulphate, containing about 24 8 grams per litre ($\frac{1}{10}$ mol ), can be standardised by means of *potassium iodate*, which can readily be procured in a pure state and weighed out directly This salt is an oxidising agent, which interacts quantitatively with an acidified solution of potassium iodide according to the equation

$$KIO_3 + 5KI + 6HCl = 6KCl + 3I_2 + 3H_2O.$$

The equivalent is one-sixth of a molecule , a decinormal solution would therefore contain 3 57 grams ($\frac{1}{60}$ mol ) per litre, and would liberate 12 7 grams ($\frac{1}{20}$ mol ) of free iodine per litre Such a solution can be used to standardise an approximately $N/10$ solution of sodium thiosulphate, and this can be used in turn to standardise solutions of iodine As a further alternative, if a standard solution of potassium permanganate (p 426) is

available, this can be used to liberate an equivalent quantity of iodine from an acidified solution of potassium iodide :

$$2KMnO_4 + 10KI + 8H_2SO_4 = 6K_2SO_4 + 2MnSO_4 + 5I_2 + 8H_2O$$

The thiosulphate can then be standardised by titration against the iodine thus liberated Conversely, an unknown solution of permanganate may be standardised against a standard solution of thiosulphate

**Estimation of reducing agents by oxidation with iodine.**—Four examples are given of reducing agents ($H_2S$, $SO_2$, $As_2O_3$, $SnCl_2$) which can be estimated by titration with a standard solution of iodine (For convenience, the empirical formula $As_2O_3$ is used in place of the molecular formula $As_4O_6$)

(*a*) *Hydrogen sulphide* —The oxidation of hydrogen sulphide by iodine, $I_2 + H_2S = 2HI + S$, is not quantitative, since other oxidation products are formed More accurate results are obtained by precipitating arsenious sulphide by the addition of an excess of standard arsenious oxide The precipitate is coagulated by warming with dilute hydrochloric acid and removed by filtration The excess of arsenious oxide in the filtrate can then be estimated with standard iodine as described in Expt 61

$$As_2O_3 + 3H_2S = As_2S_3 + 3H_2O$$

EXPT 61 **Determination of the solubility of hydrogen sulphide in water**

A saturated solution of hydrogen sulphide is prepared by bubbling the gas for three or four hours through water in a bottle (Fig 103) fitted with a cork, delivery tube and narrow exit tube In this way the water is saturated with hydrogen sulphide at atmospheric pressure, and not at some lower pressure, as would be the case if the neck of the bottle were open to the air 25 c c of the saturated solution are diluted to 100 c c with water, and 25 c c of the diluted solution are added to 25 c c of $N/10As_2O_3$ (p 421) The mixture is acidified with hydrochloric acid, warmed to coagulate the arsenious sulphide, and filtered. The excess of arsenious oxide in the filtrate is then estimated by means of $N/10$ iodine in the presence of sodium bicarbonate (see below) The solubility of hydrogen sulphide is calculated on the assumption that 1 68 c c of it uses up 1 c c of $N/10As_2O_3$

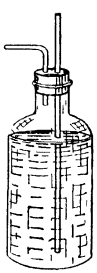


FIG 103 BOTTLE FOR PREPARING A SATURATED SOLUTION OF HYDROGEN SULPHIDE

(*b*) *Sulphurous acid* —When sulphurous acid or a sulphite is added to an *excess* of iodine, it is oxidised quantitatively to sulphuric acid

$$H_2SO_3 + I_2 + H_2O = H_2SO_4 + 2HI$$

If iodine is not in excess, part of the sulphurous acid is reduced to sulphur by the hydrogen iodide

$$H_2SO_3 + 4HI = 2I_2 + S + 3H_2O$$

The excess of iodine is titrated with sodium thiosulphate One equivalent of iodine oxidises 41 grams ($\frac{1}{2}$ mol ) $H_2SO_3$ or 32 grams ($\frac{1}{2}$ mol ) $SO_2$

(*c*) *Arsenious oxide and arsenites* —The interaction of arsenious oxide with iodine is reversible

$$As_2O_3 + 2I_2 + 2H_2O \rightleftharpoons As_2O_5 + 4HI$$

The oxidation of arsenious oxide by iodine proceeds to completion, however, when sodium bicarbonate is added to convert the hydrogen iodide into sodium iodide and thus to destroy its reducing action on the arsenic oxide Caustic soda must not be used for this purpose, because it interacts directly with iodine as well as with hydrogen iodide Conversely, when the iodine is removed by the addition of sodium thiosulphate, the reduction of arsenic oxide by hydrogen iodide proceeds to completion Arsenious oxide and arsenites can therefore be titrated directly against iodine *in presence of an excess of sodium bicarbonate*, whilst arsenic oxide and arsenates can be titrated by running sodium thiosulphate into an acidified solution containing excess of potassium iodide

EXPT 62 **Determination of the percentage purity of a specimen of arsenious oxide**

About one gram of arsenious oxide is weighed out and dissolved in 50 c c of warm dilute (1 *N*) caustic soda in a 250 c c flask After the addition of a drop of phenolphthalein, the solution is just neutralised with dilute sulphuric acid to remove free sodium hydroxide, and 5 grams of sodium bicarbonate are added in about 100 c c of water The volume is made up to 250 c c and the solution is titrated against 25 c c portions of *N*/10 iodine, starch being used to indicate the end-point Since arsenious oxide is very poisonous, it is essential to measure it out from a burette and not to use a pipette The purity of the oxide is calculated on the assumption that 1 c c of *N*/10 iodine corresponds to 0 00495 gram $As_2O_3$

(*d*) *Stannous chloride* —Soluble stannous salts may be estimated by making use of the fact that iodine oxidises stannous tin quantitatively to the stannic state

$$SnCl_2 + 2HCl + I_2 = SnCl_4 + 2HI$$

Two gram-equivalents (254 grams) of iodine are required for the oxidation of one gram-atom (119 grams) of tin A standard solution of iodine is run into a solution of the stannous salt in dilute hydrochloric acid, and the end-point is indicated by means of starch Atmospheric oxidation can be minimised by placing the stannous solution in a conical flask, which is filled with carbon dioxide and fitted with a cork containing a hole just large enough to admit the end of the pipette or burette

**Estimation of oxidising agents by liberation of iodine.**—Nine examples are given below of oxidising agents ($H_2O_2$, $KMnO_4$, $K_2Cr_2O_7$, $K_2S_2O_8$, $Cl_2$, $Br_2$, $MnO_2$, $CuSO_4$, $FeCl_3$), which can be estimated by liberation of iodine from hydrogen iodide, in neutral or acid solutions

(*a*) *Hydrogen peroxide* —Hydrogen peroxide liberates iodine quantitatively from acidified solutions of potassium iodide

$$H_2O_2 + 2KI + 2HCl = 2KCl + I_2 + 2H_2O$$

The iodine, liberated by adding an excess of potassium iodide and dilute

hydrochloric acid to a measured volume of hydrogen peroxide, is titrated with standard thiosulphate (see p 89)

(*b*) *Potassium permanganate, dichromate and persulphate* —The oxidations proceed according to the following equations

$$2KMnO_4 + 10KI + 16HCl = 12KCl + 2MnCl_2 + 5I_2 + 8H_2O$$
$$K_2Cr_2O_7 + 6KI + 14HCl = 8KCl + 2CrCl_3 + 3I_2 + 7H_2O$$
$$K_2S_2O_8 + 2KI = 2K_2SO_4 + I_2$$

Oxidation by dichromate or persulphate is slow , care must therefore be taken to use an excess of potassium iodide, and to allow time for further liberation of iodine when the end-point appears to be reached At the end of the chromate titration the blue colour of the starch changes to the *green* of a chromic salt

(*c*) *Chlorine* —Chlorine, and agents which produce chlorine, liberate iodine quantitatively from potassium iodide

$$2KI + Cl_2 = 2KCl + I_2$$

EXPT 63 **Estimation of available chlorine in bleaching powder (Iodometric method )**

Bleaching powder (about 5 grams) is weighed out in a weighing bottle or in a corked tube, by preference on an old balance which would not be harmed by traces of chlorine The bleaching powder is ground up in a mortar with successive small quantities of water, until it has all been transferred as a milky suspension to a 500 c c flask After diluting to 500 c c , and shaking vigorously to ensure thorough mixing, portions of 25 c c are withdrawn quickly and run into an excess of potassium iodide, acidified with dilute acetic or hydrochloric acid The iodine, which is liberated according to the equation

$$Ca(OCl)_2 + 4KI + 4HCl = CaCl_2 + 4KCl + 2I_2 + 2H_2O,$$

is then titrated with $N/10$ thiosulphate, 1 c c of which corresponds to 0 00355 gram of available chlorine

EXPT 64 **Estimation of available chlorine in bleaching powder (Arsenite method )**

Bleaching powder oxidises arsenites to arsenates

$$2Na_3AsO_3 + Ca(OCl)_2 = 2Na_3AsO_4 + CaCl_2$$

Since chlorides and chlorates do not effect this oxidation, it can be used to estimate the available chlorine in bleaching powder

An alkaline $N/10$ solution of arsenious oxide (4 95 grams $As_2O_3$ per litre), prepared as described in Expt 62, is run into 25 c c of the suspension of bleaching powder, until a drop of the liquid no longer gives a blue colour with STARCH IODIDE PAPER, *i e* filter-paper which has been soaked in a solution containing 1% each of starch and of potassium iodide, and then dried by exposure to air The liberation of iodine, which may be represented by the equation

$$Ca(OCl)_2 + 4KI + 2H_2O = Ca(OH)_2 + 2KOH + 2KCl + 2I_2, \quad (1)$$

has to be detected by an EXTERNAL INDICATOR, since, if starch and potassium iodide were added "internally" to the solution, the blue starch-iodine complex would become clogged with chalk and the end-point would not be sharp The bicarbonate, used in preparing the solution of arsenious oxide, converts the alkalis produced in (i) into the corresponding carbonates, and thereby prevents them from making the starch iodide paper insensitive by converting most of the iodine into iodide and hypoiodite

$$Ca(OH)_2 + 2NaHCO_3 = CaCO_3 + Na_2CO_3 + 2H_2O \qquad (ii)$$

The use of an external indicator is made much easier by "bracketing," *i e* by two preliminary rapid titrations in which the standard solution is added in large portions, *e g* (i) 5 c c between each test with the external indicator, and then (when the end-point has thus been roughly located) (ii) 1 c c at a time, after adding all but the last 5 c c In the final titrations the standard solution is added o 1 c c at a time, after adding all but the last 1 c c

The use of an external indicator can be avoided by adding an excess of arsenious oxide to a measured volume of the suspension of bleaching powder, and titrating the excess with a standard solution of iodine

1 c c $N/10 As_2O_3 = 0.00355$ gram of available chlorine

(*d*) *Bromine* can be estimated, like chlorine, by titrating the iodine which it liberates from potassium iodide

$$2KI + Br_2 = 2KBr + I_2$$

It cannot be titrated directly against sodium thiosulphate, because this undergoes two parallel oxidations

$$2Na_2S_2O_3 + Br_2 = Na_2S_4O_6 + 2NaBr \qquad (i)$$

$$Na_2S_2O_3 + 4Br_2 + 5H_2O = 2NaHSO_4 + 8HBr \qquad (ii)$$

In (i) each atom of bromine oxidises 1 mol $Na_2S_2O_3$, but in (ii) it oxidises only 1/8 mol The proportions in which (i) and (ii) occur can be found by titrating a solution of bromine, (a) after adding potassium iodide, and (b) without potassium iodide, but using starch-iodide paper as an external indicator If 20 c c of the bromine require $y$ c c $N/10$ thiosulphate in (a) and $z$ c c thiosulphate in (b), the proportion $x$ which interacts "normally" according to equation (i) can be calculated from the relation,

$$z = xy + \tfrac{1}{8}(1 - x)y,$$

since in the second titration a fraction $x$ of the total bromine $y$ is oxidised normally according to equation (i) and uses up $xy$ c c of thiosulphate, whilst a fraction $(1 - x)$ is oxidised according to equation (ii) and uses up only 1/8 of the normal amount of thiosulphate *i e* $\frac{1}{8}(1 - x)y$ The results can be checked by estimating the acid liberated in the direct titration, (b), by a subsequent further titration with $N/10$ alkali Since 8 equivalents of bromine give 10 equivalents of acid in equation (ii), but none in equation (i), the volume of $N/10$ alkali required for neutralisation should be $\frac{10}{8}(1 - x)y$.

(*e*) *Insoluble oxidising agents* —The available oxygen in an insoluble peroxide can be estimated by using it to liberate chlorine from hydrochloric acid, collecting the chlorine in a solution of potassium iodide, and titrating as in (*c*), *e g*

$$MnO_2 + 4HCl = MnCl_2 + Cl_2 + 2H_2O\ , \quad 2KI + Cl_2 = 2KCl + I_2$$

EXPT 65 **Determination of available oxygen in pyrolusite**

About 1 gram of powdered pyrolusite, $MnO_2$, is weighed out into a round-bottomed 250 c c flask containing about 100 c c of concentrated hydrochloric acid and a lump of magnesite, $CaCO_3$, $MgCO_3$ The flask is immediately attached to a delivery tube connected with two U-tubes (Fig 104), containing potassium iodide (20 grams in 100 c c of water) The corks should

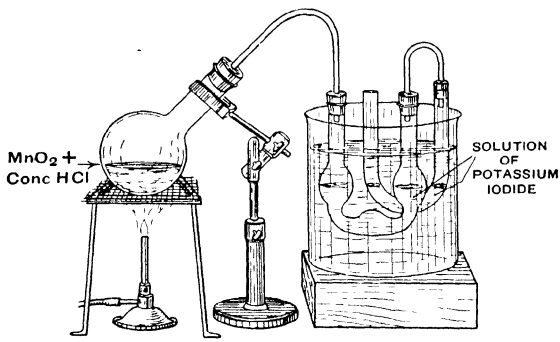



FIG 104 ANALYSIS OF INSOLUBLE OXIDISING AGENTS

be coated inside with paraffin wax to protect them from the action of chlorine When the flask is heated cautiously, a stream of chlorine (mixed with carbon dioxide from the magnesite) is given off and absorbed in the U-tubes, which are cooled in a bath of cold water to prevent loss of iodine by volatilisation The magnesite yields a steady stream of carbon dioxide, which helps to displace the chlorine from the flask into the U-tubes, and promotes regular absorption there When no more chlorine is evolved, the contents of the U-tubes are washed into a 250 c c flask and made up to that volume Portions of 25 c c are then titrated with N/10 thiosulphate The available oxygen is calculated on the assumption that 1 c c of N/10 thiosulphate is required for 0 0008 gram of oxygen

(*f*) *Cupric copper* —In the absence of mineral acids, solutions of cupric salts liberate iodine quantitatively from potassium iodide as represented by the equation

$$2CuSO_4 + 4KI = 2CuI + 2K_2SO_4 + I_2.$$

The cuprous iodide settles out as a cream precipitate, but does not interfere with the estimation of the iodine by the thiosulphate method Mineral acids must be removed before the addition of potassium iodide and

thiosulphate This is done by adding sodium carbonate until a slight precipitate of basic cupric carbonate is obtained, and then a little acetic acid to give a clear solution

EXPT 66 **Estimation of copper in crystalline copper sulphate**

About 6 grams of " blue vitriol," $CuSO_4,5H_2O$, are weighed out accurately and dissolved in hot water in a beaker The solution is transferred to a flask and made up to 250 c c Portions of 25 c c are placed in a conical flask with excess of potassium iodide solution The mixture is shaken well whilst standard $N/10$ thiosulphate is added from a burette When the colour of the iodine has almost gone, starch is added to indicate the end-point, which is quite sharp in spite of the precipitate of cuprous iodide One gram-atom of cupric copper (63 6 grams) liberates one equivalent of iodine, so that 1 c c of $N/10$ thiosulphate $\equiv$ 0 00636 gram of copper

(*g*) *Ferric iron* —Solutions of ferric salts react reversibly with iodides as shown by the equation

$$2Fe^{+++} + 2I^- \rightleftharpoons 2Fe^{++} + I_2$$

The reduction of the ferric ion proceeds to completion if the iodine is removed by the addition of thiosulphate, but it is so slow that a little freshly precipitated cuprous iodide (prepared as above) is used to catalyse it The mechanism of this catalysis is presumably

$$Fe^{+++} + Cu^+ = Fe^{++} + Cu^{++}, \quad 2Cu^{++} + 2I^- = 2Cu^+ + I_2$$

**Potassium permanganate as an oxidising agent in volumetric analysis.**— It has already been stated (p 49) that potassium permanganate, $KMnO_4$, is readily reduced (i) in acid solution to salts of manganous oxide, MnO, with the liberation of *five* equivalents of oxygen, (ii) in alkaline or neutral solution to manganese dioxide, $MnO_2$, with liberation of *three* equivalents of oxygen from each molecule

$$2KMnO_4 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 3H_2O + 5O \quad (i)$$

$$2KMnO_4 + H_2O = 2KOH + 2MnO_2 + 3O \quad (ii)$$

(*a*) Titrations with potassium permanganate are carried out, if possible, in presence of sulphuric acid, when the end-point is marked by the disappearance of the intense colour of the permanganate and the production of a colourless solution of potassium and manganese sulphates Under these conditions the equivalent is 1/5 mol (31 6 grams) $KMnO_4$ Nitric and hydrochloric acids are to be avoided, because the former is itself an oxidising agent, and the latter reduces potassium permanganate with liberation of chlorine

(*b*) Reduction in neutral or alkaline solution gives a muddy suspension of manganese dioxide, which obscures the end-point , but some oxidations can only be effected under these conditions, *e g* the oxidation of an iodide to an iodate

$$2KMnO_4 + KI + H_2O = 2KOH + 2MnO_2 + KIO_3.$$

The advantages of potassium permanganate as an oxidising agent in volumetric analysis are

(i) It gives a very sharp end-point without the use of an indicator

(ii) It is a powerful oxidising agent, and can therefore be used to oxidise a wide range of reducing agents

(iii) Its solution can be kept several months without deterioration especially if stored in a dark bottle to exclude light

The chief disadvantages are

(i) Potassium permanganate oxidises hydrochloric acid and can therefore only be used under controlled conditions when chlorides are present, *e g* in solutions of iron ores in hydrochloric acid

(ii) Standard solutions of permanganate cannot be prepared by direct weighing , a solution of approximately the right strength is therefore prepared, and then standardised by means of ferrous ammonium sulphate or oxalic acid

**Standardisation of solutions of potassium permanganate.**—(*a*) *Ferrous ammonium sulphate*, $FeSO_4,(NH_4)_2SO_4,6H_2O$, is commonly used to standardise solutions of potassium permanganate, because it is more easily purified (and apparently less quickly oxidised by air) than ferrous sulphate , but the ammonium sulphate plays no part in the reduction and may be omitted from the equation

$$2KMnO_4 + 10FeSO_4 + 8H_2SO_4 = K_2SO_4 + 2MnSO_4 + 5Fe_2(SO_4)_3 + 8H_2O$$

Since the salt contains 1/7 of its weight of iron, and its equivalent (as a reducing agent) is identical with its molecular weight, a decinormal solution can be prepared by dissolving $7 \times 5\ 6 = 39\ 2$ grams ($\frac{1}{10}$ mol ) in 200 c c of dilute sulphuric acid and diluting to a litre The acid required for the titration with permanganate is added at the beginning, because it checks the hydrolysis of the salt, and therefore impedes its oxidation by air, since ferrous hydroxide is much more readily oxidised than ferrous sulphate

As an alternative, pure iron wire (at the rate of 5 6 grams per litre of $N/10$ solution) may be weighed out and dissolved in hot dilute sulphuric acid in a conical flask Atmospheric oxidation is sufficiently checked by liberation of hydrogen , and the presence of a little carbon (say 0 4%) in the iron is covered by taking its atomic weight as 56, instead of the more precise value 55 84

(*b*) *Oxalic acid*, $C_2H_2O_4,2H_2O$, is oxidised quantitatively by acid permanganate at 60°–70° according to the equation

$$2KMnO_4 + 5C_2H_2O_4 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 10CO_2 + 8H_2O$$

A decinormal solution is prepared by weighing out 6 3 grams ($\frac{1}{20}$ mol ) of the hydrated acid, or 6 70 grams of *anhydrous* sodium oxalate, since its equivalent as an oxidising agent (like its equivalent as an acid) is half of its molecular weight

The titration is carried out by adding dilute sulphuric acid and warming to 70°, permanganate is then run in until a faint pink colour persists even when the solution is reheated The oxidation is catalysed by manganous

sulphate, and therefore proceeds more rapidly when a little permanganate has been reduced

**Estimation of reducing agents by means of potassium permanganate.**—(*a*) *Ferrous sulphate —Ferrous salts* may be titrated directly in presence of sulphuric acid as described above When, however, hydrochloric acid has been used in preparing the solution, ferrous iron is usually estimated by oxidation with a standard solution of potassium dichromate (p 429), although the oxidation of hydrochloric acid by potassium permanganate, which is promoted by ferrous salts, can be checked by an excess of manganous sulphate *Ferric solutions* can be titrated, after complete reduction to the ferrous state, by one of the following methods

(i) An excess of sulphurous acid is added to the ferric solution, and the excess is boiled off before dilution to a known volume and titration with standard permanganate

$$Fe_2(SO_4)_3 + H_2SO_3 + H_2O = 2FeSO_4 + 2H_2SO_4$$

The solution should contain as little free acid as possible, since this impedes the reduction of ferric sulphate, as well as the oxidation of ferrous sulphate (p 426)

(ii) The ferric solution is shaken vigorously for a minute in a stoppered bottle containing granulated zinc (which must obviously be free from iron), a little mercury, and sufficient sulphuric acid to make the solution approximately twice normal The ferric iron is reduced by the amalgamated zinc according to the equation

$$Fe_2(SO_4)_3 + Zn = 2FeSO_4 + ZnSO_4$$

The resulting solution is decanted from the bottle, rinsed out with water, diluted to a known volume and titrated as usual

(*b*) *Hydrogen peroxide*, although it is a strong oxidising agent, reduces acidified permanganate according to the equation

$$2KMnO_4 + 5H_2O_2 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 5O_2 + 8H_2O$$

In the absence of organic materials, which are also oxidised by permanganate, the strength of solutions of hydrogen peroxide may be estimated by adding sulphuric acid to a measured volume of the peroxide, and running in permanganate until a permanent pink colour is produced The titration can also be carried out in the converse order, when the end-point is indicated by the disappearance of the pink colour The equivalent weight of hydrogen peroxide is half the molecular weight, hence 0 0017 gram of it will reduce 1 c c of $N/10$ permanganate

EXPT 67 **Analysis of a mixture of hydrogen peroxide and persulphuric acid**

When aqueous hydrogen peroxide is mixed with four times its weight of concentrated (95%) sulphuric acid, about two-thirds of the available oxygen of the hydrogen peroxide is transferred to the acid as persulphuric acid, *e g*

$$H_2O_2 + H_2SO_4 \rightleftharpoons H_2SO_5 + H_2O,$$
$$H_2O_2 + 2H_2SO_4 \rightleftharpoons H_2S_2O_8 + 2H_2O$$

This equilibrium can be " fixed " by rapid dilution, or better by pouring on to ice The determination of the ratio of " persulphuric oxygen " to

" peroxide oxygen " then provides an interesting variant on the direct estimation of hydrogen peroxide as described above The analysis depends on the fact that the persulphuric acids (p 264) will oxidise ferrous sulphate, but (unlike hydrogen peroxide) will not reduce potassium permanganate

Portions of 2 to 5 c c of a mixture of commercial hydrogen peroxide (1 part) and sulphuric acid (4 parts) are run on to ice, to form a dilute solution, which contains hydrogen peroxide and persulphuric acid in a definite proportion, depending on the concentration of the original mixture The hydrogen peroxide is first estimated by running in $N/10$ potassium permanganate until a pink colour appears, some manganese sulphate being added, if necessary, to start the interaction An excess of $N/10$ ferrous ammonium sulphate is then added to reduce the persulphuric acid, and the excess is estimated by running in $N/10$ permanganate until a pink colour is again produced The volume of $N/10$ permanganate which is reduced by hydrogen peroxide, and of $N/10$ ferrous sulphate which are oxidised by persulphuric acid, gives the proportions of " peroxide oxygen " and " persulphuric oxygen " in the solution

(*c*) *Oxalic acid* —The oxidation of oxalic acid by potassium permanganate can be used also for the estimation of metals, such as calcium, which form insoluble oxalates

EXPT 68 **Estimation of calcium in marble**

About 1 gram of powdered marble is weighed out into a beaker and dissolved in about 40 c c of dilute hydrochloric acid The solution is boiled to expel all the carbon dioxide and then made just alkaline with ammonia and ammonium chloride A slight excess of hot ammonium oxalate solution is added, and the mixture is boiled to obtain a granular precipitate of calcium oxalate

$$CaCl_2 + (NH_4)_2C_2O_4 = CaC_2O_4 + 2NH_4Cl$$

The precipitate is transferred to a filter-paper and freed from the excess of ammonium oxalate by washing with hot water until the filtrate no longer gives a precipitate with a solution of calcium chloride It is then dissolved in hot dilute sulphuric acid and made up to 250 c c with water,

$$CaC_2O_4 + H_2SO_4 = CaSO_4 + H_2C_2O_4$$

Portions of 25 c c of this solution are then titrated with standard $N/10$ permanganate in the usual way

Since calcium oxalate contains 20 grams of calcium per equivalent weight of oxalic acid, it follows that 1 c c of $N/10$ permanganate corresponds to 0 002 gram of calcium The weight of calcium in the marble is therefore $0\ 002 \times 10x = 0\ 02x$, where $x$ is the volume of permanganate required to oxidise 25 c c of the above solution

(*d*) *Potassium nitrite* —Nitrites are oxidised to nitrates by an acid solution of potassium permanganate, thus

$$2KMnO_4 + 5KNO_2 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 5KNO_3 + 3H_2O.$$

A nitrite is estimated by running a solution of it into a known volume of hot standard permanganate, acidified with sulphuric acid, until the colour of the permanganate disappears Alternatively, a given volume of the nitrite may be added to excess of permanganate, which is then titrated back with oxalic acid The permanganate must be hot, otherwise the reaction is slow, and part of the nitrous acid may be lost, owing to its decomposition into gaseous oxides of nitrogen

**Potassium dichromate as an oxidising agent in volumetric analysis.**—A solution of potassium dichromate is often used as an oxidising agent in presence of hydrochloric or sulphuric acid, when three atoms of oxygen are rendered available for each molecule of ichromate

$$K_2Cr_2O_7 + 4H_2SO_4 = K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3O$$

The equivalent is therefore $\frac{1}{6}K_2Cr_2O_7$, and a decinormal solution can be prepared by weighing out 4 9 grams per litre of the anhydrous crystals, which are pure enough to be weighed out directly if previously powdered and dried at 130° Alternatively, a solution which is to be used for the estimation of iron is often standardised by means of ferrous sulphate prepared from pure iron wire (p 426)

The yellow dichromate is converted into a green chromic salt, and there is no sharp change of colour at the end-point *Potassium ferricyanide*, which gives a blue colour or precipitate with *ferrous* salts, and a dull brown colour with *ferric* salts, is therefore used as an *external indicator*, when iron is estimated by this method , but it must be entirely free from *ferrocyanide*, which gives a blue precipitate with *ferric* salts The indicator is therefore prepared by crushing a large crystal into coarse fragments, washing repeatedly with hot distilled water to remove ferrocyanide from the outer surface, and finally dissolving a pellet, half the size of a pea, in a test tube of water The dichromate is added to the ferrous salt (using the method of bracketing, p 423) until a drop of the solution no longer gives a blue colour when added to a drop of indicator on a white tile

Diphenylamine, $NH(C_6H_5)_2$, which is oxidised reversibly by potassium dichromate to a deep-blue dye, can be used as an *internal indicator* Since the oxidation is reversible, the titration can be carried out with either solution in the burette, using a few drops of a 1% solution of diphenylamine in concentrated sulphuric acid as an indicator The end-point is made more distinct if a few c c of a mixture of concentrated sulphuric acid and phosphoric acid are added to the liquid in the flask

**Estimation of reducing agents by means of potassium dichromate.**—(*a*) *Ferrous iron* can be estimated by this method *in presence of hydrochloric acid*, which is itself the best solvent for iron ores The preliminary reduction of the ferric salt can then be carried out with ease and certainty by means of stannous chloride

$$2FeCl_3 + SnCl_2 = 2FeCl_2 + SnCl_4$$

Concentrated hydrochloric acid is added to the ferric solution, which becomes bright yellow in colour, and a freshly-prepared dilute solution

of stannous chloride in hydrochloric acid is run into the hot solution from a burette until the yellow colour of the ferric salt just disappears The solution is then cooled, and the excess of stannous chloride is removed by adding mercuric chloride drop by drop until no more mercurous chloride is precipitated

$$SnCl_2 + 2HgCl_2 = SnCl_4 + Hg_2Cl_2$$

The ferrous salt can then be titrated with dichromate If no white precipitate is formed on adding the first drop or two of mercuric chloride, the reduction is not complete, and more stannous chloride is needed If the mixture turns grey by liberation of mercury, too much stannous chloride has been used, or the solution has been heated too strongly, and the solution must be discarded since the finely-divided mercury may reduce the dichromate

As a variant on the estimation of ferrous iron, *oxidising agents* may be added to a known excess of acidified ferrous sulphate and estimated by titrating the residue of ferrous iron with standard dichromate Thus, the available oxygen in a specimen of potassium chlorate may be determined by the oxidation of ferrous sulphate according to the equation

$$KClO_3 + 6FeSO_4 + 3H_2SO_4 = KCl + 3Fe_2(SO_4)_3 + 3H_2O$$

(*b*) *Stannous chloride* may be estimated by adding a known volume of the stannous solution to an excess of a hot solution of ferric chloride in hydrochloric acid, which has been boiled to expel dissolved oxygen The amount of ferrous chloride formed by the reduction can be estimated as in (*a*), but without adding any mercuric chloride The ferric solution must, of course, be free from ferrous iron In this reduction the equivalent of stannous tin is half its atomic weight or 59 5 grams , 1 c c of $N/10$ potassium dichromate is therefore required by 0 00595 gram of stannous tin

A stannic salt may be estimated by reducing it to metallic tin with zinc and sulphuric acid The tin and excess of zinc are dissolved in hydrochloric acid in a flask fitted with a Bunsen valve * to prevent atmospheric oxidation, and the stannous chloride is titrated with bichromate as before

## C Titrations with Silver Nitrate

**General considerations** —An important group of volumetric analyses depends on the precipitation of insoluble silver salts A standard solution of *silver nitrate* can be prepared by weighing the recrystallised salt and making up to a known volume with distilled water , when required for the estimation of a chloride, the strength of the solution can be checked (or the solution may be standardised) by titration against pure dry sodium chloride Alternatively (as in Stas's experiments, p 10) a known weight of pure *silver* can be dissolved in dilute nitric acid, and the surplus acid removed by evaporating to dryness before dissolving in water A deci-

* A Bunsen valve consists of a glass tube, fitted with a small piece of rubber tubing containing a glass rod at the other end and a slit in the side The slit in the rubber tube opens and allows gas to escape when the pressure rises inside the flask, but it does not permit air to enter the tube

normal solution contains 10 79 grams of silver or 16·99 grams ($\frac{1}{10}$ mol ) $AgNO_3$ per litre

**Estimation of halides.**—(*a*) *Without an indicator* —Since silver chloride, bromide and iodide are all insoluble in water, it is possible to use silver nitrate to estimate any soluble halide except a fluoride, *e g*

$$AgNO_3 + KCl = AgCl + KNO_3, \text{ or } Ag^+ + Cl^- = AgCl$$

The solution of halide is added in small quantities at a time to a measured volume of standard silver nitrate, acidified with a little nitric acid to assist the coagulation of the precipitate After each addition of the halide the mixture is shaken vigorously, and more halide added until no further turbidity is produced in the clear supernatant liquid A rough end-point is found by two rapid titrations, preferably with potassium chromate as indicator if the presence of free acid can be avoided The exact end-point is then determined by " creeping " from within one c c of it, as in Expt 70 The weight of the halogen is deduced from the fact that 1 c c of *N*/10 silver nitrate precipitates 0 00355 gram of chlorine, 0 00799 gram of bromine and 0 0127 gram of iodine from their respective halide salts *Silver* may be estimated in exactly the same way by precipitation with a standard solution of sodium chloride

(*b*) *Mohr's method* —The tedious operation of shaking can be avoided (with some loss of accuracy) by using an indicator Thus, if silver nitrate is run into a *neutral* solution of a chloride or bromide (not iodide) containing a suitable concentration of potassium chromate, the mixture will develop the crimson colour of silver chromate, $Ag_2CrO_4$, as soon as all but a trace of the halide has been precipitated The method is only successful in neutral solution, since silver chromate is not formed in acid solution, and silver oxide is precipitated in alkaline solution.

EXPT. 69 **Estimation of the equivalent of potassium**

Weigh out about 2 gms of pure dry A R potassium chloride, dissolve in distilled water and make up to 250 c c in a calibrated flask Titrate 25 c c portions of this solution against *N*/10 silver nitrate, using

(i) 1 c c of a 5% solution of potassium chromate as indicator. When an accurate end-point has been obtained, repeat the titration without the chloride, using 1 c c of the chromate solution and a volume of water equal to the final volume of the last titration, this titration gives the volume of silver nitrate required by the indicator, and must be subtracted from the chloride titration figure

(ii) 0 5 c c of dichlorofluorescein solution (p 433) as indicator Dilute the mixture with 25 c c of water before titrating

(iii) No indicator as described under method (*a*) above

Calculate the equivalent of the chloride for each set of titrations, and thence deduce the equivalent of potassium (Cl = 35 5)

(*c*) *Volhard's method* —Halides may be estimated in presence of acids by adding excess of silver nitrate, boiling to coagulate the insoluble silver halide, and then titrating the excess of silver nitrate against standard

*ammonium thiocyanate*, which gives a white precipitate of silver thiocyanate with silver nitrate

$$AgNO_3 + NH_4CNS = AgCNS + NH_4NO_3$$

Since ammonium thiocyanate is very deliquescent, an approximately $N/10$ solution is first standardised against $N/10$ silver nitrate *Ferric alum* is used to indicate the presence of unprecipitated thiocyanate at the end of the interaction, when it gives a deep-red coloration owing to the formation of the complex anion $Fe(CNS)_6^{---}$

$$Fe^{+++} + 6CNS^- \rightleftharpoons Fe(CNS)_6^{---}.$$

Since the reaction is reversible, the sharpness of the end-point is improved by using a fair quantity of the indicator, *e g* 2 c c of a strong solution of the alum in nitric acid for every 20 c c of solution If the titration is carried out in the presence of the coagulated halide, the pink colour at the end-point fades gradually, owing to a slow interaction between the complex anion and the precipitate, viz

$$6AgCl + Fe(CNS)_6^{---} = 6AgCNS + Fe^{+++} + 6Cl^-$$

For this reason it is usually advisable to filter off the precipitate of silver chloride before titrating with thiocyanate The converse estimation of silver in acid solution is described in Expt 70

EXPT 70 **Estimation of silver in coinage**

A weighed piece of a silver coin, containing about 2 grams of silver, is dissolved by heating it with about 20 c c of 20% nitric acid in a conical flask The solution is made up to 200 c c in a standard flask, and portions of 20 c c are titrated with $N/10$ thiocyanate, after adding 2 c c of a strong solution of ferric alum

The result can be checked and improved in accuracy by finding the volume of $N/10$ sodium chloride, which must be added to a similar portion of the solution (but diluted to 100 c c ) until no further turbidity is produced The sodium chloride should be added to within 0 5 c c of the " thiocyanate " end-point and then in portions of 0 1 c c or even 0 05 c c It is essential to shake the mixture vigorously in order to obtain a clear supernatant liquid, and thus a sharp end-point 1 c c of $N/10$ sodium chloride is required to precipitate 0 01079 gram of silver, the weight of silver in the coin is therefore $0\ 01079 \times 10x = 0\ 1079x$, where $x$ is the volume of sodium chloride used by 20 c c of the silver solution

**Estimation of alkali cyanides.**—Alkali cyanides may be estimated by making use of the fact that they form a soluble double cyanide with silver cyanide, which is itself insoluble in water

$$AgCN + KCN = KAg(CN)_2$$

Thus, if standard silver nitrate is run into a measured volume of potassium cyanide, a precipitate of silver cyanide will form as soon as more silver is added than is required to form the double salt

$$KAg(CN)_2 + AgNO_3 = 2AgCN + KNO_3.$$

If the titration is stopped at this point, each c c of $N/10$ silver nitrate will correspond to 0 0052 gram of CN

## D Adsorption Indicators

The end-points of titrations involving a precipitation are now frequently determined by the use of an adsorption indicator, which works on an entirely different principle from the indicators that have been described above Thus, at the end-point, an adsorption indicator produces a change in the colour of the *precipitate*, usually owing to a marked increase in its adsorption on the surface of the latter For example, when silver nitrate is added to a solution of a chloride containing a few drops of dichlorofluorescein, the white precipitate of chloride turns pink at the end-point The mechanism of this change is as follows When silver nitrate is added to a solution of a chloride, a semi-colloidal precipitate of silver chloride is formed, which preferentially adsorbs chloride ions, $Cl^-$, and thus becomes negatively charged The addition of more silver nitrate removes chloride ions from the solution and eventually from the semi-colloidal silver chloride too, so that the latter loses its negative charge at the end-point As soon as a slight excess of silver nitrate is added, the precipitate adsorbs silver ions, $Ag^+$, and becomes positively charged In this condition it is able to adsorb a sufficient quantity of dichlorofluorescein anions to turn pink, presumably owing to the formation of silver dichlorofluoresceinate The advantage of this indicator is that it can function in weakly acidic solutions (up to $p_H = 4$), and hence can be used in the estimation of the chlorides of metals, such as zinc and aluminium, which are appreciably hydrolysed in aqueous solution and therefore cannot be estimated by using potassium chromate as the indicator The dichlorofluorescein indicator is prepared by dissolving 0 1 gram of the dyestuff in 100 c c of 70% alcohol, and not more than $\frac{1}{2}$ c c of this solution is added to 25 c c of the chloride solution, whose strength should preferably be about N/40

Eosin can be used for silver-bromide, silver-iodide and silver-sulphocyanide titrations It turns the halide or sulphocyanide precipitate a pinkish colour at the end-point, but the actual colour change varies somewhat with the concentrations of the reactants This dyestuff works very well in solutions which are less acid than decinormal, and is generally employed in the presence of dilute acetic or nitric acids

## E Hardness of Water

**Determination of the hardness of water.**—The relative hardness of water is expressed in "degrees" Each DEGREE OF HARDNESS represents the hardness produced by one part of calcium carbonate (or its equivalent) in 100,000 parts of water * The hardness of water may be measured by Clark's or by Hehner's method

* Formerly a degree of hardness was defined as 1 grain of calcium carbonate per gallon, this is equal to 1 part in 70,000 parts of water

(*a*) *Clark's method* depends upon measuring the volume of a standard solution of soap which is required to give a permanent lather to a measured volume of water

EXPT 71 **Estimation of the hardness of tap-water by Clark's method**

A standard solution of calcium chloride of 20 degrees of hardness is prepared by dissolving 0 2 gram of Iceland spar in dilute hydrochloric acid, evaporating to dryness to expel the surplus hydrochloric acid, and dissolving the residue in a litre of distilled water The distilled water used here and in subsequent operations must be free from carbon dioxide, since this imparts hardness to water

Castile soap (7 grams) is dissolved in 200 c c of warm methylated spirits and diluted to roughly a litre by adding a 50% solution of methylated spirits in water This solution is run from a burette into a reagent bottle, containing 50 c c of the standard solution of calcium chloride, until the lather produced by shaking the mixture vigorously lasts for five minutes The end-point is found by the method of bracketing (p 423), and should be confirmed by three concordant titrations The soap solution is then diluted so that 21 c c of it are required to lather 50 c c of the standard solution of calcium chloride The reason for choosing this figure is that about 1 c c of the soap solution is required to produce a lather in 50 c c of distilled water, so that $21 - 1 = 20$ c c are used up in removing hardness Each c c of soap solution then corresponds to one degree of hardness, since the hardness of the calcium solution is 20 degrees Hence, if 50 c c of any water are taken and titrated with the soap solution, its degree of hardness will be equal to $n - 1$, where $n$ is the volume of soap solution required for the titration When the volume of the hard water for titration is a multiple, $x$, of 50 c c , the degree of hardness is given by the expression $(n - x)/x$ It is difficult to determine the end-point when much magnesium is present in the water, owing to the formation of a permanent scum on the surface of the water and to the fact that the reaction between soap and magnesium salts is slow In such cases the hard water is diluted with distilled water so that 50 c c of the " dilute " mixture only require about 7 c c of soap solution, and the titration is continued until the lather lasts for 10 minutes

The ratio of permanent to temporary hardness in a specimen of water is found by titrating it as above, and then repeating with further portions which have been boiled For this purpose a weighed flask of water is boiled vigorously for about twenty minutes The loss of water due to evaporation is made good by replacing the flask on the balance and adding distilled water until it reaches its former weight The difference in the volumes of soap solution required for the titration of unboiled and boiled water represents the temporary hardness

The results obtained by this method are not very accurate, because the volume of soap solution required to produce the lather is not strictly proportional to the hardness, and in any case the correction of 1 c c introduced above is only approximate Greater accuracy is obtained by

preparing a standard solution of potassium oleate and using a titration table as described in the literature

(*b*) *Hehner's method* depends upon titrating the bicarbonates which give rise to temporary hardness with standard acid, using methyl orange as the indicator

$$Ca(HCO_3)_2 + H_2SO_4 = CaSO_4 + 2CO_2 + 2H_2O,$$
$$Mg(HCO_3)_2 + H_2SO_4 = MgSO_4 + 2CO_2 + 2H_2O$$

The permanent hardness is measured by adding to a measured volume of the water a known volume of a standard mixture of sodium hydroxide and carbonate, when the calcium and magnesium salts are precipitated and removed by filtration

$$CaSO_4 + Na_2CO_3 = CaCO_3 + Na_2SO_4,$$
$$MgSO_4 + 2NaOH = Mg(OH)_2 + Na_2SO_4$$

The excess of alkali in the filtrate is then estimated by titration with standard acid and methyl orange The permanent hardness is deduced directly from the volume of standard alkali which has been used, since the total alkalinity of the filtrate is not affected by temporary hardness

EXPT 72 **Determination of temporary and permanent hardness of tap-water by Hehner's method**

(i) *Temporary hardness* —Portions of 500 c c of the tap-water are titrated with decinormal sulphuric acid, using methyl orange to indicate the end-point The same quantity of methyl orange, about 0 5 c c , is used in each titration and the titration is stopped when the same tint is produced, as judged by direct comparison with one of the titrated portions A blank titration is then carried out with distilled water to find out exactly how much acid is required to change the indicator to the required tint When the value of this is deducted from the mean of the other titrations, the result is numerically equal to the degree of temporary hardness, since 1 c c of decinormal acid neutralises 5 milligrams of calcium carbonate, which is one hundred thousandth of the weight of 500 c c of water

(ii) *Permanent hardness* —Boil 250 c c of the tap-water in a conical flask to expel part of the carbon dioxide, and then add 50 c c of $N/10$ sodium hydroxide and a similar quantity of sodium carbonate The mixture is boiled to coagulate the precipitate and then made up to 500 c c in a standard flask The precipitate is allowed to settle and portions of 50 c c of the clear solution are titrated with $N/20$ sulphuric acid, or $N/40$ acid if the water is very hard The volume of standard $N/10$ alkali which has been removed by the calcium sulphate, etc , is then calculated and multiplied by *two* to give the degrees of permanent hardness

# CHAPTER XXXI

## GRAVIMETRIC ANALYSIS

**General considerations.**—The gravimetric analysis of a substance depends upon the isolation and weighing of its constituents in the form of pure derivatives of known composition The most usual procedure in the gravimetric analysis of an inorganic substance is to dissolve a known weight of the sample in a suitable solvent, and then to precipitate the component elements and radicals so that they can be weighed separately The precipitation must be carried out under carefully controlled conditions, otherwise it may be incomplete, or the precipitate may be contaminated or may undergo partial decomposition

**Collecting the precipitate.**—The essential conditions vary according to the nature of the precipitate, so that no hard and fast rules can be laid down, but it is advantageous (i) to precipitate in a beaker covered with a clock-glass, so that the precipitate may be easily accessible , (ii) to precipitate in boiling solution, so that a granular precipitate is produced , and (iii) to wash the precipitate by decantation, *i e* the clear supernatant liquid is poured through the filter (Fig 105) and the precipitate agitated with fresh portions of water, etc , before it is brought on to the filter The collecting and weighing of the precipitate may be carried out by the following methods

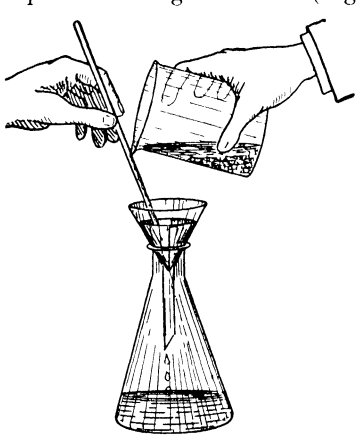


FIG 105 DECANTATION OF A PRECIPITATE

(*a*) The simplest method is to collect the precipitate on a filter paper which has been counterpoised with another filter paper from the same packet It is essential that the folded filter paper should be smaller than the funnel in which it is contained The filtration is faster when the paper has been pressed tightly into the funnel, so that the column of liquid in the stem of the funnel exerts a suction in the pores of the paper This suction can be increased by attaching a piece of glass tubing, preferably with a loop in it, to the stem of the funnel (Fig 106) When the precipitate and the counterpoise have been dried in an oven at the same temperature, they are weighed against one another on a balance to give the net weight of the precipitate.

(*b*) Since the weight of a filter paper varies considerably when dried and when exposed to moist air, it is usually better to burn the filter paper with its contents in a weighed crucible with lid and to subtract from the gross weight thus recorded the stated weight of the ash of the filter paper If there is any danger of the precipitate being reduced by the combustible part of the filter paper, it is first dried in an oven, so that the main bulk of it can be scraped from the paper into a crucible before the paper is burnt on the lid The ash and precipitate are then weighed together Since even a crucible fluctuates in weight, it is important that it should be heated (*e g* to 200°) and allowed to cool in a desiccator before weighing, both before and after collecting the precipitate

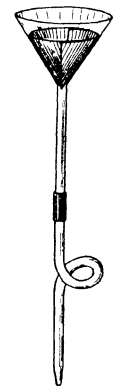


FIG 106 FILTER FUNNEL WITH EXTENSION

(*c*) The necessity for burning a filter paper can be avoided by using a GOOCH CRUCIBLE (Fig 107), in which the precipitate is collected on a layer of asbestos, resting on the perforated base of the crucible, instead of on paper In order to prepare this asbestos filter, the Gooch crucible is pushed into a wide piece of rubber tubing attached to a thistle funnel, as shown in Fig 107 The thistle funnel is fitted to a thick-walled flask, which is attached by the side tube to a pump A suspension of finely divided asbestos (prepared by scraping asbestos fibres and boiling the shreds with water) is poured into the crucible and sucked down to form a thin but uniform pad on the bottom of the crucible This is washed by pouring distilled water down a glass rod into the centre of the crucible, and not down the side, since this tends to displace the pad The crucible is drained on the pump and then subjected to the same treatment that will be used subsequently to dry the precipitate The Gooch crucible is very convenient for collecting and weighing precipitates, *e g* AgCl, which are easily filtered and do not require drastic treatment, since one precipitate can be collected on the top of another, and finally emptied out without necessarily preparing a fresh asbestos mat In this way a single weighing can be used to give the additional weight of each precipitate collected Under drastic treatment the weight of the asbestos may vary , the Gooch crucible should therefore be ignited, when necessary, by heating it inside a nickel crucible over a Bunsen burner

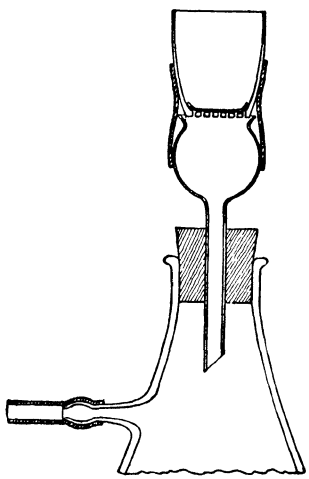


FIG 107 GOOCH CRUCIBLE

(*d*) Crucibles are now available in which the filtration is effected by a

layer of sintered glass powder This type of filter has obvious advantages over a loose pad of asbestos, but cannot be renewed in the same simple way

**Limits of error.**—The errors made in ordinary gravimetric work are seldom less than 0 25%, unless special precautions are taken Thus an error of half a milligram in weighing amounts to 0 1% on half a gram of material This error can be reduced by weighing larger quantities, as in many determinations of atomic weight , but the trouble of collecting and washing the precipitate is then largely increased, and for this reason large weights should be avoided in ordinary analyses Again, errors are introduced through the solubility of the precipitate Thus even silver chloride dissolves to the extent of 1 5 milligrams per litre at 18° If therefore 200 c c of water are used in the precipitation and washing, 0 3 milligram of the chloride may be lost Finally some precipitates, such as barium sulphate, readily absorb salts from the solution, and, unless precautions are taken, errors may be made which are quite considerable, even when allowance is made for the opposing effect of solubility

**Estimation of silver and of halogens** —The amount of silver in one of its alloys or soluble salts may be estimated by precipitating as silver chloride, *e g*

$$AgNO_3 + NaCl = AgCl + NaNO_3$$

The ease with which the precipitate clots or curdles, *e g* on boiling the solution, leaving a perfectly clear supernatant liquid, makes it the easiest of all precipitates to collect and weigh, since it has no tendency either to pass through the filter, like finely divided barium sulphate, or to choke it, like the gelatinous precipitates of ferric and aluminium hydroxides (see below) The halogens, in the form of a halide salt or acid, may also be determined by weighing as silver chloride, bromide and iodide, but fluorides cannot be estimated in this way, since silver fluoride is soluble in water On the other hand, the halogen in an oxy-salt must be reduced first to the corresponding halide, whilst that in an organic compound is converted into the silver halide by Carius' method of heating with concentrated nitric acid and silver nitrate in a sealed tube (p 450)

EXPT 73 **Estimation of silver in an alloy.**

The alloy is cut into small pieces or filed, and a quantity of it is weighed out which will give roughly half a gram of silver chloride It is dissolved in the minimum of hot 25% nitric acid (about 15 c c ) in a small beaker, covered with a watch glass to avoid loss of silver by spraying The solution is diluted to 100 c c , and then a dilute solution (about 10%) of sodium chloride is added until it produces no further cloudiness in the clear supernatant liquid obtained by boiling the mixture The precipitate is washed twice by decantation with very dilute nitric acid, before it is transferred to a counterpoised filter paper or weighed Gooch crucible It is washed free from sodium chloride with a little distilled water, and then dried at 130° in an air oven The precipitate should not be exposed to direct sunlight,

since silver chloride is decomposed by light One gram of silver chloride contains 0 752 gram of silver

EXPT 74 **The percentage of chlorine in rock salt**

Rock salt, NaCl, is ground up in a mortar and dried in a steam oven About 0 4 gram is weighed out and dissolved in 100 c c of distilled water, to which a little nitric acid has been added The chloride is then precipitated by the addition of an excess of a dilute solution of silver nitrate The precipitate is coagulated by boiling the mixture and then treated exactly as in Expt 73, except that the washing is continued until the filtrate no longer gives a precipitate with a solution of sodium chloride

**Estimation of metals as oxides.**—Iron, aluminium, copper and zinc may be estimated by precipitating the hydroxides from solution (zinc is precipitated as a basic carbonate), and then igniting to the oxide

(i) $$FeCl_3 + 3NH_4OH = Fe(OH)_3 + 3NH_4Cl\,,$$
$$2Fe(OH)_3 = Fe_2O_3 + 3H_2O$$

(ii) $$Al_2(SO_4)_3 + 6NH_4OH = 2Al(OH)_3 + 3(NH_4)_2SO_4\,,$$
$$2Al(OH)_3 = Al_2O_3 + 3H_2O$$

(iii) $$CuSO_4 + 2NaOH = Cu(OH)_2 + Na_2SO_4\,,$$
$$Cu(OH)_2 = CuO + H_2O$$

(iv) $$2ZnSO_4 + 2Na_2CO_3 + H_2O = ZnCO_3,Zn(OH)_2 + 2Na_2SO_4 + CO_2\,,$$
$$ZnCO_3,Zn(OH)_2 = 2ZnO + CO_2 + H_2O$$

EXPT 75 **Estimation of iron in ferrous ammonium sulphate**

About a gram of ferrous ammonium sulphate, $FeSO_4,(NH_4)_2SO_4,6H_2O$, is weighed out and dissolved in 100 c c of distilled water in a 500 c c beaker The solution is boiled with a few c c of concentrated nitric acid to oxidise the iron to the ferric state The oxidation is shown to be complete when a drop of the liquid no longer gives a blue coloration with a drop of potassium ferricyanide on a white tile (p 429) The solution is then boiled with a few c c of reagent ammonium chloride and an excess of ammonia The precipitate of ferric hydroxide is allowed to settle, and is washed twice by decantation with hot distilled water before it is brought on to the filter paper The washing is continued until the filtrate no longer gives a precipitate with an acidified solution of barium chloride, showing that all the ammonium sulphate has been removed The filter paper is dried in a steam oven and burnt on the lid after as much as possible of the precipitate has been transferred to a weighed crucible The ash is then added to the precipitate and ignited at a dull red heat, until the weight of the crucible and contents remains constant Unless the heating is exceptionally strong, there is no danger of the ferric oxide decomposing into the magnetic oxide, $Fe_3O_4$ The weight of iron is calculated from the weight of the precipitate (less the weight of the ash) by assuming that 1 gram of ferric oxide contains 0 6994 gram of iron

The procedure with other ferrous salts is similar, but the preliminary oxidation with nitric acid is omitted when the iron is already in the ferric state

EXPT 76 **Estimation of aluminium in potash alum**

The method differs from that of Expt 75 only in that the ammonia (which should be free from carbonate) is added gradually to a boiling solution of alum and ammonium chloride, in order to give a coherent precipitate of aluminium hydroxide If the hydroxide is not precipitated slowly, and in the presence of a large excess of ammonium salts, a gelatinous precipitate may be obtained which cannot be collected and washed The filter paper and precipitate are burnt in a weighed crucible with a lid, and the residue is ignited strongly to drive off all the water There is no danger of decomposing the aluminium oxide by heating

It is now usual to precipitate aluminium hydroxide by the addition of a solution of sodium thiosulphate (3 grams of the hydrate in 100 c c of water for 1 gram of alum in 100 c c of water) in place of ammonium chloride and ammonia The aluminium thiosulphate, which is formed by double decomposition with the sodium thiosulphate, is hydrolysed completely when the solution is boiled vigorously

$$Al_2(S_2O_3)_3 + 3H_2O = 2Al(OH)_3 + 3SO_2 + 3S$$

When most of the sulphur dioxide has been expelled, a slight excess of ammonia is added and the mixture is boiled for about two minutes before it is filtered The use of thiosulphate as the precipitating agent has the merit of retarding the separation of the hydroxide and thus giving a more coherent precipitate

EXPT 77 **Estimation of copper in blue vitriol**

A boiling solution of half a gram of blue vitriol, $CuSO_4.5H_2O$, in 100 c c of water in a 500 c c beaker, is precipitated by adding potassium hydroxide slowly and with continuous stirring until the supernatant liquid has lost its blue colour and is alkaline to litmus paper The mixture is then boiled for three minutes, with vigorous stirring to minimise " bumping " The clear supernatant liquid is decanted into a weighed Gooch crucible, and the precipitate boiled twice with fresh portions of distilled water before it is brought on to the filter The coating of copper oxide on the side of the beaker is best removed by dissolving it in dilute hydrochloric acid and reprecipitating with alkali The precipitate in the crucible should be washed with boiling water until the filtrate no longer responds to the sulphate test The crucible is then placed in a nickel crucible (with a few pieces of porcelain in the bottom to prevent the direct contact of the two crucibles) and ignited to constant weight Strong ignition is required to expel the last traces of water The percentage of copper is calculated on the assumption that 1 gram of the oxide contains 0·799 gram of the metal The result, which will not be very accurate because of the difficulty of

avoiding absorption by the copper oxide, should be compared with that obtained in Expt 66

The same method can be employed for estimating copper in solutions of other copper salts, provided that alkali nitrates, ammonium salts and certain non-volatile organic compounds are not present in considerable quantities. In such cases, the copper can be precipitated with hydrogen sulphide and redissolved in boiling dilute sulphuric acid The most accurate method for estimating copper is to deposit it by electrolysis on a weighed cathode of platinum gauze

EXPT 78 **Estimation of zinc in calamine**

About half a gram of calamine, $ZnCO_3$, is weighed out and dissolved in the minimum of dilute sulphuric acid in a 500 c c beaker The solution is diluted to about 200 c c with distilled water, and a dilute solution of sodium carbonate is then added from a burette until the mixture becomes turbid The mixture is boiled to precipitate basic zinc carbonate, and, after the addition of a few drops of phenolphthalein, more sodium carbonate is added until the mixture is just pink This ensures that just sufficient sodium carbonate is added The mixture is again boiled, and the precipitate washed twice with boiling water before it is transferred to a weighed Gooch crucible The washing is continued until the filtrate no longer gives a precipitate with barium chloride, the precipitate is then ignited to constant weight Sodium carbonate is used as the precipitating agent since caustic soda and ammonia dissolve zinc hydroxide The percentage of zinc in calamine is calculated on the assumption that 1 gram of zinc oxide contains 0 803 gram of zinc

**Estimation of metals by conversion into sulphates.**—Barium and lead may be estimated by precipitating their sulphates under carefully controlled conditions as explained in Expts 79 and 80

$$BaCl_2 + H_2SO_4 = BaSO_4 + 2HCl\ ,$$
$$Pb(NO_3)_2 + H_2SO_4 = PbSO_4 + 2HNO_3$$

Sodium and potassium can also be estimated as sulphates in any of their compounds which yield the pure sulphate on evaporation with concentrated sulphuric acid

EXPT 79 **Estimation of barium in hydrated barium chloride.**

Half a gram of barium chloride, $BaCl_2,2H_2O$, is weighed out and dissolved in 200 c c of water with a few c c of dilute hydrochloric acid The solution is brought to the boil in a 500 c c beaker, and then 5 c c of dilute ($2N$) sulphuric acid is added from a burette The mixture is boiled and stirred vigorously for a few minutes to assist in the formation of a granular precipitate The barium sulphate is allowed to settle, and the clear supernatant liquid is tested by adding a few more drops of sulphuric acid to make sure that the precipitation is complete, before the whole is transferred to a filter paper The filter paper and precipitate are ignited in a

weighed crucible, and the residue is again ignited after it has been moistened with about two drops of concentrated sulphuric acid In this way, any traces of barium sulphide formed by reduction are reconverted into the sulphate The percentage of barium in the hydrated chloride is calculated on the assumption that 1 gram of barium sulphate contains 0 589 gram of barium

EXPT 80 **Estimation of lead in lead nitrate**

Half a gram of finely powdered lead nitrate is weighed out into a large crucible and dissolved in the least possible quantity of hot water About 5 c c of concentrated sulphuric acid are then added cautiously, and the mixture is heated to expel most of the nitric acid, since this acid dissolves lead sulphate The cooled residue is cautiously washed into a beaker with 30 c c of water followed by 20 c c of alcohol, and then collected in a weighed Gooch crucible The precipitate is washed with a mixture of sulphuric acid and alcohol, and finally alcohol, before drying in a hot-air oven

EXPT 81 **Estimation of sodium in a mixture of sodium nitrate and sodium chloride**

Excess of concentrated sulphuric acid is added drop by drop to about half a gram of the mixture dissolved in the minimum of water in a weighed crucible with lid When the action has subsided, the mixture is evaporated to dryness and ignited strongly for ten minutes after fuming has ceased After weighing, a little more concentrated sulphuric acid is added, and the ignition and weighing are repeated, with further additions of sulphuric acid, until the weight becomes constant The evaporation to dryness should be carried out by heating the crucible from the top downwards, to prevent the acid from creeping over the side of the crucible, and the lid should be placed so that there is a small gap for the escape of vapour One gram of sodium sulphate contains 0 324 gram of sodium

**Estimation of sulphur as sulphate.**—A large range of sulphur compounds can be oxidised to sulphuric acid by boiling with concentrated nitric acid The sulphuric acid can then be precipitated and weighed either as barium sulphate or as lead sulphate, exactly as in the preceding experiments

EXPT 82 **Estimation of soluble sulphates as barium sulphate**

The quantity of sulphate weighed out should be sufficient to give about half a gram of barium sulphate It is dissolved in 200 c c of water, containing about 5 c c of concentrated hydrochloric acid to assist in the coagulation of the precipitate A dilute (10%) solution of barium chloride is then added very slowly from a burette to the solution of the sulphate, which should be boiled and stirred vigorously When no further precipitation occurs, the barium sulphate is allowed to settle and washed twice by decantation with boiling water It is then transferred to a counterpoised filter paper or weighed Gooch crucible, and washed with boiling water until the filtrate is free from chloride Finally, it is dried at 130° in an air-bath

and weighed If the filter paper is to be incinerated instead of counterpoised, it should be burnt apart from the precipitate, otherwise some of the barium sulphate may be reduced to barium sulphide, and it will be necessary to reignite it after moistening with concentrated sulphuric acid

**Estimation of metals by conversion into pyrophosphates.**—Magnesium, zinc and manganese may be estimated by making use of the fact that in the presence of ammonium salts they can be precipitated quantitatively from solution as double ammonium phosphates, *e g*

$$MgSO_4 + (NH_4)_2HPO_4 + NH_4OH = NH_4MgPO_4 + (NH_4)_2SO_4 + H_2O$$

The precipitate is ignited in a Gooch crucible in order to expel ammonia and water and is then weighed as the pyrophosphate

$$2NH_4MgPO_4 = Mg_2P_2O_7 + 2NH_3 + H_2O$$

The conditions under which the precipitation is carried out vary somewhat with the metal Thus, zinc ammonium phosphate is precipitated from a weakly acid solution, whilst magnesium and manganese are precipitated in ammoniacal solutions Manganese requires in addition a large excess of ammonium chloride to prevent the precipitation of manganous hydroxide Detailed instructions for the estimation of magnesium are given in Expt 83

EXPT 83 **Gravimetric estimation of magnesium**

A solution of a magnesium salt (about 0 1 gram magnesium in 100 c c of water) is heated to boiling with 20 c c of reagent ammonium chloride in a 500 c c beaker A solution containing 20 c c of a 5% solution of microcosmic salt, $NaH(NH_4)PO_4$, and 40 c c of 10% ammonia is then added to the magnesium solution, which must be boiled and stirred vigorously to ensure that a crystalline precipitate is obtained The stirring should be continued for about five minutes, so that any sodium magnesium phosphate in the precipitate is converted into the corresponding ammonium compound The precipitate is then transferred to a weighed Gooch crucible, and washed with 5% ammonia (pure water hydrolyses the phosphate to a basic salt), until the filtrate no longer gives a white turbidity with an acidified solution of silver nitrate Finally, the crucible is dried and ignited strongly to convert the precipitate into the pyrophosphate, $Mg_2P_2O_7$, one gram of which contains 0 218 gram of magnesium

**Estimation of phosphorus as magnesium pyrophosphate** —Soluble phosphates can be estimated by the converse of the method used for the estimation of magnesium (Expt 83) The phosphorus in other compounds may also be estimated by this method, provided that it can first be oxidised to phosphoric acid or a soluble phosphate The details for the determination of the phosphorus in microcosmic salt,

$$NaH(NH_4)PO_4,4H_2O,$$

are described in Expt 84

EXPT 84 **To determine the percentage of phosphorus in microcosmic salt**

Dissolve about 1 0 gram of microcosmic salt, $NH_4NaHPO_4.4H_2O$, in 100 c c of water in a 500 c c beaker, make alkaline with excess of ammonia and bring almost to the boil To this solution add a boiling solution of magnesium sulphate, 2 grams, containing 40 c c of reagent ammonium chloride, and then 50 c c of 10% ammonia The mixture must be boiled and stirred vigorously in order to produce a crystalline and easily filterable precipitate (p 436), which is then treated as in Expt 83.

# CHAPTER XXXII

## ORGANIC ANALYSIS

**General.**—The radicals of an organic compound are generally linked together by covalent bonds, and (with certain exceptions) cannot therefore be detected by the ordinary ionic reactions Thus pure **chloroform,** $CHCl_3$ (p 702), does not give a precipitate with silver nitrate, even when the two reagents are brought together in alcohol, in which they are both soluble In the same way, **methyl cyanide,** $CH_3CN$ (p 766), does not give the ordinary reactions of a cyanide, and **amyl nitrite,** $C_5H_{11}ONO$ (p 768), does not give the ordinary reactions of a nitrite Exceptions to this rule are found in

(i) *Metallic derivatives*, in which the metal can nearly always be detected by the methods described in Chapter XXVIII

(ii) *Acid chlorides*, *e g* **acetyl chloride,** $CH_3COCl$ (p 711), which are hydrolysed so readily by water (like $PCl_3$ or $PCl_5$) that the presence of hydrogen chloride can be detected at once in an aqueous solution of the chloride

(iii) *Methyl iodide*, $CH_3I$ (p 725), which gives an immediate precipitate with silver nitrate in alcoholic solutions,

$$CH_3I + AgNO_3 + H_2O = AgI + CH_3OH + HNO_3$$

In general, however, the compound must be destroyed, as described in the following section, in order to detect the elements which it contains

**Detection of carbon and hydrogen.**—These elements can be identified by heating a mixture of the organic compound and *dry* cupric oxide The carbon and hydrogen are thereby oxidised to carbon dioxide and water, which are detected as indicated in Expt 85

**Detection of halogens, sulphur and nitrogen.**—(*a*) *Lassaigne's test* — The organic compound is heated with sodium when (i) halogens are converted into the corresponding sodium halide , (ii) sulphur forms sodium sulphide , (iii) nitrogen yields sodium cyanide,

$$Na + [C] + [N] = NaCN$$

The red-hot product thus obtained is plunged into water and the resulting solution tested for the presence of the above compounds, as described in Expt 85

(*b*) *Middleton's test* —In this test the organic compound is heated with a mixture of one part of anhydrous sodium carbonate and two parts of *pure* zinc dust The red-hot product is then plunged into water and the

resulting solution tested for sodium cyanide and halide, whilst the insoluble residue is examined for zinc sulphide

This method is much less dangerous than the sodium test, but takes rather longer

EXPT 85 **The detection of elements in organic compounds.**

(*a*) *Hydrogen and carbon* —Heat about 4 grams of copper oxide powder in a hard glass test tube in the Bunsen flame until perfectly dry Cool in a desiccator Mix about one gram of sugar with the copper oxide, then attach a cork and delivery tube to the test tube and heat again strongly Test the issuing gas for carbon dioxide by passing it into lime water Note whether drops of moisture have condensed in the upper part of the test tube and whether the copper oxide is changed in appearance Repeat the experiment, but moisten the copper oxide with alcohol instead of mixing it with sugar

(*b*) *Beilstein's test for halogens* —Fix a stout piece of copper wire, about 12 cms in length, with a cork to act as holder, and securely attach to the other end a small roll of copper gauze (about the size of a postage stamp) Heat the gauze strongly in a Bunsen flame until the latter is no longer coloured green, then dip it into a small quantity of the organic compound (*e g* chloral hydrate) and replace it in the vertical edge of flame The appearance of a green tint to the flame indicates the probable presence of a halogen, whilst a negative result proves the absence of a halogen The test depends upon the fact that the hot oxidised gauze unites with the halogen in the organic compound to form a halide of copper, which volatilises and colours the flame Organic compounds containing nitrogen, but no halogen, very occasionally give a positive result owing to the formation of volatile cuprous cyanide, the test does not therefore provide conclusive evidence of the presence of halogen

(*c*) *Lassaigne's test for nitrogen, halogen and sulphur* —As an introduction to this test it is suggested that known compounds of these elements should be taken, *e g* acetamide, $CH_3CONH_2$, chlorobenzene, $C_6H_5Cl$ and potassium ethyl sulphate Chloroform, carbon tetrachloride and polynitro derivatives must not be used, as they may cause a dangerous explosion

If the organic compound is a solid, place about 0 4 gm of it in an ignition tube and add a small pellet (about 0 3 c c ) of sodium Heat the mixture gently and then more strongly until no further fumes are given off (if the compound is a liquid, then slowly drip not more than 0 5 c c of it onto molten sodium and proceed as above) Plunge the red-hot test tube into about 40 c c of water in a small mortar, holding the tube securely with tongs Grind up the product, and, after stirring, filter it into a boiling tube Divide the filtrate into three portions and test each as follows

(1) Add 4 c c of ferrous sulphate solution, and if necessary sodium hydroxide until a precipitate forms Boil the mixture for a minute or two so that any cyanide present is converted into ferrocyanide Add a drop of ferric chloride solution, and make the product just acid with hydrochloric acid The formation of a Prussian blue precipitate, which

incidentally can be seen more clearly by collecting it on a filter paper, indicates the presence of a cyanide, and hence of nitrogen in the organic compound

(ii) Acidify with dilute nitric acid and add silver nitrate (N B if a cyanide is present it will interfere with this test and must therefore be destroyed by boiling the acidified mixture before the addition of the silver nitrate), when a white precipitate indicates a chloride or bromide, and a yellow precipitate an iodide The chloride is readily soluble in ammonia, whilst the bromide is sparingly soluble

(iii) Add a freshly prepared solution of sodium nitroprusside when a purple coloration shows the presence of sulphur

(*d*) *Middleton's test for nitrogen, halogen and sulphur* —Mix very thoroughly in a mortar 50 gms of anhydrous " analar " sodium carbonate with 100 gms of the purest obtainable zinc dust , keep the mixture in a wide-mouthed stoppered bottle

Powder up about quarter of a gram of the organic compound, and mix it with about five times its bulk of the reagent in a small hard glass test tube If the compound is a liquid, drip it slowly on to the reagent in the test tube In either case now cover the mixture with the reagent to a depth of about 2 cms Hold the test tube in a horizontal position and heat it cautiously in the middle When the upper layer of the mixture gets red hot, slowly extend the heating downwards until the whole of it is red hot, then plunge the tube into about 30 c c of water in an evaporating basin, and boil the contents for a few minutes

Allow the solid matter to settle and decant off the upper liquid through a filter paper Test for zinc sulphide in the solid residue by adding dilute hydrochloric acid and immediately covering the top of the basin with a filter paper which has been moistened in the middle with lead acetate solution Blackening of the paper proves the presence of hydrogen sulphide, and hence of sulphur in the original compound, provided that a blank test has been carried out on the reagent to show that it does not contain sufficient sulphur to give a positive result Test the filtrate for cyanide and halogen as in Lassaigne's method

**Determination of equivalents and molecular weights.**—The equivalent of an organic acid can be determined by titration, but, since organic acids are almost always weak, phenolphthalein is generally used as an indicator The equivalent of an organic acid can also be determined by igniting the silver salt, and weighing the residue of metallic silver The silver salts are chosen since they are generally normal salts, contain no water of crystallisation and are readily purified A solution of the acid is neutralised with ammonia, any excess of the latter being expelled by boiling A slight excess of silver nitrate is added and the precipitated silver salt is collected on a filter and carefully washed and dried A weighed portion $W$ of the salt is then carefully ignited in a crucible until nothing remains but metallic silver, which is also weighed Let its weight be $w$ Then, since the equivalent weight of silver is 108, the equivalent weight of the

silver salt is $\frac{108W}{w}$ This multiplied by $n$, the basicity of the acid, gives the molecular weight of the silver salt, $\frac{108nW}{w}$ To obtain the molecular weight of the free acid deduct the weight of the silver ($108n$) and add $n \times 1$ to represent hydrogen

The molecular weights of bases may be obtained in a similar way by preparing and igniting the **platinichlorides,** which may be regarded as organic derivatives of the salt $(NH_4)_2PtCl_6$ in which some or all of the hydrogen is replaced by organic radicals

EXPT 86 **Determination of the equivalent of an organic acid.**

(*a*) Weigh accurately, say, 0 75 gram of powdered citric, tartaric or oxalic acid, dissolve in warm distilled water, add a few drops of a solution of phenolphthalein in alcohol and titrate with half-normal caustic soda until a pink colour persists From the result calculate the equivalent weight of the acid *N B* —The caustic soda should be as free as possible from sodium carbonate , alternatively, the acid may be titrated against an almost saturated solution of barium hydroxide (p 123)

(*b*) To a solution of tartaric acid in water add a solution of ammonia until the liquid is neutral, then add a solution of silver nitrate as long as any precipitate forms Collect the precipitate on a filter, wash it well with water and dry it in the oven Weigh accurately about 0 4 to 0 5 gram of the dry salt in a weighed silica crucible Ignite the crucible strongly until the salt is completely decomposed and nothing remains in the crucible except metallic silver Cool and weigh again Calculate what weight $w$ of the salt is equivalent to 108 grams of silver The equivalent weight of the free acid is then $w - 108 + 1$, since 1 gram of hydrogen in the acid is replaced by 108 grams of silver in the salt Compare your result with that obtained in (*a*) *N B* —If oxalic acid be used in place of tartaric acid, the two methods will give different results, since the crystals of oxalic acid in (*a*) contain water of crystallisation

Since many organic compounds boil without decomposition and at relatively low temperatures, it is often possible to determine the approximate molecular weight from the vapour density, *e g* by Victor Meyer's method (p 466) The formula can then be deduced from a knowledge of the percentage composition (reinforced if possible by a knowledge of the equivalent) and of the molecular weight Since many organic acids decompose before they can be distilled, they are first converted into *esters* by replacing the acid hydrogen with the organic radicals methyl, $CH_3$, or ethyl, $C_2H_5$ These can generally be vaporised without decomposition, when the molecular weight of the acid can be deduced from that of the ester by subtracting $CH_3 - H = CH_2 = 14$ for each methyl radical in the methyl ester, or $C_2H_5 - H = C_2H_4 = 28$ for each ethyl radical in the ethyl ester Thus the molecular weight of **methyl oxalate** (p 729), $(CH_3)_2C_2O_4 = 118$, can be deduced from its vapour density , we can then infer that the formula of oxalic acid must be $H_2C_2O_4$ and not $HCO_2$

The percentage composition of the methyl ester is usually determined by combustion as described below It is, however, also possible to estimate the methyl groups by ZEISEL'S METHOD For this purpose the methyl compound is heated with hydriodic acid, which converts all the $-OCH_3$ groups into the very volatile methyl iodide, $CH_3I$ This is distilled off into a solution of silver nitrate in methyl alcohol and the precipitate of silver iodide is weighed Each methyl radical ($CH_3 = 15$) then gives 235 parts of silver iodide

**Estimation of carbon and hydrogen.**—Carbon and hydrogen are estimated by combustion, according to the method of Dumas (p 82), but arrangements are made to collect both (i) water, in drying tubes of calcium chloride, and (ii) carbon dioxide, in a set of potash bulbs The apparatus is shown in Fig 108

EXPT 87 **Estimation of carbon and hydrogen**

A small amount (between 0 1 gram and 0 2 gram) of the substance is weighed to a tenth of a milligram in a small porcelain (or platinum) boat This is placed in a combustion tube of hard glass about 3 feet in length, which contains a long column of dry copper oxide in a coarse granular

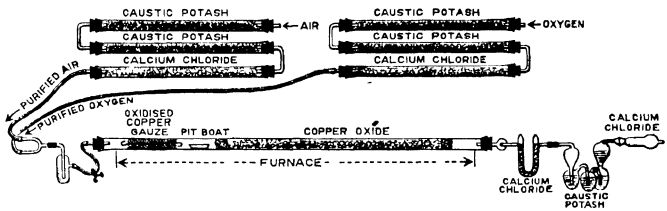



FIG 108 ESTIMATION OF CARBON AND HYDROGEN

condition , a roll of oxidised copper gauze is placed behind the boat so that it is enclosed on both sides by layers of copper oxide A slow current of air, freed from carbon dioxide and moisture by passing through layers of caustic potash and of calcium chloride, is passed through the tube, which rests in a furnace in which it can be carefully heated At the further end of the tube are fixed a small U-tube containing calcium chloride to absorb the moisture produced by the combustion of the organic compound, and a " bubbler " containing a 30% solution of caustic potash (*not* soda) to absorb the carbon dioxide , the bubbler also carries a tube of solid calcium chloride to prevent loss of water by evaporation from the caustic potash

These two pieces of apparatus are weighed carefully at atmospheric temperature before and after the experiment The combustion must be carried out very slowly in order to guard against incomplete absorption of carbon dioxide by the bubbler , and the heating must be continued until the porcelain boat is seen to be empty and clean and any reduced copper has been oxidised again If the apparatus has not been used previously, prolonged ignition in a current of dry air is needed, in order to free it from

all traces of moisture and combustible matter before introducing the substance Towards the end of the combustion it is usual to pass dry oxygen instead of air through the tube, but air is passed again through the apparatus before weighing the absorption tubes, since otherwise the different densities of air and oxygen would give rise to a small error in the weights recorded

The increase in weight of the potash bulbs is due to carbon dioxide, of which $\frac{12}{44}$ or $\frac{3}{11}$ consists of carbon Similarly $\frac{1}{9}$ of the increase shown by the calcium chloride tube is due to hydrogen Since the weight of substance burned is known, it is easy to calculate the percentage of carbon and of hydrogen

If the percentages of carbon and hydrogen in an organic compound add up to 100, the substance is a **hydrocarbon,** *i e* it contains no other element than carbon and hydrogen If the total is less than 100 and no other element has been detected, the remainder is generally assumed to be *oxygen* If elements other than carbon, hydrogen and oxygen are present in the compound, modifications must be introduced in the method of combustion Thus, if *nitrogen* is present, oxides of nitrogen may be formed These will dissolve in the potash and introduce an error in the weight of carbon dioxide To prevent this, a roll of bright copper gauze is placed at the front end of the combustion tube This, when heated gently, removes oxygen from the oxides of nitrogen and free nitrogen passes over Similarly, when *chlorine* is present, a roll of silver foil is used instead of the roll of copper gauze to decompose any hydrogen chloride which may be formed *Sulphur* is sometimes present in organic compounds During combustion sulphur dioxide is formed, but it can be absorbed by using heated lead chromate instead of copper oxide for the combustion

**Estimation of nitrogen.**—The most trustworthy method of estimating nitrogen in organic substances is that of Dumas, in which the substance is burned completely by heating it in contact with finely-powdered copper oxide in an atmosphere of carbon dioxide In this way the whole of the nitrogen can be liberated as gas and its weight calculated from its volume

EXPT 88 **Estimation of nitrogen by combustion.**

The estimation is carried out in a combustion tube, about 3 feet in length, containing coarse copper oxide A weighed amount, about 0 2 to 0·3 gram of substance, is *mixed with previously-ignited copper oxide powder,* and introduced into the tube between a long layer of granular copper oxide and a roll of oxidised gauze, in very much the same way as in the estimation of carbon and hydrogen A roll of bright copper gauze at the further end of the tube serves to reduce any oxides of nitrogen formed during the combustion The end of the combustion tube near the substance is then connected with an apparatus for producing carbon dioxide free from air

This may take the form of a short length of hard glass tubing closed at one end and containing magnesite, which can be heated to generate carbon

dioxide. The other end of the combustion tube is connected to a **nitrometer** (Fig 109) for collecting the nitrogen, this is filled with a 30% solution of caustic potash in order to remove the carbon dioxide by means of which the nitrogen is carried forward

Before heating the substance, carbon dioxide is passed through the apparatus in order to drive the air out of the tube During this process the column of potash in the nitrometer is reduced as much as possible by opening the tap at the top and lowering the reservoir When all the air has been expelled, and a trial shows that the carbon dioxide is absorbed completely by the potash, the nitrometer is filled with potash to the top, and the current of carbon dioxide is stopped The substance is then heated gradually until combustion is complete During this process, nitrogen collects in the nitrometer, but some of it remains in the tube and must be carried forward by passing carbon dioxide through it again, until the bubbles are absorbed completely, and no further increase takes place in the volume of nitrogen collected The nitrometer is then allowed to cool, and the nitrogen is measured Corrections must be applied for temperature and pressure A small correction should also be applied for the pressure of the vapour of the potash solution, this is assumed to be one-half of the vapour-pressure of water at the same temperature The percentage of nitrogen in the compound is calculated by taking the weight of 1 litre of nitrogen at 0° C and 760 mm pressure as 1 26 grams

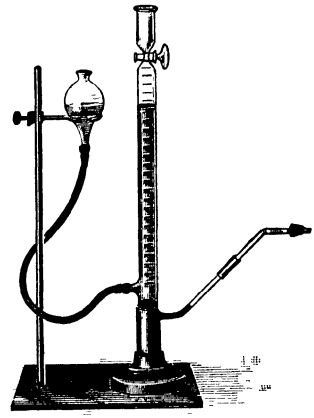


FIG 109 NITROMETER

Nitrogen can be distilled off from certain types of organic compound, *e g* the amides (p 763), in the form of ammonia by direct hydrolysis with a caustic alkali From other compounds, *e g* the proteins, the nitrogen is liberated as ammonia only by charring first in the presence of strong sulphuric acid, when the nitrogen is converted into ammonium sulphate Thus the nitrogen in flour and in many similar organic materials is estimated by KJELDAHL'S METHOD, by heating with excess of concentrated sulphuric acid, to which potassium sulphate has been added in order to raise the boiling-point When the liquid has become clear again, by the total destruction of the organic material, the ammonia is set free by an excess of caustic soda, distilled off and titrated exactly as in Expt 60 (p 418)

**Estimation of chlorine.**—Chlorine is generally estimated by the method of **Carius** A thick-walled tube of soft glass is sealed and rounded at one end About 2-3 c c of fuming nitric acid and a crystal of silver nitrate are introduced into the tube The substance to be analysed is weighed

in a small tube and carefully introduced into the larger tube (Fig 110). The open end of the latter is then drawn out very slowly in the blow-pipe flame and well sealed, care being taken not to allow the nitric acid to attack the substance before the tube is sealed When cool, the tube is wrapped in asbestos paper, inserted in an iron sheath and placed in a horizontal furnace which can be tilted at a slight angle. The furnace is then heated for several hours to 200° or higher During this heating the carbon and hydrogen are oxidised by the nitric acid and the chlorine forms silver chloride Great pressure is produced, so that it is dangerous to handle the tubes at this stage When cold, the tip of the tube which projects from the iron sheath is heated in a flame until it softens and the compressed gases force an opening and escape The tube can then be handled safely It is cut open and the contents are washed into a beaker of distilled water The silver chloride is collected, dried and weighed in the usual way Since the composition of silver chloride is accurately known, the weight of chlorine can be calculated



FIG 110 CARIUS' TUBE

**Estimation of sulphur.**—The estimation of sulphur is carried out in much the same way as that of chlorine In this case, however, no silver nitrate is used The sulphur is oxidised by the nitric acid to sulphuric acid, which can afterwards be converted, by the addition of barium chloride, into barium sulphate and weighed as such The percentage of sulphur is then calculated

**Estimation of metals.**—Many organic substances contain metallic constituents These can generally be estimated by the ordinary methods of inorganic analysis, sometimes after the original substance has been burned in air or oxygen until nothing remains but an ash , in other cases the metals can be weighed as sulphate after igniting the organic compound with sulphuric acid

# *PART V*

# PHYSICAL CHEMISTRY

## CHAPTER XXXIII

### THE GASEOUS STATE

**The three states of matter.**—The three states of matter, solid, liquid and gaseous, can be defined as follows

(i) **Solids** have a definite volume and a definite shape They can be compressed or expanded they can also be distorted, but force has to be exerted in order to change either the volume or the shape of a solid

(ii) **Liquids** are fluids which have a definite volume but no definite shape A liquid can be compressed, but the resistance to compression has to be overcome by the exercise of force On the other hand, no force is required to make a liquid change its shape The form of a liquid is therefore determined in the first instance by the form of the vessel in which it is contained Thus when a liquid is at rest under the influence of gravity, it fills the lower part of the vessel, and the free upper surface is horizontal

(iii) **Gases** are fluids which have no definite shape and no definite volume They differ from liquids in possessing the power of expanding until they fill completely any vessel in which they are placed

Gases and liquids are classed together as FLUIDS, on account of their ability to flow under the influence of very small forces Thus, gases (which were formerly described as ELASTIC FLUIDS) will flow under the influence of their own elasticity until the space in which they are confined is filled completely Liquids will flow under gravity, but viscous liquids flow only slowly PLASTIC SOLIDS, such as lead or sodium, can be made to flow under pressure, *e g* by squirting through a nozzle or die, but this flow does not take place until a minimum limiting pressure is applied

**The properties of gases.**—The behaviour of gases is in general much simpler than that of solids and liquids Thus, whilst the physical properties of liquids and solids vary widely from substance to substance, and have to be studied individually, it is often possible to state a simple rule which will describe the properties or behaviour of all gases, *e g* their combination by volume (Chap III) and their behaviour on compression or on change of temperature For this reason, it is convenient to begin the study of physical chemistry by considering the properties of gases

**The gas laws.**—The behaviour of gases, and especially the changes of volume which take place when the temperature and pressure are varied,

can be expressed by means of three important laws These three laws can also be combined in an equation, which gives a very useful summary of the physical properties of gases

(*a*) **Boyle's law,** which described the behaviour of a gas under varying pressures, may be stated as follows

*The volume of a given quantity of a gas at constant temperature is inversely proportional to its pressure*

It may also be expressed algebraically by the equation,

$$pv = k,$$

where $p$ is the pressure and $v$ the volume of a fixed quantity of a gas at constant temperature , $k$ is then a constant, the value of which depends upon (i) the quantity of gas considered, (ii) the temperature, and (iii) the units in which $p$ and $v$ are measured

(*b*) **Charles's law** describes the manner in which the volume of a gas varies when it is heated at constant pressure It expresses the fact that all gases expand and contract uniformly and to a similar extent when the temperature is changed Thus, the volumes of all gases increase by about 37% between the freezing-point and the boiling-point of water If this rate of expansion and contraction were maintained, the volume of the gas would diminish to zero at $-273^\circ$ C , this temperature is therefore called the ABSOLUTE ZERO At any other temperature the volume of the gas would be proportional to the ABSOLUTE TEMPERATURE, *i e* to the temperature measured in Centigrade degrees, but from the absolute zero at $-273^\circ$ C instead of from $0^\circ$ C Charles's law may therefore be stated as follows

*At constant pressure the volume of a given quantity of any gas is proportional to its temperature on the absolute scale*

If $t$ is the temperature on the Centigrade scale, then the absolute temperature $T$ is equal to $t + 273$ We may therefore write Charles's law algebraically in the following manner

$$v = k(273 + t) = kT$$

The numerical value of the constant $k$ depends upon (i) the quantity of gas considered, (ii) the pressure, and (iii) the units in which $v$ and $T$ are expressed

(*c*) The above equations may be combined to give the relation

$$pv = kT$$

The constant $k$ in this equation is the same for all values of the temperature, pressure or volume , but its value still depends upon the units in which $p$, $v$, and $T$ are expressed, and upon the quantity of gas which is taken We can, however, make this equation still more general by applying AVOGADRO'S HYPOTHESIS, according to which *equal volumes of all gases at the same temperature and pressure contain the same number of molecules* One gram-molecule of any gas at a given temperature and pressure will therefore occupy a definite volume, which will be the same for all gases If, therefore, we always consider one gram-molecule of gas, the value of $k$ in the equation $pv = kT$ will also be the same for all gases. This standard

value of $k$ is usually indicated by a special symbol $R$, and is named the GAS CONSTANT The equation,

$$pv = RT,$$

thus summarises the three important laws of gases and enables us to predict the behaviour of one gram-molecule of any gas when subjected to changes of volume, pressure and temperature These predictions are only approximately true in the case of actual gases , the ideal gas, for which alone they would be mathematically exact, is described as a PERFECT GAS (p 461).

**The gas constant.**—The value of the gas constant $R$ has been determined by a careful study of the density of gases under known temperatures and pressures If $M$ is the molecular weight of a gas, $d$ its density at a pressure $p$, and at an absolute temperature $T$, then the volume occupied by a gram-molecule is given by $V = M/d$, and $R = pV/T = Mp/dT$ By using this formula, the value of the gas constant $R$ can be calculated from the results of accurate measurements of the densities of gases

The value of the gas constant $R$, when deduced from the densities of different gases, varies slightly, because the gas laws are not obeyed strictly by any real gas At moderate pressures, however, and at temperatures much above the temperature of liquefaction, many gases obey the gas laws very closely, and therefore give concordant values for the gas constant $R$ Table 37 records some of the most accurate determinations of the densities of gases, together with the volume in litres, $V_0$, occupied by one gram-molecule at 0° C and 760 mm pressure (*i e.* at " normal temperature and pressure," or N T P )

TABLE 37 —MOLECULAR VOLUMES OF GASES.

| Gas | Mol wt | Density $d$ (in grams per litre at N T P ) | Volume $v_0$ (in litres at N T P ) |
|---|---|---|---|
| Hydrogen - - - | 2 016 | 0 08988 | 22 43 |
| Oxygen - - - | 32 000 | 1 4291 | 22 39 |
| Nitrogen - - - | 28 02 | 1 2507 | 22 40 |
| Nitric oxide - - - | 30 01 | 1 34265 | 22 35 |
| Carbon monoxide - | 28 00 | 1 2507 | 22 44 |
| Nitrous oxide - - | 44 02 | 1 9706 | 22 34 |
| Methane - - - | 16 03 | 0 71464 | 22 44 |
| Ammonia - - - | 17 07 | 0 7621 | 22 39 |

The molecular volume $V_0$ is not quite constant, but varies a little from one gas to another Since these variations become less as the pressure is reduced, it is supposed that they would disappear altogether at very low pressures

**Numerical value of the gas constant.**—When allowance is made for the deviations of real gases from the ideal gas laws, the value of $V_0$ for a perfect or ideal gas is 22 412 litres at 0° C , and 1 atmosphere pressure The value of $R$ is then given by the equation

$$R = \frac{pV}{T} = \frac{1 \times 22\,412}{273} = 0\,0821 \text{ litre-atmosphere.}$$

Since we have expressed $p$ in atmospheres and $V$ in litres, the number 0 0821 represents the value of $R$ in LITRE-ATMOSPHERES This unit is a convenient one to use when the gas equation is applied to the calculation of the volumes of gases at different temperatures and pressures

The significance of the constant $R$ may be seen by considering the nature of the quantities of which it is made up Pressure is force per unit area, whilst temperature is expressed by a pure number, hence

$$R = \frac{\text{pressure} \times \text{volume}}{\text{temperature}} = \frac{\text{force}}{\text{area}} \times \text{volume}$$
$$= \text{force} \times \text{length} = \text{work}$$

We can therefore express $R$ in absolute units of work Thus in the centimetre-gram-second system (C G S system) the value of $R$ can be expressed in *ergs* In order to do this, we must transform $p$ and $V$ into C G S units One atmosphere is the pressure of a column of 760 mm of mercury at 0° Since the density of mercury at 0° is 13 596 grams per c c , the weight of a column of mercury 76 cm in height and 1 sq cm in area is $76 \times 13\ 596$ grams To convert this pressure into absolute units we must multiply by the gravitational constant 980 6, which converts grams of weight into absolute units of force or dynes The absolute value of an atmosphere of pressure is therefore

$$76 \times 13\ 596 \times 980\ 6 = 1{,}014{,}000 \text{ dynes per sq cm}$$

If we then express $V_0$ in cubic centimetres, instead of in litres, we have

$$R = \frac{76 \times 13\ 596 \times 980\ 6 \times 22{,}412}{273} = \mathbf{83{,}150{,}000} \text{ ergs}$$

Now work and heat are forms of energy which may be converted quantitatively into one another We can, therefore, express the value of the gas constant $R$ in units of heat instead of in units of work For this purpose we must make use of the fact that the unit of heat, the CALORIE (*i e* the amount of heat required to raise 1 gram of water from 15° to 16° C , see p 548), is equal to $4\ 183 \times 10^7$ ergs The value of $R$ in calories is therefore

$$R = \frac{8\ 315 \times 10^7}{4\ 183 \times 10^7} = 1\ 985 \text{ calories}$$

The approximate figure, $R = 2$ calories, finds many applications in the discussion of problems concerning gases, and should be remembered

**The kinetic theory of gases.**—The KINETIC THEORY assumes that gases are composed of minute particles (molecules) which are moving at random in space These particles are supposed to be completely elastic, *i e* no loss of translational energy occurs when they collide with themselves or with the walls of the vessel Further, it is supposed that the volume of the molecules is very small in comparison to the space which they occupy, and that the distances between them are so large that intermolecular forces are negligible The pressure exerted by a gas is then attributed to the impact of the molecules on the walls of the containing vessel, whilst gaseous diffusion is due to their random motion

**The deduction of the gas laws from the kinetic theory.**—Each molecule in a gas moves in a straight line until it meets another molecule, when its direction suddenly changes Its path is therefore an irregular zigzag, made up of a series of straight lines Not only does the direction of motion vary, but also the speed at which the molecule is moving, since at one moment it may be moving rapidly and then after a collision be brought almost to a standstill

It can be shown by mathematical reasoning that it is sufficient to consider only the average velocity of the whole group of molecules, provided that this average is calculated in a special way Suppose there are $n$ molecules which at a given instant have velocities, $c_1$, $c_2$, $c_3$, $c_n$, then this special kind of average, which is called the ROOT MEAN SQUARE VELOCITY, is given by the formula

$$c = \sqrt{\frac{c_1^2 + c_2^2 + c_3^2 \quad + c_n^2}{n}},$$

where the symbol $c$ is used to signify this average velocity

Since the gas molecules are perfectly elastic, the time occupied by a collision is negligible compared with the time in which the molecules are moving in a straight line There is also a great deal of evidence to show that the volume of the molecules themselves is very small compared with the volume occupied by the gas Thus 1 c c of water at 100° gives 1700 c c of steam at the same temperature, so that the volume of the water molecules is certainly less than 1/1700 of the volume occupied by the steam Hence in discussing the effect of the gas molecules on the walls of the containing vessel, we can neglect the influence of the collisions between molecules in the interior of the vessel, and suppose that each molecule moves in a straight line from one wall to another, and is then reflected back again

Suppose we have $n$ molecules of gas contained in a cubical vessel of side $l$ cm Let the mass of each molecule be $m$, and let $c$ be the root mean square velocity This is represented in magnitude and direction by $OK$ in Fig. 111 This velocity can be regarded as made up of three component velocities, $x$, $y$ and $z$, parallel to the sides of the cube These are related to $c$ by the equation

$$c^2 = x^2 + y^2 + z^2$$

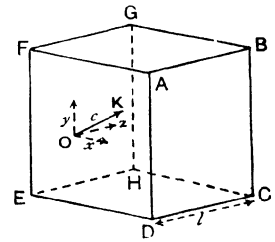



FIG 111 DIAGRAM TO ILLUSTRATE THE KINETIC THEORY OF GASES

Now suppose that the particle starts with a velocity $x$ from the face $EFGH$ It will strike the face $ABCD$ and be reflected back again in the opposite direction Just before colliding with $ABCD$ its momentum is $mx$, and after the collision it is $-mx$, since the particle is moving in the opposite direction Hence the change of momentum during each collision is $2mx$ The force exerted on the walls is measured by the rate of change of momentum Since the molecule is moving with velocity $x$, and no time is wasted in collisions, it will strike the face $ABCD$, or the opposite

face $EFGH$, $x/l$ times per second Hence the change of momentum per second (which gives the force exerted on these two faces) is

$$2mx \times \frac{x}{l} = \frac{2mx^2}{l}$$

Similarly, if the particle had only the component $y$ of its velocity, it would exert a force of $2my^2/l$ on the faces $ABGF$ and $CDEH$, and if it had only the velocity component $z$, it would exert a force of $2mz^2/l$ on the faces $ADEF$ and $BCHG$ Adding these, the total force exerted by one molecule on all six faces of the cube is :

$$f = \frac{2m}{l}(x^2 + y^2 + z^2) = \frac{2mc^2}{l}$$

If $n$ particles are present, we can, as we have seen, neglect the effect of interior collisions and suppose each particle to behave as if the others were not there The *total force* on the walls due to $n$ particles is therefore $2nmc^2/l$, where $c$ is now the *root mean square* of all the individual velocities The pressure (or force per unit area) will be given by dividing this quantity by the area of the six faces, $6l^2$

$$p = \frac{2nmc^2}{6l^3}$$

Substituting $v$, the volume, for $l^3$, we have the fundamental kinetic equation,

$$pv = \tfrac{1}{3}nmc^2, \qquad (1)$$

from which the gas laws may be derived as follows

(*a*) *Boyle's law* —The quantities on the right-hand side of equation (1) are $n$ and $m$, the number and mass of the gas molecules (which are constant) and the root mean square velocity $c$ If the gas is at constant temperature in a closed vessel, it neither gains nor loses energy, the mean square velocity $c^2$, and the root mean square velocity $c$, must therefore remain constant, and equation (1) may then be written

$$pv = \text{constant (at constant temperature)}$$

We have thus deduced BOYLE'S LAW from the kinetic theory of gases

(*b*) *Charles's law* —This law cannot be deduced directly from the kinetic theory, but a new interpretation of the temperature of a gas may be derived by assuming the correctness of the law

The average kinetic energy of the molecules of a gas is $\frac{1}{2}nmc^2$, and, writing for this the symbol $E$, we have

$$pv = \tfrac{1}{3}nmc^2 = \tfrac{2}{3}E.$$

But, for one gram-molecule of a gas,

$$pv = RT,$$
$$\therefore\ RT = \tfrac{2}{3}E,$$
$$T = \tfrac{1}{3}E, \text{ where } R = 2.$$

In terms of the kinetic theory, the temperature of a gas may therefore

be defined as *a quantity which may be measured by the average kinetic energy of the molecules*

(*c*) *Avogadro's hypothesis* —If we take equal volumes of two gases at the same pressure and temperature, and allow them to mix together, there is in most cases no change of temperature Hence the average kinetic energy of the molecules must be the same for each gas If these equal volumes contain, in the case of one gas, $n_1$ molecules of mass $m_1$ and velocity $c_1$, and, in the case of the other gas, $n_2$ molecules of mass $m_2$ and velocity $c_2$, then, since the kinetic energies are the same,

$$\tfrac{1}{2}m_1{c_1}^2 = \tfrac{1}{2}m_2{c_2}^2 \qquad (2)$$

Also, since equal volumes at the same pressure were taken,

$$p_1v_1 = p_2v_2 ,$$

and therefore

$$\tfrac{1}{3}n_1m_1{c_1}^2 = \tfrac{1}{3}n_2m_2{c_2}^2 \qquad (3)$$

Dividing (3) by (2), we find that

$$n_1 = n_2,$$

*i e equal volumes of different gases at the same temperature and pressure contain the same number of molecules*, which is AVOGADRO'S HYPOTHESIS

(*d*) *Graham's law of diffusion* —Graham found that the rate at which gases diffuse through a porous plug, or escape from a small orifice, varied inversely as the square root of the density of the gas It is obvious that the rate of diffusion will depend upon the velocity with which the molecules are moving

Since $pv = \frac{1}{3}nmc^2$, it follows that $c^2 = 3pv/nm$ Since the density $d$ is equal to the weight per unit volume,

$$d = \frac{nm}{v} , \quad \therefore \; c^2 = \frac{3p}{d} \quad \text{and} \quad c = \sqrt{\frac{3p}{d}}$$

Thus, at constant pressure and temperature, *the velocity of the gas molecules is inversely proportional to the square root of the density* The kinetic theory of gases therefore accounts for GRAHAM'S LAW OF DIFFUSION

(*e*) *Mean velocity of molecules* —The mean velocity of the molecules of a gas can be calculated from this equation by putting in the values of $p$ and $d$ for a particular gas To get the velocity in centimetres per second, we must express $p$ and $d$ in absolute units Thus oxygen at 1 atmosphere pressure and 0° C has a density of 1 429 grams per litre

$$\begin{aligned} p = 1 \text{ atm} &= 76 \text{ cm of mercury} \\ &= 76 \times 13\,6 \times 981 \text{ dyn /sq cm.} \\ &= 1{,}014{,}000 \text{ dyn /sq cm} \end{aligned}$$

$$d = 1{\cdot}429 \text{ gm /lit} = 0\,001429 \text{ gm /c c}$$

$$\therefore \; c = \sqrt{\frac{3 \times 1{,}014{,}000}{0\,001429}}$$

$$= 46{,}100 \text{ cm /sec}$$

$$= 0\,3 \text{ mile per second.}$$

Similarly the mean velocity of the hydrogen molecule at 0° is 192,000 cm /sec or 1 2 miles per second

**Specific heats of gases.**—We have seen already (p 458) that the kinetic energy of a gas molecule is proportional to the absolute temperature, and that the kinetic energy per gram-molecule is given by

$$E = \tfrac{3}{2}RT$$

If therefore a gram-molecule of a gas is heated in a closed vessel from $T$ to $T+1$ degrees, the kinetic energy increases from $\frac{3}{2}RT$ to $\frac{3}{2}R(T+1)$, an increase of $\frac{3}{2}R$ or 3 calories (since $R = 2$ calories approximately)

The MOLECULAR HEAT of a gas is defined as the amount of heat required to raise one gram-molecule through 1° C If the only effect of heat were to increase the energy of translation of the molecules, then the MOLECULAR HEAT AT CONSTANT VOLUME $C_v$ should be 3 calories for all gases Molecules are, however, complex systems often containing several atoms, and may therefore possess other forms of energy, due to rotation of the molecule as a whole or to vibrations of parts of the molecule When this is the case, additional energy will be used up in increasing the amplitude of these rotations or vibrations, or generally speaking in doing internal work on the molecules If this amount of work is represented by $x$ units of heat, then the molecular heat at constant volume will be

$$C_v = 3 + x,$$

where $x$ will vary from one gas to another, and will be large for complex molecules

When a gas is heated at constant pressure, instead of at constant volume, it expands and so does work against the atmosphere For this reason the molecular heat at constant pressure, $C_p$, is greater than $C_v$, the molecular heat at constant volume This difference may be calculated in the following way

$$\textit{Work done} = \textit{pressure} \times \textit{increase in volume} = p_1(v_1 - v_0),$$

but

$$p_1v_1 = RT_1 \quad \text{and} \quad p_1v_0 = RT_0,$$

$$\textit{work done} = p_1v_1 - p_1v_0 = R(T_1 - T_0),$$

where the initial pressure, volume and temperature are $p_1$, $v_0$, $T_0$, and the final values are $p_1$, $v_1$, $T_1$

When one gram-molecule is raised through one degree

$$\textit{Work done} = R = 2 \text{ calories, or } C_p - C_v = 2 \text{ cals}$$

Since

$$C_v = 3 + x \text{ cals}, \qquad C_p = 5 + x \text{ cals}$$

The ratio $C_p/C_v$ of the heat-capacities of the gas at constant pressure and at constant volume is often indicated by the symbol $\gamma$, so that

$$\gamma = \frac{C_p}{C_v} = \frac{5+x}{3+x}.$$

The determination of the ratio $\gamma$ provides valuable evidence with regard to the atomicity of the simpler molecules Thus, for a monatomic gas, $x = 0$, so that $\gamma = \frac{5}{3} = 1{\cdot}667$, as in helium and argon. For a diatomic gas,

the theoretical value of $x$ is 2 calories, *i e* $\gamma = \frac{7}{5} = 1\ 4$, as in $H_2$, $N_2$, $O_2$ and CO ; but $Cl_2$ gives a lower value As the atomicity of the molecule increases, the value of $x$ also increases, whilst that of $\gamma$ decreases still further, as may be seen in Table 38

TABLE 38 —MOLECULAR HEATS OF GASES

| Gas | Formula | $C_p$ | $C_v$ | $C_p/C_v$ |
|---|---|---|---|---|
| Helium - - - | He | 4 97 | 2 98 | 1 67 |
| Argon - - - - | A | 4 97 | 2 98 | 1 67 |
| Hydrogen - - - | $H_2$ | 6 86 | 4 87 | 1 41 |
| Oxygen - - - | $O_2$ | 7 04 | 5 04 | 1 40 |
| Nitrogen - - - | $N_2$ | 6 925 | 4 929 | 1 41 |
| Carbon monoxide - | CO | 6 94 | 4 94 | 1 40 |
| Chlorine - - - | $Cl_2$ | 8 04 | 5 93 | 1 36 |
| Carbon dioxide - - | $CO_2$ | 8 79 | 6 75 | 1 30 |
| Ammonia - - - | $NH_3$ | 8 74 | 6 67 | 1 31 |
| Acetylene - - - | $C_2H_2$ | 8 88 | 6 83 | 1 28 |
| Ethylene - - - | $C_2H_4$ | 10 25 | 8 20 | 1 25 |
| Ethane - - - | $C_2H_6$ | 11 47 | 9 40 | 1·22 |

**Number, mass, and dimensions of molecules** —The number of molecules in a gram-molecule of a gas is indicated by the symbol $N$, and is named the AVOGADRO NUMBER It has been determined with considerable accuracy by several different methods and has the value $0\ 6064 \times 10^{24}$ It is difficult to obtain any idea of the significance of such an enormous number Suppose we have a gas at a pressure of only a millionth of a millimetre of mercury (which is the vacuum attained in an electric light bulb), then each cubic millimetre of the attenuated gas still contains more than 30 million molecules

**The ideal or perfect gas.**—Accurate measurements of the volume occupied by a gas at different temperatures and pressures show that Boyle's law and Charles's law are only approximately true The ideal gas, which would obey both of these laws exactly, is called a PERFECT GAS It should have the following properties

(1) If cooled at constant pressure, its volume would decrease continuously and become zero at $-273°$ C All real gases, however, condense to liquids at temperatures above 0° Absolute. Since the volumes of these liquids is not much changed by cooling, extrapolation of the $V/T$ graph to zero temperature leads to a small but definite value for $V$

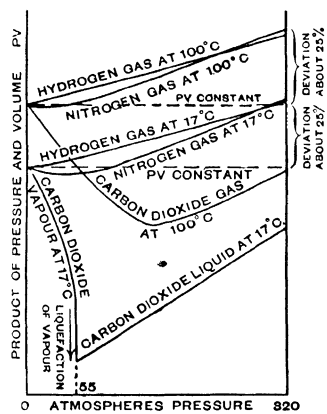



FIG 112 DEVIATIONS FROM BOYLE'S LAW

(2) The value of $pV$ at constant temperature should be constant and not vary with pressure In Fig 112 the values of $PV$ for a number of

gases are plotted against the pressure The graphs for a perfect gas should consist of a set of horizontal straight lines, whereas all real gases give either a sloping straight line, *e g* hydrogen, or a curve with a minimum, *e g* carbon dioxide For a given gas, however, the shape of the "isotherm" showing the relation between $pV$ and $p$ at constant temperature is determined by the temperature Thus hydrogen at low temperatures gives a curve with a minimum, like that of carbon dioxide, whilst carbon dioxide gives a straight line like the isotherm of hydrogen, when the temperature is raised above 500° C

(3) No change of temperature should occur when it is allowed to expand into a vacuum without doing any external work

**Explanation of the deviations from the gas laws** —In deducing the gas laws from the kinetic theory, it was assumed (i) that the molecules of a gas do not attract or repel one another, and (ii) that their volume is negligible in comparison with the total space occupied by the gas These assumptions are approximately true for gases at low pressures, and at temperatures relatively far above the temperature of liquefaction, but they become increasingly inaccurate as the pressure is raised and the temperature lowered It is not surprising, therefore, that gases should show wide deviations from these laws when the pressure is high and the temperature low

**Van der Waals' equation.**—(*a*) The value of $pV$ for carbon dioxide decreases at first with pressure (Fig 112) This is accounted for by assuming that the molecules exercise an attraction for one another, which is no longer negligible when the molecules are brought closer together by compression The gas is therefore more compressible than a perfect gas Thus the volume at a given pressure is reduced, and the product $pV$ therefore decreases as the pressure increases Looked at in another way, the attractive forces between the molecules weaken their impact on the walls of the containing vessel, and therefore reduce the effective pressure of the gas In order to allow for this inter-molecular attraction, van der Waals proposed to add to the observed external pressure a term $a/V^2$ to represent the INTERNAL PRESSURE of the gas, where $a$ is a constant depending on the nature of the gas, and $V$ is the volume occupied by one gram-molecule of the gas This term implies that *the attraction between molecules varies inversely as the fourth power of the distance* The combined Boyle-Charles law then becomes

$$\left(p+\frac{a}{V^2}\right)V=RT$$

(*b*) At higher pressures the isotherms for carbon dioxide pass through a minimum and then begin to rise, with the result that $pV$ soon becomes greater than the theoretical value This is due to the fact that the volume $b$ of the molecules themselves is now no longer negligible in comparison with the total volume $V$ occupied by the gas, *i e* the space $V-b$ between the molecules is distinctly smaller than the total volume $V$ This is readily allowed for in terms of the kinetic theory of gases Thus, on p 458, the number of times a molecule hits two opposite walls of the containing vessel in unit time was given by the expression $x/l$, where $l$ is the distance

between these walls and $x$ is its velocity perpendicular to them If the diameter, $d$, of the molecule is no longer negligible in comparison with $l$, the distance through which the molecule has to move between consecutive collisions with the walls is reduced from $l$ to $l - d$, and hence the collisions are more frequent This causes an increase of pressure, which tends to nullify the effect of inter-molecular attraction The upward slope of the isotherms for carbon dioxide, at high pressures, shows that eventually the effect of the finite volume of the molecules more than counterbalances that due to their mutual attraction The form of the hydrogen curves shows that, even at low pressures, the size of the molecules is the predominating factor, but, when the temperature is sufficiently low, hydrogen also gives isotherms like those of carbon dioxide

In order to allow not only for inter-molecular attraction, but also for the size of the molecules, van der Waals proposed the equation

$$\left(p + \frac{a}{V^2}\right)(V - b) = RT$$

VAN DER WAALS' EQUATION corresponds closely with the behaviour of real gases over a moderate range of pressure and temperature, but it is not exact, since the term $a/V^2$ is only an approximate representation of the variations of the internal pressure with the volume of the gas, and the effective value of $b$ appears to be influenced by pressure and temperature

**Molecular weights of gases and vapours.**—In an earlier section (Chap III, p 16) Avogadro's hypothesis has been applied in order to deduce approximate molecular weights from the relative densities of gases and vapours, by means of the relation,

$$\text{Mol wt} = 2 \times \text{relative density} = 2 \times \frac{\text{wt unit vol of gas or vapour}}{\text{weight of unit volume of hydrogen}},$$

where the volumes are measured under the same physical conditions, and the molecular weight of hydrogen is taken as 2 instead of as 2 0162 The methods employed in the direct measurement of the densities of gases and vapours are described below

**The densities of gases by Regnault's method.**—Two identical globes fitted with stopcocks are suspended from the arms of a balance and counterpoised, one having been previously evacuated The balance must be enclosed in order to eliminate air-currents, and for the most accurate work the globes may be hung below it in a desiccator cupboard, as in Morley's experiments (p 81) The evacuated globe is then filled with hydrogen at a definite temperature and pressure, and reweighed The weight of the hydrogen is thus found and the weight of it which would fill the globe at N T P is calculated The globe is evacuated once more, filled with the given gas at a definite pressure and temperature, and weighed The weight of the gas which would fill the globe at N T P is calculated as before The relative density of the gas is then deduced from the relation

$$\text{Relative density of gas} = \frac{\text{weight of gas filling globe at N T P}}{\text{weight of hydrogen filling globe at N T P}}.$$

The advantage of having two identical globes is that they are affected equally by changes of temperature, pressure and humidity, whereas if only one globe were used a series of tedious corrections would be necessary

Lord Rayleigh showed that a correction must be made to allow for the fact that a glass globe shrinks when evacuated, and thereby displaces less air than when filled with gas This shrinkage can be measured by immersing the evacuated globe in a bath, adjusting the water to the level of the overflow, and then measuring the water which overflows on letting air into the globe

Regnault's method gives very accurate results but is very tedious, so that the method is simplified for rough laboratory work by using a single flask as described in Expts 89 and 90 below

EXPT 89 **Determination of the density of air**

Place about 30-40 c c of water in a round-bottomed flask of about 250 c c capacity, provided with a rubber stopper, glass tube, rubber tube and clip, as in Fig 113 Insert the stopper, leaving the clip open, and boil vigorously over wire gauze for 5 minutes Then take away the flame and immediately close the clip on the rubber tube When the flask is cold, suspend it on the balance and weigh carefully Open the clip for a few seconds, when air will rush in to take the place of the condensed vapour, then weigh again The increase in weight gives the weight of air which has entered the flask Take the temperature of the water in the flask and measure its volume The volume of the air which has entered is obtained by subtracting this volume from the total volume of the flask Read the barometer The pressure of the air in the flask is given by the height of the barometer, minus the vapour-pressure of the water * The weight of a known volume of air at a known temperature and pressure has thus been obtained Hence calculate the weight of 1 litre of air at 0° C and 760 mm pressure

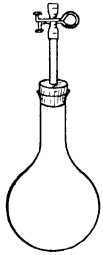


FIG 113 FLASK ARRANGED FOR DETERMINING THE DENSITY OF AIR

EXPT 90 **Density of carbon dioxide**

Choose a light flask of about 200 c c capacity Fit it with a rubber stopper carrying two right-angle tubes, one reaching to the bottom of the flask and the other ending flush with the stopper (Fig 114) In order to determine the volume of the flask, fill it with water up to the stopper and measure the volume of the water Then clean and dry the flask

Fit the outer ends of the two glass tubes with short lengths of rubber tubing each closed by a clip Weigh the flask carefully Then pass a stream of carbon dioxide (prepared in a Kipp apparatus and dried over sulphuric acid) through the longer tube until the gas issuing from the other tube extinguishes a taper Pass the gas for a minute or two longer, then

* The vapour-pressures of water at different temperatures are given in Table 44, p 482.

close the clips, starting with the one through which the gas enters the flask Read the temperature of the air by means of a thermometer left hanging near the flask, and read the barometer Weigh the flask again The increase in weight *plus* the weight of air displaced gives the weight of the carbon dioxide The weight of air displaced can be calculated from the volume of the air and its density as determined in Expt 89 Hence calculate the weight of 1 litre of carbon dioxide at 0° C and 760 mm

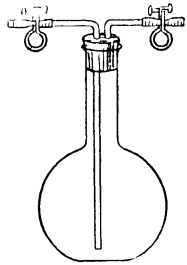


FIG 114 FLASK FOR DETERMINING DENSITY OF GASES

**Vapour density of a volatile liquid by Dumas' method.**—The apparatus generally used in the laboratory consists of a thin-walled glass bulb of about 100 c c capacity, with a drawn-out neck The bulb is first weighed full of air, the temperature and pressure being noted It is then warmed to drive out some of the air, and the tip is placed in a volatile liquid the vapour density of which it is desired to determine, so that two or three c c are sucked up as the bulb cools The bulb is now immersed, with only the tip projecting, in a bath of boiling liquid (Fig 115) or in a vapour jacket, at a temperature at least 30° above that of the boiling-point of the liquid in the bulb Greater differences than 30° are all to the good, because the further a vapour is from its boiling-point the more nearly does it obey the gas laws When no more vapour issues from the tip (observed by placing a luminous flame behind) it is sealed, and the bulb removed and weighed The volume of the bulb is found by breaking the drawn-out neck under water, which rushes up and fills the space formerly occupied by the vapour If the bulb is not filled to within 2 c c of its capacity, it is usually better to start the experiment over again The bulb full of water is reweighed with the broken fragments of glass The results obtained in an actual experiment are worked out below to show how the vapour density is calculated

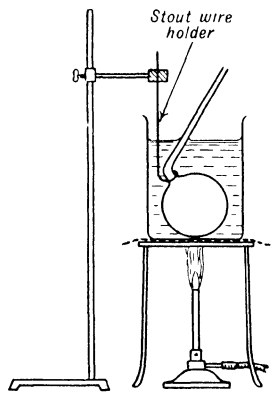



FIG 115 DUMAS' METHOD FOR MEASURING VAPOUR DENSITIES

Weight of bulb full of water = 86 50 grams
Weight of bulb full of air = 9 080 grams ,
Weight of water (approx ) = 77 42 grams ,
Volume of globe = 77 4 c c

Since 1 c c of air at N.T P weighs 0·00129 gram, the weight of the air that filled the bulb at 15 5° C and 751 mm pressure was

$$77\ 4 \times 0{\cdot}00129 \times \frac{273 \times 751}{288 \times 760} = 0\ 094 \text{ gram.}$$

The weight of the bulb minus the air which it contained was therefore 9 080 – 0 094 = 8 986 grams

When filled with chloroform vapour and sealed at 99° C and 751 mm pressure, the weight of the bulb was 9 294 grams Hence

$$\text{Weight of chloroform} = 9\ 294 - 8\ 986 = 0\ 308 \text{ gram}$$

Since this weight of chloroform occupied a volume of 77 4 c c at 99° C and 751 mm , its volume (if still gaseous) at N T P would be

$$\frac{77\ 4 \times 273 \times 751}{372 \times 760} \text{ c c ,}$$

.. 1 litre of chloroform at N T P weighs

$$0\ 308 \times \frac{1000 \times 372 \times 760}{77\ 4 \times 273 \times 751} = 5\ 49 \text{ grams}$$

Since 1 litre of hydrogen at N T P weighs 0 090 gram, the relative density of chloroform = 5 49/0 09 = **61 0.** This gives **122** as the molecular weight of chloroform, as compared with the calculated value of **119 5** for a compound having the formula $CHCl_3$

Dumas' method is subject to the following disadvantages

(1) It is wasteful, on account of the relatively large amount of liquid that must be used , the method is therefore not suitable for use with rare liquids

(2) If the liquid is not pure, the less volatile impurities will accumulate in the vapour which remains behind in the bulb

(3) It is difficult to tell when all the excess liquid has been vaporised out of the bulb

(4) Vapours near their boiling-point often diverge greatly from the gas laws

(5) The temperature of the bath may vary a little , but this is of minor importance compared with (3) and with errors caused by weighing a large glass bulb without a counterpoise, as a result of which the method is subject to errors which may exceed 5%

**Victor Meyer's method.**—In this method a known weight of liquid is vaporised and displaces its own volume of air, which is collected and measured at the temperature of the room Since it is not necessary to know the temperature of the vapour by which the air is displaced, it is possible to measure the vapour density of volatile solids, such as sulphur and zinc, by using a porcelain or silica bulb, heated at a constant but unknown temperature in a muffle furnace

The large bulb, *b* (Fig 116), is heated in a vapour jacket, *c*, until no more air is expelled The temperature of the jacket must be at least 30° C above that of the boiling-point of the liquid, not only in order to minimise the deviations from the gas laws, but also because speedy evaporation is essential in order to avoid diffusion and condensation of the vapour in the upper cold part of the apparatus A tiny bottle, containing a known weight of the volatile liquid, is dropped into the bulb at *d* The air displaced through the side tube, *a*, is collected and measured at a known temperature and pressure. Since the volume of gas displaced would be

the same if the bulb had been filled with hydrogen, it is easy to calculate the weight of *hydrogen* displaced by the known weight of the volatile liquid, and thus to deduce directly its vapour density and molecular weight

Water (b -pt 100°), aniline (b -pt 182°), nitrobenzene (b -pt 208°) or sulphur (b -pt 444° C) may be used in the outer jacket Errors in the molecular weights deduced by this method may be introduced by deviations from the gas laws if the vapour is not heated far enough above its boiling-point The method is capable of giving results within 4% of the correct values, but it is obviously unsuited for substances which dissociate when heated, since the temperature of the vapour is not recorded, and dilution with air would result in increased dissociation (*e g* $N_2O_4 \rightleftharpoons 2NO_2$)

**Hofmann's method** —A known weight of liquid in a tiny bulb, similar to that used in Victor Meyer's method, Fig 116, is allowed to evaporate at the top of a barometer heated by a vapour jacket (Fig 117) The barometer is graduated from the top in c c and from the bottom in centimetres In this way, the volume of a known weight of vapour is determined at a known temperature, and under a pressure equal to the difference between the heights of the column of mercury before and after the experiment This method has the advantage that the greatly reduced pressure in the barometer tube makes it possible to find the vapour density of substances which decompose at their normal boiling-points

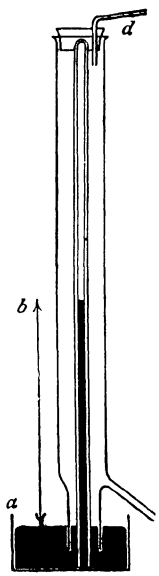



FIG. 117. DETERMINATION OF VAPOUR DENSITY BY HOFMANN'S METHOD.

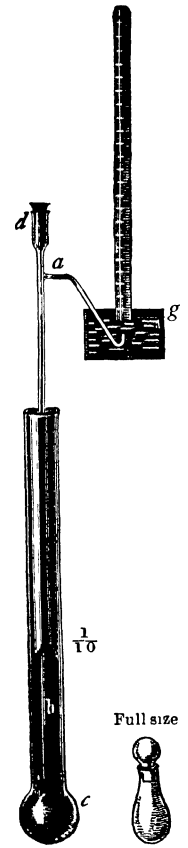



FIG 116 VICTOR MEYER'S APPARATUS FOR DETERMINATION OF VAPOUR DENSITY

**Indirect measurement of densities by diffusion.**—In addition to the direct method of weighing a given volume of gas or vapour, it is possible to compare the densities of gases by making use of Graham's law of gaseous diffusion, which states that the rate at which gases diffuse is inversely proportional to the square root of their densities

$$\frac{\text{No of c c of gas } A \text{ diffusing per sec}}{\text{No of c c of gas } B \text{ diffusing per sec.}} = \sqrt{\frac{D_B}{D_A}}$$

EXPT 91 **Relative densities of oxygen, nitrogen and air by diffusion**

A glass tube, 70 cms long and 1 cm wide (Fig 118), is sealed at one end with a thin plug of plaster of Paris, which acts as a porous diaphragm when dry Three rubber bands, *a*, *b*, *c*, are placed round the tube, which is then filled with *hydrogen* and immersed to *a* in a glass jar of water The time, $T_{H_2}$, taken for the water to rise inside this tube from *c* to *b* is noted The experiment is repeated with *oxygen* and with *air*, and in each case the time taken for the same volume of gas to diffuse through the same plug under the same excess of pressure is measured The relative densities are calculated thus

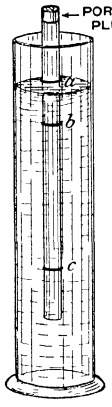



FIG. 118 DETERMINATION OF RELATIVE DENSITIES OF GASES BY DIFFUSION

$$\frac{\sqrt{D_{\text{oxygen}}}}{\sqrt{D_{\text{hydrogen}}}} = \frac{T_{O_2}}{T_{H_2}}, \text{ etc}$$

**Determination of exact molecular weights from vapour densities.**—Since the Boyle-Charles law is not obeyed strictly by any gas at ordinary temperatures and pressures, Avogadro's hypothesis is also only approximately true when applied to real gases Thus, even if a measurement of vapour density were absolutely correct, it would not give a true value for the molecular weight, because unit volumes of different gases do not contain equal numbers of molecules Since, however, there are good reasons for believing that the gas laws would be obeyed rigidly at very low pressures, trustworthy values for molecular weights may be obtained by extrapolating the relative densities to zero pressure This is known as the METHOD OF LIMITING DENSITIES It was introduced by Bertholet in 1898, and has been applied to the determination of the exact molecular weights of many gases, with a view to determining the atomic weights of their components by an independent method

The limiting density, $D_l$, may be deduced from the normal density, $D_n$, in the following way

Let $V_1$ = the volume of $M$ grams of the gas at one atmosphere pressure,
$V_0$ = the volume which $M$ grams of the gas would occupy at one atmosphere if it were an ideal gas

Then $$D_n = \frac{M}{V_1}, \quad D_l = \frac{M}{V_0} = D_n \times \frac{V_1}{V_0}$$

If values for $pV$ are plotted against $p$, it is possible to extrapolate to $p = 0$, and so to obtain the ideal value $(pV)_0$ The value of this product at 1 atmosphere is $1 \times V_1$, whereas the ideal value is $1 \times V_0$ It follows that

$$D_l = D_n \times \frac{V_1}{V_0} = D_n \frac{(pV)_1}{(pV)_0}$$

The following table indicates the exactness with which molecular weights, determined by the method of limiting densities, agree with those

derived from the atomic weights of the elements as deduced by the ordinary method of exact analysis

TABLE 39 —THE COMPARISON OF MOLECULAR WEIGHTS FROM NORMAL AND LIMITING DENSITIES

| Gas | Formula | Normal density, $O_2 = 32$ | Limiting density, $O_2 = 32$ | Molecular weight |
|---|---|---|---|---|
| Hydrogen - - | $H_2$ | 2 0125 | 2 0150 | 2 0156 |
| Nitrogen - - | $N_2$ | 28 007 | 28 013 | 28 016 |
| Hydrogen chloride | HCl | 36 741 | 36 484 | 36 465 |

EXPT 92 **Measurement of vapour densities by Dumas' method.**

Take a beaker which is sufficiently large to hold the Dumas bulb, and fill it two-thirds full of distilled water Heat the water to boiling point, and in the meantime weigh the bulb full of air, being careful to note the temperature and pressure of the air at the time of weighing Now continue the experiment as described on page 465, using one of the following liquids acetone, chloroform, pentane Note that 2 or 3 c c of liquid should be sucked into the bulb for each 100 c c capacity of the latter

Calculate the density of the vapour in grams per litre, then deduce the relative density and hence molecular weight of the vapour

EXPT 93 **Measurement of vapour densities by Victor Meyer's method.**

Carefully read the account of this method on pp 466-467, then fit up the apparatus depicted in Fig 116 Whilst the water jacket is being heated weigh an empty Victor Meyer bottle, then fill it full of ether, chloroform or acetone, and reweigh it, being careful to replace the stopper and wipe off all liquid from the outside of the bottle When no more air is being expelled from *a*, Fig 116, remove cork *d*, drop the bottle into *b*, quickly replace the cork and then put *f* under the calibrated collecting tube *N B* —If the delivery tube is not of fine capillary bore it must be taken out of the water whilst the bottle is being dropped into the bulb and the cork reinstated , why is this necessary?

Reduce the volume of the collected air to N T P (neglect the water-vapour correction), and thence calculate the density, relative density and molecular weight of the vapour

## CHAPTER XXXIV

### LIQUEFACTION AND THE LIQUID STATE

**The critical state.**—The precise conditions under which a gas can be converted into a liquid were first defined by Andrews in 1869, as a result of a detailed study of the influence of pressure and temperature on the volume of carbon dioxide Andrews' apparatus is shown in Fig 119 The volume of the gas was measured in the strong capillary tube, *a*, in which it was confined by a mercury thread, *c* The lower end of the tube, *b*, opened into water contained in the outer water-tight case of the apparatus By screwing in the plunger at *e* the water was compressed, and pressures up to 400 atmospheres could thus be applied to the gas in the tube The pressure was measured by means of a similar tube, containing air, which was fitted into the same reservoir of water Since $pv$ for air was known accurately over a large range of pressures, the common pressure in the two tubes could be calculated from observations of the volume of the air The upper part of the tube containing the carbon dioxide was surrounded by a bath maintained at a suitable temperature, and a series of observations of $p$ and $v$ at a number of temperatures was made

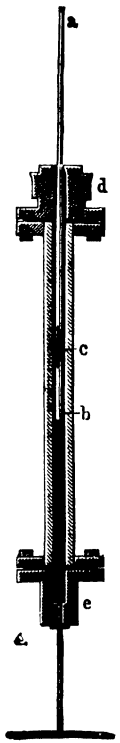



FIG. 119 ANDREWS' APPARATUS FOR DETERMINING THE CRITICAL TEMPERATURE OF GASES

The curves obtained by plotting pressure against volume for a fixed quantity of gas at one temperature are called ISOTHERMS Fig 120 shows a number of isotherms for carbon dioxide For a perfect gas at constant temperature $pv$ is constant and hence the isotherm should be a rectangular hyperbola At 100° carbon dioxide gives the isotherm, $AB$, which has nearly the correct shape At lower temperatures the curve droops below the ideal hyperbola for large values of $p$, and this drooping is more marked the lower the temperature At 31° the isotherm has the form $CDE$ and at $D$ the gas just liquefies

Below 31° the curves are no longer continuous, but exhibit sudden breaks which divide them into three portions. Thus $FG$ represents the

progressive decrease in volume as the gas is compressed at $-50°$. At $G$ a liquid layer separates, and when further compression is attempted the only effect is to convert more of the gas into liquid The pressure therefore remains constant until all the gas has been liquefied and a large contraction in volume has taken place This large change of volume at constant pressure is represented by the horizontal line, $GL$ Then, since liquids are not easily compressed, further contraction in volume is only brought about by the application of high pressures The remainder of this isotherm, $LM$, is therefore a steeply ascending curve

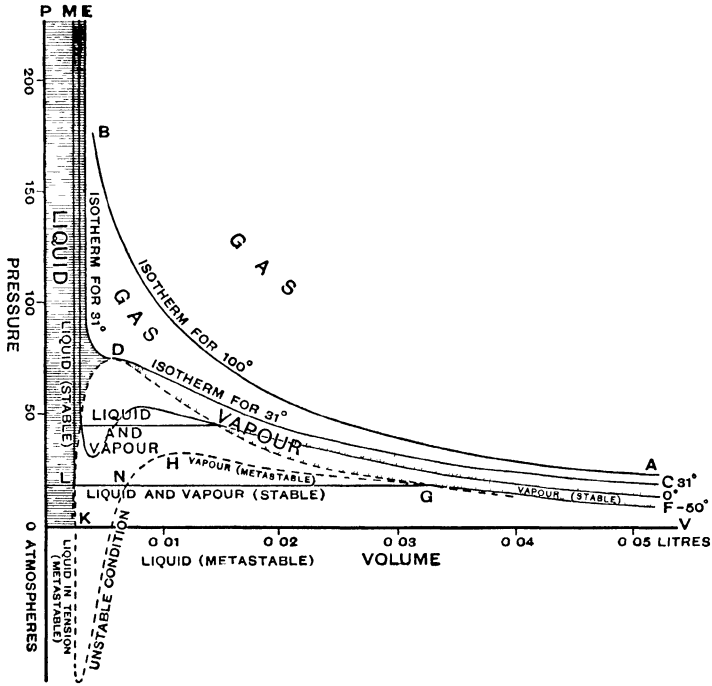



FIG 120 ISOTHERMS FOR CARBON DIOXIDE

Above 31° liquid is never formed, no matter how great the pressure, whilst below this temperature liquid is formed at some definite pressure and the isotherms exhibit a horizontal portion, representing the change from the gaseous to the liquid state At low temperatures the pressure at which liquefaction occurs is low, and the contraction in volume when the gas is liquefied is large As the temperature increases, the pressure at which liquefaction occurs becomes greater At the same time the difference in density (or in molecular volume) of the liquid and its saturated vapour becomes steadily less, mainly because of a progressive increase in the density of the saturated vapour The length of the horizontal portion of the isotherm therefore diminishes steadily as the temperature is

increased Finally, at 31° the length of the horizontal portion of the isotherm is reduced to zero, so that the isotherm is only horizontal for a moment at $D$* The isotherms for higher temperatures, at which no liquefaction takes place, show no horizontal portion

For carbon dioxide, then, 31° is the upper limit of temperature at which the gas can be liquefied by pressure Other gases behave in the same manner, and for each gas there is a specific temperature above which it cannot be liquefied by any pressure however great This temperature is called the CRITICAL TEMPERATURE, the pressure required to cause liquefaction at the critical temperature is called the CRITICAL PRESSURE, and the volume of one gram-molecule of the substance at the critical temperature and pressure is the CRITICAL VOLUME These three critical constants play a very important part in the theoretical discussion of the properties of liquids and gases The constants for some gases which have been studied accurately are therefore given in Table 40, in which the critical temperature, pressure and volume are indicated by the symbols $T_c$, $P_c$, and $V_c$

TABLE 40 —CRITICAL CONSTANTS

| Substance | $T_c$ ° C | $P_c$ atm | $V_c$ litres | $\frac{RT_c}{P_cV_c}$ |
|---|---|---|---|---|
| Helium | −268° | 2 26 | 0 061 | 3 04 |
| Hydrogen | −241° | 13 4 | 0 061 | 3 21 |
| Nitrogen | −146° | 34 | 0 087 | 3 52 |
| Oxygen | −118° | 50 | 0 074 | 3 44 |
| Carbon dioxide | +31° | 73 | 0 096 | 3 56 |
| *n*-Pentane | 197° | 33 | 0 310 | 3 77 |
| Carbon tetrachloride | 283° | 45 | 0 276 | 3 67 |
| Benzene | 288° | 48 | 0 256 | 3 75 |
| Chlorobenzene | 359° | 45 | 0 308 | 3 75 |
| Methyl alcohol | 240° | 78 | 0 117 | 4 61 |
| Water | 374° | 218 | 0 056 | 4 35 |
| Acetic acid | 322° | 57 | 0 171 | 5 01 |

**Determination of critical constants.**—(*a*) *Critical temperature* —An approximate value for the critical temperature can be found by sealing up a quantity of liquid and vapour in a strong glass tube and heating it in a suitable bath At the critical temperature the surface between liquid and vapour flickers and disappears If the tube is then cooled again to the critical temperature, a turbidity appears in the gas, which is quickly dispersed by the settling of liquid to the bottom of the tube and the reappearance of the meniscus (Expt 91)

(*b*) *Critical pressure* —The critical pressure may also be determined by a modification of this experiment due to Cagniard de la Tour, in which the liquid occupies one limb of a strong closed U-tube (Fig 121), and is

* At this point, a horizontal line would form an " osculating tangent " to the curve, *i e* it would pass through *three* consecutive points on the curve at $D$, just in the same way as an ordinary tangent passes through *two* consecutive points

separated from a quantity of air in the other limb by a column of mercury From observations of the volume of the air in the left-hand limb when the critical temperature is reached, the pressure within the tube (*i e* the critical pressure) can be calculated

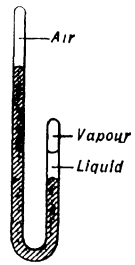



FIG 121 APPARATUS FOR MEASURING CRITICAL PRESSURE

(*c*) *Critical volume* —The accurate determination of the critical volume is a much more difficult matter, since at the critical temperature a small change in pressure causes a large change in volume The best method of determining this constant is due to Amagat It makes use of the fact that the mean of the densities of the liquid and of its saturated vapour varies much less rapidly than the individual values of these two densities The experimental method depends, therefore, on measuring the densities of liquid and vapour at a series of temperatures approaching the critical temperature, and plotting these two densities against the temperature

Amagat found that when lines were drawn connecting the points which represent the density of liquid and vapour at the same temperature, the middle points usually fell on a straight line, which was termed by Amagat the RECTILINEAR DIAMETER of the curve By extending this line to the critical temperature, and reading off the corresponding value of the density, the critical density and therefore the critical volume can be determined

In Fig 122 the densities of the liquid and vapour of *n*-pentane are plotted against the temperature The left-hand branch, *AC*, of the curve shows the density of the saturated vapour, which increases as the temperature rises The right-hand branch, *BC*, shows the decrease in the density of the liquid as the critical point is approached The two curves meet at the critical point, since the liquid and its saturated vapour then become identical in all respects, and must, therefore, have the same CRITICAL DENSITY This critical density is given by the intersection of the rectilinear diameter, *DC*, with the continuous curve, *ACB*, or, more simply, by extrapolating the rectilinear diameter to the known critical temperature of the substance

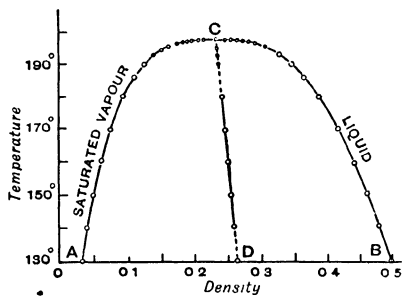



FIG 122 DIAGRAM TO ILLUSTRATE THE DETERMINATION OF CRITICAL VOLUMES

**Identity of the liquid and gaseous states at the critical temperature.**— At the critical temperature, the density of the liquid becomes the same as that of the saturated vapour All the other properties that can be examined in the two states also become identical at the same point We can

therefore assert that *at the critical temperature the liquid and vapour become identical in all respects*

One characteristic property of a liquid is its surface tension (Ch XXXV, p. 486) This property tends to diminish the free surface of a liquid, and therefore to draw the liquid together into round drops It also causes the liquid to rise in a capillary tube which is wetted by the liquid, or to be depressed if (like mercury) it does not wet the tube Since the surface tension of a liquid decreases as the temperature rises, the " meniscus " or curved surface of the liquid gets flatter and flatter as the temperature is raised Moreover, since very little work has to be done in increasing the surface between the two layers, the boundary becomes unsteady and irregular as the critical temperature is approached Finally, when the critical temperature is reached, the surface tension becomes zero, and the meniscus which forms the boundary between liquid and vapour disappears completely

**Continuity of liquid and gaseous states.**—In the series of changes described above, liquid and vapour both pass at the critical temperature into a permanent gas, which cannot be liquefied by pressure alone In this process they become identical, but without any abrupt change in the properties either of the liquid or of the vapour It is therefore possible, by making use of a suitable series of changes, to convert a liquid entirely into vapour or vice versa, *without any separation into two layers or any discontinuity in physical properties*

Thus, suppose we have liquid carbon dioxide at $-50^\circ$ and 230 atmospheres (point $M$ in Fig 120, p 471) This material is undoubtedly in the liquid state, for if we lower the pressure to about 20 atmospheres without altering the temperature, a layer of vapour begins to separate from it at the point represented by $L$ If, however, we keep the pressure constant at 230 atmospheres and raise the temperature to $100^\circ$ C , the resulting change must be represented by a horizontal movement on the diagram from $M$ to a point on the prolongation of the curve $AB$ This change of conditions, therefore, produces an increase of volume, but it is not accompanied by any abrupt change in any of the physical properties of the material If, however, the pressure is now lowered, after increasing the temperature to $100^\circ$ C , the substance expands continuously along $BA$ and at $A$ is found to have all the properties of gaseous carbon dioxide We have, therefore, converted a liquid into a gas without at any stage producing an abrupt alteration of properties, or causing the material to separate into two distinct layers Obviously, by reversing these processes, we could convert a gas into a liquid in such a way that it would be impossible to detect at what point (if any) the material had changed from one state to the other

This phenomenon is described as CONTINUITY OF STATE In practice, we generally describe as VAPOUR any gas which can be liquefied by pressure alone, without lowering the temperature Gases which cannot be so liquefied are described as PERMANENT GASES We can, therefore, say that at $31^\circ$ the *liquid* and *vapour* of carbon dioxide both become *gas*, and that whilst the change from liquid to vapour is always abrupt (except at the critical temperature), there is no physical change involved in the con-

version of liquid or vapour into gas on raising the temperature through the critical point, or in the conversion of gas into liquid or vapour on cooling the material through the critical point This distinction is illustrated in Fig 120 by dividing the diagram into areas labelled " gas," " vapour," " liquid," and " liquid and vapour "

**Isotherms of van der Waals' equation.**—In an earlier section it was pointed out that the isotherms deduced from the simple gas equation $pV=RT$ are rectangular hyperbolas, *i e* when $p$ is plotted against $V$ for a number of different temperatures a series of rectangular hyperbolas is obtained The experimental isotherms for carbon dioxide (Fig 120) and other gases are of this form when the temperature is well above the critical temperature, but diverge considerably at lower temperatures It is therefore of interest to consider whether the isotherms derived from van der Waals' equation agree more closely with the experimental values If we rearrange van der Waals' equation thus

$$\left(p+\frac{a}{V^2}\right)(V-b)-RT=0, \qquad (1)$$

and divide by $p$ after multiplying out the factors, we obtain a cubic equation in $V$

$$V^3-\left(\frac{RT}{p}+b\right)V^2+\frac{aV}{p}-\frac{ab}{p}=0 \qquad (2)$$

When $a$, $b$, and $T$ have suitable values, this equation gives the type of isotherm shown by the dotted curve, $MLKJNHGF$, in Fig 120 This differs from the experimental isotherm in that there is no sudden break at $L$ or $G$, where layers of liquid and vapour are normally formed, *i e* it predicts that the change from vapour to liquid, or conversely, is a continuous process and, more remarkable still, that for a given pressure the volume can have three different values as represented by the points $L$, $N$, $G$ Parts of the theoretical loop, $LKJNHG$, can be realised experimentally as follows

(i) When a saturated vapour which is free from dust particles is cooled, it does not at once deposit liquid, since the moisture can persist, at least for a short time, in the form of a SUPERSATURATED VAPOUR If, however, nuclei of dust, etc , are present, liquid forms and the pressure drops to the vapour pressure Since the pressure of the supersaturated vapour is greater than that at which condensation normally occurs at the temperature produced by cooling, this precarious condition, although actually produced by a change of temperature, *i e* by a transference from one isothermal to another, is similar to that which would be produced by an extension of the isothermal beyond $G$ towards $H$

(ii) Conversely, a liquid does not always begin to boil as soon as the normal boiling-point is reached, but may rise to a higher temperature as a SUPERHEATED LIQUID The introduction of a piece of porous material charged with air, however, leads at once to the formation of bubbles of vapour, and the temperature falls to the normal boiling-point Since the atmospheric pressure is less than the normal vapour-pressure of the liquid when superheated, this phenomenon may be compared with the condition

which would be produced by a prolongation of the isothermal in the direction of lower vapour-pressures from $L$ towards $J$

(iii) A liquid can persist not only (along $LK$) at pressures less than its normal vapour-pressure, but also (along $KJ$) under negative pressures The condition of a LIQUID UNDER TENSION is sometimes realised when a long barometer tube filled with mercury is inverted over mercury, since the mercury sometimes clings to the tube and does not fall to the normal barometric height until it is tapped

(iv) The region $JH$ represents an unstable condition, in which pressure and volume increase together, and has never been realised experimentally

**Application of van der Waals' equation to critical phenomena.**—Since van der Waals' equation is a cubic equation, it can have three roots, *i e* a given value of $p$ may correspond to three values of $V$, as at the points $L$, $N$ and $G$ of Fig 120 If $a$ and $b$ are fixed, then for low values of $T$ the loops, $LJN$ and $NHG$ (which should be equal in area), are large and the three values of $V$ differ widely from one another As $T$ becomes larger the loops become smaller , and finally there is one particular value of $T$ at which the loops just vanish, and the three values of $V$ become identical For still higher values of $T$ there is only one real root of the equation , the other two values of $V$ are " imaginary " and have no physical significance

This feature of the theoretical isotherms of van der Waals' equation corresponds closely to the change in the form of Andrews' experimental isotherms as the temperature rises, when the horizontal portion $LG$ of the isotherms becomes shorter and shorter at higher temperatures and vanishes when the critical temperature is reached Obviously the CRITICAL ISOTHERM is the one which for a particular value of $p$, namely, the critical pressure $P_c$, gives three equal values of $V$, all equal to the critical volume $V_c$ Expressed algebraically, this means that at the critical point van der Waals' equation (1) must become identical with the particular solution represented by equation (3),

$$(V - V_c)^3 = 0 \tag{3}$$

For the purpose of comparing the two equations, we must expand equation (3), as in (4),

$$V^3 - 3V_c V^2 + 3V_c^2 V - V_c^3 = 0 \tag{4}$$

We must also insert the special values $T = T_c$ and $p = P_c$, in the expanded form (2) of van der Waals' equation, which then assumes the form,

$$V^3 - \left(\frac{RT_c}{P_c} + b\right) V^2 + \frac{aV}{P_c} - \frac{ab}{P_c} = 0 \tag{5}$$

We can now equate the coefficients of each power of $V$ in equations (4) and (5), and so deduce the following relations

Equating the coefficients of $V^2$

$$3V_c = \frac{RT_c}{P_c} + b \tag{6}$$

Equating the coefficients of $V$

$$3V_c^2 = \frac{a}{P_c}. \tag{7}$$

Equating the coefficients of the terms not containing $V$:

$$V_c^3 = \frac{ab}{P_c} \tag{8}$$

From these three equations the values of the critical constants in terms of $a$ and $b$ can be deduced as follows

(i) Dividing (8) by (7),

$$V_c = 3b, \tag{9}$$

*i e* the *critical volume* is equal to $3b$, or conversely, van der Waals' constant $b$ is 1/3 of the critical volume

(ii) Substituting this value of $V_c$ in (7), we find that we can express the *critical pressure* in terms of the two constants of van der Waals' equation as follows

$$P_c = \frac{a}{27b^2} \tag{10}$$

(iii) Finally, by substituting for $P_c$ and $V_c$ in (6), it is found that the *critical temperature* is given by the expression

$$T_c = \frac{8a}{27Rb} \tag{11}$$

Hence, if $a$ and $b$ are determined from measurements on compressed gases, they can be used to predict the critical constants The converse process can also be used in order to deduce the values of $a$ and $b$ from the critical constants as measured experimentally Thus, from (9), (10) and (11), it is readily shown that

$$b = \tfrac{1}{3} V_c = \frac{RT_c}{8P_c}$$

and

$$a = 3P_c V_c^2 = \frac{9RV_cT_c}{8} = \frac{27R^2T_c^2}{64P_c} \tag{12}$$

**Van der Waals' equation not numerically exact.**—An important general relation is revealed when the values of the critical constants given by equations (9), (10) and (11) are used to calculate the ratio $RT_c/P_cV_c$, thus

$$\frac{RT_c}{P_cV_c} = \frac{R \times 8a \times 27b^2}{27Rb \times 3b \times a} = \frac{8}{3} = 2\ 67$$

If, therefore, van der Waals' equation gives a true representation of the transition from the liquid to the gaseous state, this ratio should be constant for all substances and should have the value 2 67 It will be seen from the last column of Table 40 (p 472) that this ratio is nearly constant for many substances, but that it usually has a value 3 7, which is much larger than the figure predicted by van der Waals' equation There are two groups of substances which give abnormal values The ratio for hydrogen and helium is lower, but it is difficult to determine the value of $V_c$ for these substances Water, the alcohols, and acetic acid all give values higher than 3 7 They all belong to the group of " associated " liquids (Chap XXXVIII, p 525), and high values for the ratio $RT_c/P_cV_c$ are probably characteristic of this group

**The principle of corresponding states.**—It has been found experimentally that, in the neighbourhood of the critical point, all gases give the same type of isotherm as carbon dioxide The actual position of the critical isotherm varies with the critical constants of the gases studied, but the similarity is great enough to suggest that, if we could choose suitable scales of pressure, temperature and volume for each different gas, we could superimpose all the critical isotherms on one another If this were done for the critical isotherms, it is probable that all the other isotherms would coincide We should then have one isothermal diagram, and one fundamental equation, for all gases

The scale which immediately suggests itself is one in which the pressure, temperature and volume are expressed as fractions of the critical pressure, temperature and volume If we write

$$\pi = \frac{p}{P_c}, \quad \phi = \frac{V}{V_c} \quad \text{and} \quad \theta = \frac{T}{T_c},$$

then $\pi$, $\phi$ and $\theta$ are termed the REDUCED PRESSURE, the REDUCED VOLUME and the REDUCED TEMPERATURE respectively If now we replace $p$, $V$ and $T$ in van der Waals' equation by $\pi P_c$, $\phi V_c$ and $\theta T_c$, we have

$$\left(\pi P_c + \frac{a}{\phi^2 V_c^2}\right)(\phi V_c - b) = R\theta T_c$$

Expressing $P_c$, $V_c$ and $T_c$ by the functions of $a$ and $b$ given in equations (9), (10) and (11), we have

$$\left(\frac{\pi a}{27b^2} + \frac{a}{\phi^2 9b^2}\right)(3b\phi - b) = \frac{8aR\theta}{27Rb},$$

which reduces to

$$\left(\pi + \frac{3}{\phi^2}\right)(3\phi - 1) = 8\theta \quad . \quad . \quad (13)$$

This is the fundamental equation we are seeking The quantities $a$ and $b$, $P_c$, $T_c$, $V_c$, which are characteristic for any given gas, have all cancelled out, and equation (13) should predict the form of the isotherms for any gas whatsoever Thus if we take any two substances at the same reduced pressure and the same reduced temperature, they should have the same reduced volume The data in Table 41 show that this is nearly true for many substances with respect to the volume in the liquid state and in the state of saturated vapour

TABLE 41 —CORRESPONDING STATES

$\pi = 0\ 08846 \quad \theta = 0\ 73$

| Substance | $\phi$ (liquid) | $\phi$ (vapour) |
|---|---|---|
| Benzene - - - - | 0 4065 | 28 3 |
| *iso*-Pentane - - - | 0 4085 | 27 7 |
| *n*-Pentane - - - | 0 4061 | 28 4 |
| *n*-Hexane - - - | 0 4055 | 29 1 |
| Chlorobenzene - - - | 0 4028 | 28 5 |
| Ether - - - - | 0 4030 | 28 3 |

When two substances are at the same reduced temperature and the same reduced pressure they are said to be in CORRESPONDING STATES It is obvious that if we wish to make comparisons between physical properties which are altered by changes in pressure or temperature, the comparison should be made when the substances are in corresponding states When a property of a liquid or solid is concerned, pressure has usually little effect, and it is sufficient to use corresponding temperatures As an approximation, liquids at their boiling-points are roughly at corresponding temperatures, since it has been found that the boiling-point on the *absolute* scale of temperature of a liquid under a pressure of 760 mm is approximately 2/3 of the critical temperature (Table 42)

TABLE 42 —BOILING-POINTS AND CRITICAL TEMPERATURES

| Substance | Boiling-point $T_b$ | Critical temperature $T_c$ | $T_b/T_c$ |
|---|---|---|---|
| Benzene - - | 353° | 561° | 0 629 |
| *iso*-Pentane - | 303° | 468° | 0 647 |
| *n*-Pentane - | 313° | 470° | 0 666 |
| *n*-Hexane - | 342° | 508° | 0 673 |
| Chlorobenzene | 405° | 632° | 0 641 |
| Ether - - | 308° | 467° | 0 661 |

**Limitations of van der Waals' equation** —Whilst van der Waals' equation accounts qualitatively (and approximately quantitatively) for the pressure-volume-temperature relations of gases and liquids, it does not predict accurately the form of the isotherms At temperatures above the critical temperature and for moderate pressures, there is good agreement between the observed and theoretical curves At lower temperatures and higher pressures, van der Waals' curves differ appreciably from the observed curves, though they have the right shape Further, the law of corresponding states only holds approximately (Table 41), and the experimental values of the ratio $RT_c/P_cV_c$ are much higher than the value 2 67 predicted by van der Waals' equation (Table 40) These and other similar discrepancies show that van der Waals' equation, whilst it is a great advance on the simple gas laws, gives only an approximate account of the behaviour of liquids and gases

**The liquefaction of gases.**—Faraday in 1823 liquefied chlorine, sulphur dioxide, carbon dioxide, cyanogen, ammonia, and hydrogen chloride by preparing the gas at one end of a bent sealed tube (Fig 84, p 277), and cooling the other end in a freezing mixture

At the present time gases are liquefied by making use of the cooling effect produced either

(*a*) By adiabatic expansion against the internal attraction of the molecules whereby the gas does internal work, or

(*b*) By expansion in an engine in which the gas does external work

(*a*) In the first method an underperfect gas is compressed and allowed to cool again , the compressed gas then escapes from a jet into a chamber

in which the pressure is small when compared with the initial pressure During the expansion the molecules of the gas do internal work in overcoming their attraction for one another Since the expansion is adiabatic (*i e* no heat leaves or enters the system), this work is done at the expense of the kinetic energy, $E$, of the molecules, and hence the temperature of the gas falls ($T=\frac{1}{3}E$, p 458) Now gases such as air, nitrogen and carbon dioxide are underperfect (except at high pressures, Fig 112), *i e* the value of $pV$ decreases as the pressure is raised Hence, when a volume $V_1$ of one of these gases is forced through a porous plug under a pressure $p_1$, and allowed to expand freely to a volume $V_2$, under a smaller pressure $p_2$, it follows that the work done on the gas (viz $p_1V_1$) in forcing it through the plug is less than that which the gas does (viz $p_2V_2$) in expanding on the other side This extra work, $p_2V_2-p_1V_1$, is also done at the expense of the kinetic energy of the gas molecules, and although it is smaller than the internal work that is done against intermolecular attraction, it nevertheless enhances the fall in temperature

Hydrogen, however, differs from most other gases in that its molecules exert a relatively small attraction for one another at room temperatures Thus, the value of $pV$ increases with pressure because the volume, $b$, occupied by the molecules has a greater effect than the intermolecular forces, *i e* on expansion from $p_1$ to $p_2$ the value of $p_1V_1$ is greater than the value of $p_2V_2$, so that more work is done on the gas in forcing it through the porous plug than is done by the gas in expanding on the other side of the plug The net work thus done on the gas, viz $p_1V_1-p_2V_2$, is actually greater than the *internal* work done by the molecules in overcoming the intermolecular attraction, hence there is a net increase in the kinetic energy of the molecules, and in consequence the temperature rises At lower temperatures, however, hydrogen behaves as an underperfect gas and is cooled by free expansion

The cooling produced by the free expansion of a gas is known as the JOULE-THOMSON EFFECT, its magnitude for some gases is shown below

TABLE 43 —COOLING OF GASES BY EXPANSION AT 0° C

| | | | |
|---|---|---|---|
| Carbon dioxide | 1 46° per atm | Nitrogen | 0 31° per atm |
| Oxygen | 0 326° ,, | Hydrogen | −0 03° ,, |

The cooling of the underperfect gases per atmosphere of expansion is greater for the easily liquefied gas, carbon dioxide, than for nitrogen and oxygen, which are much more difficult to liquefy The cooling at ordinary temperatures is not large, *e g* it amounts only to 12° for air at 20° when the pressure falls from 50 atmospheres to 1 atmosphere, but it becomes larger at lower temperatures, so that by arranging a continuous circulation of the gas, lower and lower temperatures can be obtained until liquid air is produced

Liquid air is now manufactured on a large scale by means of an apparatus based on this principle and devised by Linde and Hampson, Fig 123 In the Hampson process, air is first freed from carbon dioxide by the action of lime in a "low-pressure purifier" and then compressed to about 200 atmospheres, cooled by jackets of cold water, separated from condensed water, and freed from the last traces of carbon dioxide by

passing over potash in a "high pressure purifier" The purified compressed gas enters through $P'$ and flows through the innermost of two concentric copper tubes, until it reaches the jet $N$, where it expands and is cooled The cooled gas now circulates through the outer tube, $P$, thus cooling the incoming compressed gas, which is still further cooled by expansion The cooling is thus progressive, and finally the air escaping from the nozzle $N$ is obtained as a liquid The whole apparatus is very carefully "lagged" in order to minimise the inflow of heat from surrounding bodies, and the liquid air is stored and handled in vacuum-jacketed vessels

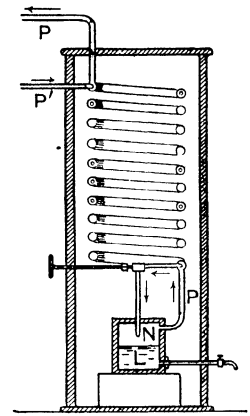



FIG 123 APPARATUS FOR LIQUEFACTION OF AIR BY ADIABATIC EXPANSION

(*b*) In the Claude process, for which a higher efficiency is claimed, purified air, compressed to 40 atmospheres, is cooled to $-140°$ by allowing it to perform external work in an expansion engine, which is coupled up to assist in driving the compressor The cold gases escaping from the engine are used to liquefy some of the compressed air, the boiling-point of which under 40 atmospheres is about $-140°$ The liquid air is then released from 40 atmospheres to atmospheric pressure, and the cold gases which escape are utilised to cool more compressed air

**Vapour-pressure** — Many liquids evaporate when exposed to the air, and are converted into vapour Marked differences are observed between different liquids with respect to this property Thus ether evaporates at the ordinary temperature much more rapidly than water, whilst mercury does not evaporate to any appreciable extent If the evaporation takes place into a closed space, it is found that evaporation at a given temperature ceases when the space contains a definite pressure of vapour If the liquid is allowed to evaporate into the vacuum above a barometer, as in Expt 93, the vapour-pressure can be measured by comparing the height of the mercury in the tube containing vapour with the height of the barometer

It will be remembered that Andrews found, when compressing a vapour at a constant temperature below the critical temperature, that liquid appeared at a definite pressure, and that, when further compression was attempted, the pressure remained constant until all the vapour was converted into liquid This pressure, corresponding to the horizontal portion of the isotherms in Fig 112 (p 461), is the VAPOUR-PRESSURE of the liquid

The existence of a definite vapour-pressure is readily accounted for by the kinetic theory In a liquid, the molecules are held together by their mutual attraction, and their movements are much more restricted than in a vapour At the surface of the liquid this attraction tends to pull the molecules inwards, and is sufficiently strong to prevent most of them from escaping as gas A few molecules, however, which have acquired by

collision a velocity greater than the average, will approach the surface at such a speed that they are able to overcome the attractive force and to escape into the space above the liquid

As molecules of vapour accumulate in this space, some of them will begin to strike the surface of the liquid and be recaptured The number which return in this manner will obviously depend on the concentration of molecules in the vapour, *i e* on its pressure The process will go on until an equilibrium is reached at which in a given time each unit of area of the liquid surface loses as many molecules by evaporation as it gains by recapturing molecules from the vapour The pressure at which this occurs is the vapour-pressure, and is thus the pressure of a vapour in equilibrium with the liquid Vapour at this pressure is often referred to as SATURATED VAPOUR, whilst when the pressure is less it is described as UNSATURATED VAPOUR

As the temperature rises, the molecules move more swiftly, and the number which have a sufficient velocity to escape from the surface increases rapidly Hence the vapour-pressure becomes greater at higher temperatures Thus the vapour-pressures of water and of chlorobenzene are found to increase between 0° and 100° in the manner shown in Table 44

TABLE 44 —VAPOUR-PRESSURES OF WATER AND OF CHLOROBENZENE

| *t* | Vapour-pressures in mm Hg | | *t* | Vapour-pressures in mm Hg | |
|---|---|---|---|---|---|
| | Chlorobenzene | Water | | Chlorobenzene | Water |
| 0 | 2 6 | 4 6 | 60 | 64 8 | 149 5 |
| 10 | 4 9 | 9 2 | 70 | 98 2 | 233 8 |
| 20 | 8 8 | 17 5 | 80 | 144 9 | 355 5 |
| 30 | 15 4 | 31 8 | 90 | 208 4 | 526 0 |
| 40 | 25 7 | 55 3 | 100 | 292 8 | 760 0 |
| 50 | 41 5 | 92 5 | | | |

When the vapour-pressure becomes equal to the atmospheric pressure, vapour is also produced by the formation of bubbles within the liquid itself, and the liquid is then said to boil The BOILING-POINT of a liquid is therefore the temperature at which the vapour-pressure is equal to the atmospheric pressure. If the pressure above a liquid is reduced it will boil at a lower temperature Distillation under reduced pressure is therefore often used in order to purify substances which would decompose if distilled under atmospheric pressure, and consequently at a higher temperature

EXPT 92. **Observation of critical phenomena**

Select a piece of soft glass tube about 15 cm long and 3-4 mm internal diameter. Seal and round off one end, taking care that the rounded end has even walls of the same thickness as the tube Make a constriction about 5 cm from the open end of the tube. Fill to above the constriction with ether and fit a short length of rubber tubing, closed by a spring clip, on to

the open end of the glass tube (Fig 124) Heat the lower part of the tube in a beaker of hot water so that the ether boils away gently When the space below the constriction is rather more than half full of ether, close the clip, and seal off the glass tube at the constriction in a small blow-pipe flame In this way a glass tube of sufficient strength containing only ether and its vapour is obtained

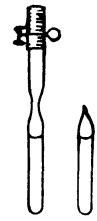


FIG 124 APPARATUS FOR OBSERVING CRITICAL PHENOMENA

Support the tube vertically in a wire holder behind a glass screen and heat it gently by brushing a Bunsen flame up and down it Note how the meniscus flattens as the temperature rises, and disappears suddenly when the critical temperature is reached Allow to cool When the temperature falls below the critical temperature, a cloud of mist suddenly appears in the tube, and rapidly settles to form a liquid layer

EXPT 93 **Measurement of vapour-pressure Barometric method**

Fill four barometer tubes, about a metre long, with mercury, and invert in a bath of mercury The first tube is left empty to act as a barometer By means of bent pipettes, introduce about 1 c c of water, alcohol, and ether respectively into the remaining tubes After a minute or two, measure by means of a cathetometer the difference in level between the mercury in the first tube and in the other tubes The lowering of the mercury surface below the level at which it stands in the first tube gives the vapour-pressure of the liquid

**Physical properties and chemical constitution.**—One of the objects of physical chemistry is to trace the relationship between the physical properties of substances and the composition and structure of their molecules Thus, when the laws governing the magnitude of a given property have been determined, we can not only predict the properties of new compounds of given structure, but may also be able to decide which of two possible constitutional formulae should be ascribed to a particular compound of doubtful structure From this point of view three types of physical property are usually distinguished

(1) **Colligative properties** are those which are determined only by the *number of molecules* present, and are independent of their nature An example of this type of property is the volume of a gas (at N T P ), which is fixed within very narrow limits by the number of molecules present per unit volume, whatever their mass or chemical properties

(2) **Additive properties** are those which are determined only by the *nature and number of the atoms* (or radicals) in the molecule, and not by the way in which they are arranged or united together Thus, the mass of a molecule is strictly additive, since (in accordance with the law of conservation of mass) it can be predicted accurately by adding together the masses of its constituent atoms Many other physical properties which are roughly additive (*e g* molecular volume) are affected to some extent

by changes in chemical constitution, and therefore belong strictly to the third group of properties

(3) **Constitutive properties** are those which depend on the arrangement as well as on the number of the atoms in the molecule These properties are affected profoundly by changes in chemical constitution, and are of special value in the study of molecular structure As examples of this type of property we may take (i) *absorption spectra*, which depend almost entirely on the nature of the bonds by which the atoms are united, (ii) *optical rotatory power*, which depends on a dissymmetric arrangement of the atoms, and (iii) *refractivity*, which depends on the number and nature of the atoms in the molecule, but also on the character of the bonds between them

**Influence of pressure and temperature on physical properties.**—Most physical properties are altered by changes in pressure and temperature In the case of gases, *pressure* is of great importance , but when liquids or solids are considered, the effect of pressure is small and can generally be neglected The effect of *temperature* has, however, to be allowed for, even in the case of liquids and solids, before the physical properties of a number of substances can be compared fairly with one another Two methods are usually employed

(i) The first is to measure the physical property which is to be studied at corresponding temperatures, *i e* at temperatures which are equal fractions of the critical temperatures (p 478) of the liquids under investigation This is, in effect, the method used by Kopp in the study of molecular volumes (see below)

(ii) The second method consists in finding a function of the property studied which does not vary with temperature This constant can then be used in comparing the magnitude of the property in different compounds An example of this method will be found in the parachor (p 487)

**Molecular volumes.**—The MOLECULAR VOLUME is *the volume in cubic centimetres occupied by one gram-molecule of a substance* It is obtained by dividing the molecular weight by the density, and is therefore defined by the relation

$$V = \frac{M}{D}.$$

Since liquids expand on heating, the molecular volume varies with the temperature and a standard temperature must be chosen Kopp, who discussed the subject in 1855, suggested that the boiling-point was a natural temperature for comparison , and by comparing molecular volumes *at the boiling-point* he discovered many regularities If these boiling-points had been determined at equal fractions of the critical pressures of the liquids, instead of at atmospheric pressure, Kopp's method would have given a comparison of the molecular volumes of the liquids in corresponding states (p 478) Since, however, the boiling-points at atmospheric pressure are *approximately* equal fractions of the critical temperatures, Kopp's method can be regarded as a practical approximation to this ideal condition

The molecular volumes of the members of a homologous series at their boiling-points were shown by Kopp to differ by a nearly constant

increment for the addition of each $CH_2$ group This is illustrated in Table 45

TABLE 45 —MOLECULAR VOLUMES AT THE BOILING-POINT

| Substance | Formula | Molecular Volume | Difference |
|---|---|---|---|
| Methyl iodide - - | $CH_3I$ | 64 1 | 21 6 |
| Ethyl ,, - - - | $C_2H_5I$ | 85 7 | 21 1 |
| Propyl ,, - - - | $C_3H_7I$ | 106 8 | 21 7 |
| Butyl ,, - - - | $C_4H_9I$ | 128 5 | |
| Methyl ethyl ether - | $C_3H_8O$ | 84 0 | 22 1 |
| Diethyl ,, - | $C_4H_{10}O$ | 106 1 | 21 7 |
| Ethyl propyl ,, - | $C_5H_{12}O$ | 127 8 | 22 3 |
| ,, butyl ,, - | $C_6H_{14}O$ | 150 1 | |
| Methyl formate - - | $C_2H_4O_2$ | 62 7 | 21 9 |
| Ethyl ,, - - | $C_3H_6O_2$ | 84 6 | 21 6 |
| Propyl ,, - - | $C_4H_8O_2$ | 106 2 | 21 4 |
| Butyl ,, - - | $C_5H_{10}O_2$ | 127 6 | |

From a large number of these differences Kopp deduced an average value of 22 0 c c for an increment of $CH_2$ Since the molecular volumes of butane, $C_4H_{10}$, and of benzene, $C_6H_6$, were equal, Kopp assumed that the volume of the carbon atom was twice that of the hydrogen atom, from which it follows that $C = 2H = 11$, $H = 5\ 5$ By using these values, atomic volumes can be calculated for other elements Thus methyl ethyl ether, $C_3H_8O$, gives $V = 84\ 0$ Subtracting

$$3C + 8H = 33 + 44 = 77,$$

we find that the oxygen atom in this compound has an atomic volume of $84 - 77 = 7$ units Working in this way Kopp compiled the list of atomic and structural constants which is set out in Table 46 below

TABLE 46.—KOPP'S ATOMIC VOLUMES

| | | |
|---|---|---|
| C = 11 0 | Cl = 22 8 | O′ in OH |
| H = 5 5 | Br = 27 8 | or in ethers = 7 8 |
| | I = 37 5 | O″ in >CO = 12 2 |

These numbers may be used to predict molecular volumes, as follows ·

| Propyl iodide, $C_3H_7I$ | | Acetic acid, $C_2H_4O''O'$ | |
|---|---|---|---|
| 3C = | 33 0 | 2C = | 22 0 |
| 7H = | 38 5 | 4H = | 22 0 |
| I = | 37 5 | O'' = | 12 2 |
| | | O' = | 7 8 |
| $V$(calc) = | 109 0 c c | $V$(calc) = | 64 0 c c |
| $V$(obs) = | 106 8 c c | $V$(obs) = | 63 5 c c |

It will be seen that the relation is not strictly additive, since different values are assigned to oxygen when singly linked and when doubly linked to carbon Moreover, investigation has shown that the molecular volume of a compound is affected by other constitutional factors Thus, if it were a strictly additive property, isomeric substances would have identical values of $V$, but Table 47 shows that there are considerable deviations from this rule, and that the structure of the molecule does influence the value of the molecular volume Molecular volumes are therefore roughly "additive," but are affected appreciably by "constitutive" factors

TABLE 47 —MOLECULAR VOLUMES OF ISOMERS

| Substance | Formula | Molecular volume |
|---|---|---|
| Acetaldehyde | $C_2H_4O$ | 56 9 |
| Ethylene oxide | ,, | 52 4 |
| Allyl alcohol | $C_3H_6O$ | 74 2 |
| Acetone | ,, | 76 8 |
| Propyl alcohol | $C_3H_8O$ | 81 3 |
| Methyl ethyl ether | ,, | 84 0 |
| Anisole | $C_7H_8O$ | 125 2 |
| *o*-Cresol | ,, | 121 5 |

**Surface tension and molecular volume.**—The irregularities found in the study of molecular volumes at the boiling-point can be ascribed to three causes.

(i) Boiling-points are not exactly corresponding temperatures (cf. Table 42, p 479)

(ii) The attraction between the molecules gives rise to a large internal pressure which is not the same for all liquids, even at corresponding temperatures , the unequal compression of the molecules under these unequal internal pressures will therefore introduce irregularities into the molecular volumes

(iii) Kopp's method of calculating the atomic volumes of carbon and hydrogen ignores the structural differences between $C_4H_{10}$ and $C_6H_6$, and therefore gives erroneous values

A method of comparing molecular volumes, in which allowance is made for the effect of internal pressure, has been worked out by Sugden This depends on using MacLeod's relation between the surface tension $\gamma$ of a liquid and the densities $D$ and $d$ of the liquid and vapour Since

$$\gamma = C(D-d)^4, \quad \ldots\ldots\ldots\ldots \quad \ldots \quad (1)$$

it follows that $C^{\frac{1}{4}} = \gamma^{\frac{1}{4}} - (D - d)$ is constant and therefore that the quantity,

$$[P] = \frac{M}{D - d}\gamma^{\frac{1}{4}} = MC^{\frac{1}{4}} \qquad \ldots\ldots\ldots\ldots\ldots\ldots (2)$$

(where $M$ is the molecular weight), will be constant over the range of temperatures within which MacLeod's relationship is valid Since $d$ is small compared with $D$, $[P]$ is practically equal to the molecular volume, multiplied by the fourth root of the surface tension, so that if two liquids are examined under such conditions that their surface tensions are equal, their molecular volumes will be proportional to the values of the constant $[P]$ The constant $[P]$ is therefore a measure of the *molecular volume at temperatures at which different liquids have the same surface tension* This constant is named the PARACHOR (from $\pi\alpha\rho\acute{\alpha}$ = by the side of, and $\chi\acute{\omega}\rho\alpha$ = space), signifying comparative volume

**Atomic and molecular parachors.**—The parachor is an additive property, *i e* the value for a given molecule can be calculated as the *sum* of a series of atomic and structural constants The atomic parachors for carbon and hydrogen, which are of fundamental importance in the study of organic compounds, can be deduced from the " molecular parachors " of a series of paraffin hydrocarbons, as given in Table 48

TABLE 48.—PARACHORS OF THE PARAFFINS

| | $[P]$ obs | Diff | $39n$ | 2H |
|---|---|---|---|---|
| $C_2H_6$ | 110 5 | | 78 0 | 32 5 |
| | | 40 3 | | |
| $C_3H_8$ | 150 8 | | 117 0 | 33 8 |
| | | 39 8 × 3 | | |
| $C_6H_{14}$ | 270 1 | | 234 0 | 36·1 |
| | | 39 2 | | |
| $C_7H_{16}$ | 309 3 | | 273 0 | 36 3 |
| | | 35 7 | | |
| $C_8H_{18}$ | 345 0 | | 312 0 | 33 0 |
| | Mean | 39 1 | Mean | 34 2 |

The differences (column 3) between successive members of this and other homologous series are nearly constant, the average increment for $CH_2$ being 39 0 The value for 2H can then be obtained by subtracting

$$n \times CH_2 = 39n$$

from the parachor for the compound $C_nH_{2n+2}$ The magnitude of this residue as calculated from successive members of the homologous series is given in the last column of the table, the average value being $H_2 = 34\ 2$, or $H = 17\ 1$ Combining this with the value $CH_2 = 39\ 0$ it follows that

$$C = 39\ 0 - 2 \times 17\ 1 = 4\ 8$$

When the values for carbon and hydrogen are fixed, the atomic parachors for other elements can be determined in a similar manner It is then found that the parachor can be expressed as the sum of a series of atomic and structural constants *which do not vary from compound to compound* Thus the same constant can be used for oxygen in ethers and in ketones (there is a small anomaly in esters), and the increment for a double bond

is the same in the groups C=C, C=O, C=N, C=S, and N=O The most important atomic and structural constants are quoted in Table 49, in general the atomic parachors vary with the atomic weight in much the same way as Lothar Meyer's atomic volumes

TABLE 49.—PARACHOR CONSTANTS

| | | |
|---|---|---|
| H = 17 1 | Triple bond - - - | 46 6 |
| B = 14 0 | Double bond - - | 23 2 |
| C = 4 8 | 3-membered ring - - | 17 0 |
| N = 12 5 | 4 ,, ,, - - | 11 6 |
| O = 20 0 | 5 ,, ,, - - | 8 5 |
| F = 25 7 | 6 ,, ,, - - | 6 1 |
| Si = 12 0 | Single bond - - - | 0 0 |
| P = 37 7 | Semi-polar double bond - | − 1 6 |
| S = 48 2 | $O_2$ in esters - - - | 60 0 |
| Cl = 54 3 | | |
| Br = 68 0 | | |
| I = 91 0 | | |

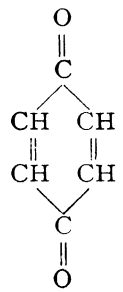
**Parachors of isomeric compounds.**—The additive nature of the parachor can be tested by comparing the values recorded for a series of isomerides, such as the esters in the following table

| | [P] obs | | [P] obs |
|---|---|---|---|
| *iso*-Amyl formate - | - 293 6 | Ethyl butyrate - | - 293 6 |
| *iso*-Butyl acetate - | - 295 1 | Ethyl isobutyrate - | - 293 9 |
| *n*-Propyl propionate | - 295 3 | Methyl valerate - | - 292 5 |

It will be seen that six compounds having the formula $C_6H_{12}O_2$ give a parachor which is constant within the limits of experimental error and is very close to the calculated value

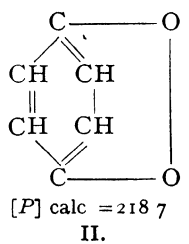
$$[P] = 294\ 0$$

On account of its additive character, the parachor cannot be used to detect differences of structure in a series of isomeric esters, and, since the structural constant for a triple bond is exactly twice as great as for a double bond, the parachors would be the same for methyl cyanate, $CH_3O\ C{\equiv}N$, and methyl *iso*-cyanate, O C N $CH_3$ If, however, two isomerides differ by the change from a double bond to a ring structure, as in the case of the two formulae I and II suggested for quinone (p 799), a difference in the parachor would be produced



[P] calc = 236 1

I



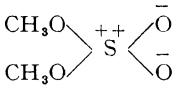
[P] calc = 218 7

II.

Measurements of the surface tension and density of this substance give $[P]$ obs $= 236{\cdot}8$, which points clearly to I as representing more accurately the constitution of this substance

**Influence of double bonds.**—The parachor is of special interest on account of the evidence that it provides of the existence of two different kinds of double bond This is shown in Table 50, where the difference between the sum of the atomic parachors $\Sigma[P]$ and the experimental value $[P]$ is a measure of the influence of the double bonds In the first three compounds this difference corresponds to an increment of about $+23$ for each double bond, but in the last three compounds a small decrement (about $-1\,6$) is observed

TABLE 50.—NON-POLAR AND SEMI-POLAR DOUBLE BONDS

| | | $[P]$ obs | $\Sigma[P]$ | Diff |
|---|---|---|---|---|
| Ethylene | $CH_2=CH_2$ | 99 5 | 78 0 | 21 5 |
| Acetone | $(CH_3)_2C=O$ | 161 7 | 137 0 | 24 7 |
| Carbon disulphide | $S=C=S$ | 144 7 | 101 2 | 21 8 × 2 |
| Phosphorus oxychloride | $Cl_3P^+—O^-$ | 217 6 | 220 6 | −3 0 |
| Thionyl chloride | $Cl_2S^+—O^-$ | 174 5 | 176 8 | −2 3 |
| Methyl sulphate |  | 238 9 | 240 4 | −0 8 × 2 |

An explanation of these differences is found in the newer theories of valency, in which two kinds of linkage and three types of double bonds are recognised (Ch VI)

It is then seen that a " non-polar " double bond, consisting of two covalences, gives rise to an *increase* of 23 units in the parachor If, however, the double bond is composed of one covalence and one electrovalence, the " semi-polar " double bond, represented by symbols such as $Cl_2S^+—O^-$, causes a small *decrease* in the parachor The third kind of double bond, consisting of two electrovalences, is probably present in compounds such as $Mg^{++}O^{--}$ or $Ca^{++}S^{--}$, but data for compounds of this type are not yet available

## CHAPTER XXXV

### THE SOLID STATE

**Crystalline and amorphous solids** —Solids can be divided into two distinct classes, namely, CRYSTALLINE SOLIDS and AMORPHOUS SOLIDS

(*a*) **Crystalline solids** —Many substances, such as rock-salt, alum and ice, separate in the form of CRYSTALS when deposited in the solid state from a solution, or from a homogeneous melt The chief characteristics of this class of solids are

(i) *They have a characteristic geometrical form* —Crystals are usually bounded by plane faces which intersect one another at definite angles These angles, as well as the angles between the edges, are fixed within

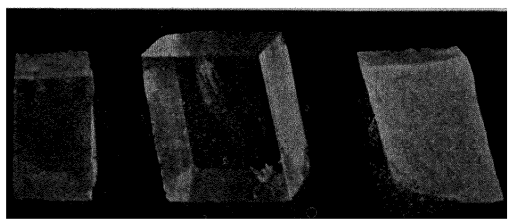


FIG 125 CLEAVAGE-FRAGMENTS OF (*a*) ROCK-SALT, (*b*) CALCITE (*c*) BARYTES

very narrow limits, and often have simple integral values, *e g* 45°, 60° or 90°

(ii) *They often have a plane fracture* —If broken by a sudden blow, crystals often break most easily along certain planes which are parallel to important crystal faces The planes along which a crystal breaks most easily are called CLEAVAGE PLANES (Fig 125) Thus mica, which has *one* very marked cleavage plane, splits up easily into thin sheets , whilst rock-salt, which has *three* cleavage planes at right angles to one another, breaks up easily into cubic or rectangular fragments Many crystals, however, have no plane of easy cleavage, and break into irregular fragments Rock-crystal (quartz) is a familiar example of this kind

(iii) *They have a definite melting-point* —This varies with the nature of the liquid with which the melting solid is bathed Thus ice floating in sea-water melts at $-2.4°$, and when bathed with a saturated solution of common salt it may melt as low as $-22°$ C , as in a " freezing-mixture " If, however, the solid is pure (and melts to a pure liquid), the melting-

point is remarkably constant, as in the case of melting ice, the temperature of which is used to fix the zero of a Centigrade thermometer

(*b*) **Amorphous solids**.—Pitch and glass may be taken as examples of amorphous solids This class of substances has the following properties

(i) Amorphous solids, as their name implies, have no definite crystalline form

(ii) When broken by a sharp blow they do not cleave along any particular plane, but fracture with equal ease in any direction The broken surfaces often exhibit convexities or concavities shaped like a shell Hence this type of fracture is often termed a CONCHOIDAL FRACTURE (Fig 126)

(iii) When heated, amorphous solids do not melt sharply at a definite temperature, but pass through an intermediate soft and pasty stage, which persists over a considerable range of temperature

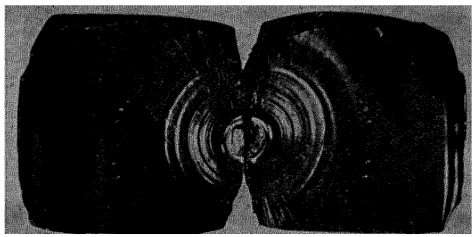


FIG 126 CONCHOIDAL FRACTURE OF PITCH

Amorphous solids can be regarded as supercooled liquids, *i e* liquids cooled to such a temperature that they have a very high viscosity and hence crystallise very slowly Although they have many of the properties of solids, it is possible to show in certain cases that they will flow like a liquid Thus, if a lump of pitch is struck smartly with a hammer, it will fly to pieces like any other solid , and the broken surfaces may exhibit a characteristic conchoidal fracture If, however, some of the fragments are placed in a funnel, and allowed to stand for some months, they will gradually coalesce and flow through the funnel just as water does Both water and pitch are liquids, but pitch has such a high viscosity that it takes months to flow through a funnel, whilst water only requires a few seconds The properties of supercooled liquids and the conditions under which they are formed are discussed again in Chap XXXIX (p 534)

**Structure of crystals.**—The most obvious property of crystals is their characteristic geometrical form , thus, salt crystallises in cubes, and alum in octahedra Silica crystallises in the form of six-sided prisms, capped by six-faced pyramids (Fig 177, p 743) Since, however, the different faces of a crystal may not all be developed equally, the actual shape of the crystals of a given substance is variable Thus crystals of quartz, Fig 127, are not bounded entirely by regular hexagonal prisms and pyramids, but are irregular in shape because some of the faces are much larger than others, although the angles at which they meet are the same in all crystals of this

substance Again, when a solution of alum is allowed to cool, the crystals which are formed are not perfect octahedra, since accidental circumstances cause different faces to grow at different rates

These facts suggest that the internal structure of crystals is more important than their external form or "habit," and that the constancy of the angles at which the faces of a crystal meet is due to a regular arrangement of the molecules or atoms of the crystal When a crystal grows, each new layer of particles is laid down in such a way as to keep the growing face parallel to its original direction This is well seen when a crystal of chrome alum is allowed to grow in a solution of potash alum The colourless potash alum then forms layers parallel to the faces of the coloured chrome alum, so that it seems beyond doubt that its particles have continued to reproduce the regular arrangements of the original crystal We



FIG 127 CRYSTALS OF QUARTZ

therefore think of the particles as being arranged in a regular and orderly fashion within a crystal, whereas in an amorphous solid or glass they have the same chaotic distribution as in a liquid

If we could see the individual particles, the face of a crystal would probably look like a field planted with cabbages all arranged in regular rows, since the particles could be joined up by a series of imaginary straight lines, all equidistant and parallel to one another We should find, however, that the particles were also spaced at regular intervals in each row, like the trees in a plantation, so that a second series of parallel lines could be drawn through them, intersecting the first series at some definite angle All the particles would then be located at points of intersection of a net-work or lattice of intersecting series of parallel straight lines

This orderly arrangement of the particles, however, is not merely in *two* dimensions, but in *three* If, therefore, we joined up the corners of this lattice to the corresponding corners of the lattice on an adjacent sheet of particles immediately below the surface, we should obtain a SPACE-LATTICE composed of many series of parallel lines, each line passing through similarly-placed molecules, atoms or ions, in the crystal Each crystalline substance has its own characteristic arrangement of particles, corresponding to a particular space-lattice, and this pattern is repeated throughout the crystal whatever its size or external form This pattern

or space-lattice determines all the properties of the crystal, in particular, it fixes the angles at which the plane faces meet, and the planes along which cleavage takes place most easily

**Analysis of crystals by X-rays.**—The above conception of the nature of crystals has been verified by the investigation of the effect of crystals upon X-rays It has long been known that a ray of light is broken up into a spectrum when it is passed through a glass plate on which a series of parallel lines is ruled at intervals not many times greater than the wavelength of the light, if the spacing is not too small, a whole series of these spectra may be seen The wavelength of ordinary light (say 4000 to 8000 A U ) is enormously greater than the distance between the atoms or molecules in a crystal, which amounts to only a few A U , but X-rays have a wavelength which is perhaps 10,000 times smaller than that of visible light, and is actually less than the dimensions of the cells of the crystal-lattice It is therefore found that, when a pencil of X-rays is passed through a crystal, a pattern of diffracted spots is produced, just as would be expected if the crystal were composed of a regular assemblage of particles

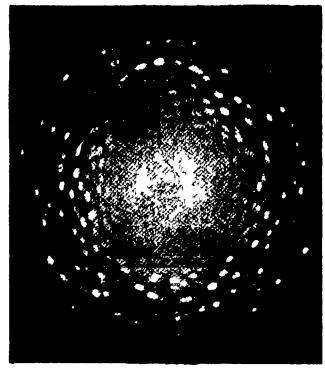


FIG 128 LAUE PATTERN (POTASH ALUM)

Fig 128 shows the type of pattern produced in this manner From a study of such photographs, and a closer investigation of the action of crystals in X-rays, the arrangement of the atoms in many crystals can be determined Fig 129 shows the space-lattice of common salt The black circles represent the centres of sodium atoms or ions, and the white ones the centre of chlorine atoms or ions (or conversely) They are probably held together as an IONIC AGGREGATE by the electrostatic forces between their opposite charges, the distance between neighbouring atoms of sodium and chlorine being $2\ 81 \times 10^{-8}$ cm This distance is very little larger than the diameter of the atoms as deduced by other methods, and we must suppose that in a crystal of common salt the atoms are very closely packed together

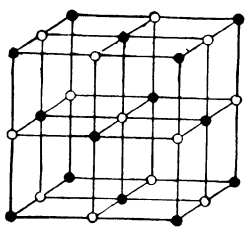


FIG 129 SPACE-LATTICE OF ROCK-SALT

**Kinetic theory of the solid state** —We have seen that the properties of crystals lead us to conclude that their constituent molecules or atoms occupy fixed positions in a space-lattice The forces of attraction between the particles are sufficient to hold each one in its place in the orderly array that constitutes the crystal Although, therefore, the molecules or atoms can still oscillate about a mean position and the radicals or ions appear sometimes to be in constant rotation, they have not the same freedom of

movement as in the liquid and gaseous states, where the molecules have freedom of " translation " as well as of oscillation and rotation

Whilst the greater number of the molecules in a crystal are thus fixed, it is readily conceivable that from time to time a particular particle may, by collision with its neighbours, attain a velocity great enough to tear it from its moorings and to transplant it to another position Definite evidence of this type of migration has been obtained in certain cases Thus minute traces of gold can be detected in lead, after strips of these metals have been in contact with one another for a long time

EXPT 94 **Determination of the melting-point. Capillary-tube method**

Draw out a boiling tube in the blow-pipe flame so as to make a thin-walled tube about 1-2 mm in diameter Break off a length of about 8 cm , seal up one end, and (when cold) shake down a few crystals of *p*-nitrotoluene or naphthalene to the closed end Attach the capillary tube to a thermometer by means of a small rubber band, so that the part containing the substance is near the middle of the bulb Support the thermometer vertically in a beaker of water containing a stirrer and raise the temperature slowly Note the temperature (51 5° or 80° C ) at which the crystals suddenly melt

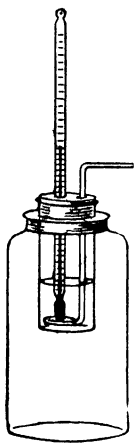


FIG 130 APPARATUS FOR DETERMINATION OF FREEZING-POINTS

EXPT 95 **Determination of the freezing-point. Method of cooling.**

Fit a specimen tube with a cork carrying a thermometer (0° to 100°) and a small stirrer made of thin glass rod Mount the tube in a larger cork which closes the neck of a wide-mouthed bottle as shown in Fig 130 This arrangement protects the tube from draughts and ensures regular cooling Place 10 grams of *p*-nitrotoluene in the tube Insert the thermometer and stirrer and heat in a bath of hot water until all the substance is melted Wipe the outside of the tube and insert in the neck of the bottle Stir slowly and regularly and read the thermometer every half minute The temperature will fall at first, but when crystals begin to form it will rise a little, and then remain steady for some time (Why ?) This steady temperature is the freezing-point of the liquid and should be identical with the melting-point of the solid.

# CHAPTER XXXVI

## SOLUTIONS

In the previous chapters some of the properties of pure substances in the gaseous, liquid and solid states have been considered The products obtained by mixing pure substances are called SOLUTIONS, if homogeneous, and must obviously have different physical properties from those of their constituents In the present chapter the following types of solutions are considered

1 *Solutions of gases in gases*
2 *Liquid solutions*, *e g* solutions of (*a*) gases, (*b*) liquids, (*c*) solids in liquids
3 *Solutions of solids in solids*

### SOLUTIONS OF GASES IN GASES

**Dalton's law of partial pressures** states that

*The total pressure exerted by a mixture of gases is the sum of the pressures which each component would exert, if it alone occupied the given volume*

This law has been shown to be approximately correct for hydrogen by making use of the fact that heated palladium is permeable to hydrogen, but not to other gases Thus, Ramsay placed an electrically heated palladium bulb (Fig 131), filled with nitrogen at a known pressure, in an atmosphere of hydrogen The pressure inside the bulb increased slowly until it was equal to the sum of the original pressure of the nitrogen plus the external pressure of the hydrogen, thus showing that (in accord with Dalton's law) the pressure of nitrogen was unaffected by the addition of hydrogen Dalton's law has also been verified by making use of Henry's law (see below)

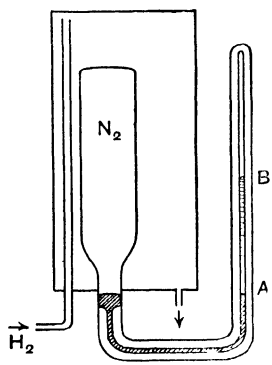


FIG 131 DIFFUSION OF HYDROGEN THROUGH PALLADIUM

### LIQUID SOLUTIONS

**Solubility of gases in liquids.**—(*a*) *Henry's law* —Gases are only miscible with liquids to a limited extent, the actual solubility depending

upon the pressure and temperature, and on the nature of the gas and liquid HENRY'S LAW states that

*The solubility of a gas in a liquid at constant temperature is proportional to the pressure*

The solubility of a gas in a liquid is usually expressed in terms of the ABSORPTION COEFFICIENT, which may be defined as

*The volume of gas, reduced to N T P, which is dissolved by unit volume of the liquid at a fixed temperature and under a pressure of one atmosphere*

If Henry's law is true, then the volume of a gas (reduced to N T P) which can be dissolved by a certain volume of a liquid is

ABSORPTION COEFFICIENT × VOLUME OF LIQUID × PRESSURE

TABLE 51 —ABSORPTION COEFFICIENTS OF GASES IN WATER AT 0° AND 100°, UNDER 760 MM PRESSURE

| Substance | Absorption coefficient at 0° | Absorption coefficient at 100° |
|---|---|---|
| Hydrogen - - - | 0 0215 | 0 0160 |
| Nitrogen - - - - | 0 0239 | 0 0100 |
| Oxygen - - - - | 0 0489 | 0 0170 |
| Argon - - - - | 0 053 | — |
| Carbon dioxide - - | 1 713 | 0 359 (60°) |
| Sulphur dioxide - - | 79 8 | 18 8 (40°) |
| Ammonia - - - | 1305 0 | 195 0 |

(*b*) *Deviations from Henry's law* —Henry's law is very nearly true for sparingly soluble gases For carbon dioxide, Henry's law holds at small pressures, but appreciable deviations are found at higher pressures (Table 52) A very soluble gas such as ammonia does not obey Henry's law even at low pressures This is shown by the figures in Table 52, where the solubility, $s$, of ammonia in one litre of water at 0° is divided by the pressure, $p$, but at 100°, when ammonia is much less soluble, Henry's law is nearly true

In general it will be found that a gas deviates from the law when (1) the concentration of the gas in the liquid is large, owing to the great solubility of the gas or to the high pressures employed, or (11) the nature of the molecule is altered by the solvent Thus ammonia and carbon dioxide both interact with water to a small extent, forming the addition compounds ammonium hydroxide, $NH_4OH$, and carbonic acid, $H_2CO_3$, which, in turn, dissociate to a small extent into ions

(*c*) *Solubility of mixtures of gases* —Dalton's law of partial pressures would lead us to suppose that, since the partial pressure of a gas is unaffected by the presence of other gases, its solubility would also be unaffected This is in accord with experimental evidence Thus air contains by volume 78 1% of nitrogen, 21 0% of oxygen and 0 9% of argon, the partial pressures of these gases in air at one atmosphere pressure are

$$p_{N_2} = 0\ 781 \text{ atm}, \quad p_{O_2} = 0\ 210 \text{ atm}, \quad p_A = 0\ 009 \text{ atm}.$$

TABLE 52.—SOLUBILITY OF GASES IN WATER

| | Pressure—$p$ | Solubility—$s$ | $s/p$ |
|---|---|---|---|
| ($a$) Carbon dioxide at 0° | 1 atm | 1 80 c c /c c | 1 80 |
| | 5 | 8 65 | 1 73 |
| | 10 | 16 03 | 1 60 |
| | 20 | 26 65 | 1 33 |
| | 30 | 33 74 | 1 12 |
| ($b$) Ammonia at 0° - | 20 mm | 82 gm /L | 4 10 |
| | 40 | 148 | 3 70 |
| | 80 | 240 | 3 00 |
| | 200 | 421 | 2 11 |
| | 500 | 770 | 1 54 |
| | 1000 | 1126 | 1 13 |
| ($c$) Ammonia at 100° - | 750 | 74 gm /L | 0 099 |
| | 1000 | 96 | 0 096 |
| | 1200 | 115 | 0 096 |
| | 1400 | 135 | 0 096 |

One litre of water should therefore dissolve the following volumes of these gases, at 0° C and atmospheric pressure

Volume of nitrogen $= 1000 \times p_{N_2} \times$ absorption coefficient
$= 1000 \times 0\ 781 \times 0\ 0239 = \mathbf{18\ 7}$ c c

,, oxygen $= 1000 \times p_{O_2} \times$ absorption coefficient
$= 1000 \times 0\ 210 \times 0\ 0489 = \mathbf{10\ 3}$ c c

,, argon $= 1000 \times p_A \times$ absorption coefficient
$= 1000 \times 0\ 009 \times 0\ 053 = \mathbf{0\ 49}$ c c

The volumes of the gases expelled by boiling one litre of water, when saturated with air at 0° C under a pressure of one atmosphere, have been found to be

$$N_2 = \mathbf{18\ 63}\text{ c c},\quad O_2 = \mathbf{10\ 22}\text{ c c},\quad A = \mathbf{0\ 53}\text{ c c},$$

in close accord with Dalton's Law of Partial Pressures

($d$) *Influence of temperature on solubility of gases*.—From the figures in Table 52 it will be seen that the solubility of carbon dioxide and of ammonia in water is diminished by increasing the temperature. In most cases dissolved gases can be expelled completely from a liquid by boiling. This is not because the absorption coefficient is zero at the boiling-point, but because the gas which diffuses into the bubbles of vapour is carried away more rapidly than the liquid is vaporised.

The same effect can be produced at ordinary temperatures by bubbling a sparingly soluble gas through the liquid. Thus ammonia can be removed completely from water by drawing a current of air through the solution. There are, however, some exceptions to this rule. Thus, solutions of hydrochloric acid in water give a mixture of constant composition

when boiled, and the gas cannot be removed from solution by a current of air. The behaviour of this type of mixture is discussed in the next section.

(*e*) *Determination of the solubility of gases.*—The solubility of gases which are sparingly soluble in water may be determined by using an apparatus similar to that in Fig 132 The contraction in volume of the gas in the graduated tube *B* is measured, after it has been in contact for a sufficient time to saturate a known volume of distilled water in the vessel *A*. The pressure is adjusted to the required value by moving the limb *C*, which contains mercury and is joined to *B* by rubber tubing The absorption coefficient is

$$\frac{\text{Contraction of gas}}{\text{Volume of water}}.$$

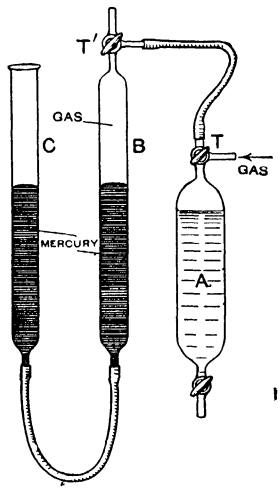



FIG 132 APPARATUS FOR MEASURING SOLUBILITY OF SPARINGLY SOLUBLE GASES

The solubility of very soluble gases such as sulphur dioxide, hydrogen chloride and ammonia cannot be determined conveniently by this direct method Known weights of their saturated solutions are therefore diluted to a known volume with water, and the quantity of gas is estimated by titration, *e g* of sulphur dioxide against standard permanganate, hydrogen chloride against standard alkali, and ammonia against standard acid

**Solubility of liquids in liquids.**—The solubility of liquids in liquids varies enormously Thus two liquids may be (i) completely miscible in all proportions, *e g* alcohol and water, (ii) partially miscible, *e g* ether and water, or (iii) almost immiscible, *e g* aniline and water

The behaviour of liquids towards one another depends largely on the electrical character of the molecules If the molecules are *non-polar* (*i e* if the positive and negative components have the same "centre of gravity," so that the molecule has no "dipole moment," p 665) the van der Waals' forces between the molecules will be weak and the boiling-point low in relation to the mass of the molecules Such non-polar liquids usually mix freely with one another, especially when their chemical character is similar, as in the case of the hydrocarbons, $C_xH_y$ If, however, the molecules are *polar* (*i e* if the centroids of the positive and negative components do not coincide, so that the molecule has a relatively large dipole moment) the van der Waals' forces between them will be large by reason of the electrostatic fields associated with the dipoles Such molecules tend to form loose aggregates, giving rise to ASSOCIATED LIQUIDS, of which water is an excellent example These liquids boil at relatively high temperatures, and are usually not miscible with non-polar liquids, because the mutual attraction of the polar molecules resists the intrusion of non-polar molecules Thus water is almost completely non-miscible with hydrocarbons. On the other hand water mixes freely with the simpler

alcohols, because the energy-content of the aggregates of alcohol with water is similar to that of the aggregates formed by alcohol and by water separately

Liquids which are not completely miscible at ordinary temperatures may become so at higher temperatures Thus, Fig 133 shows that the solubilities of water in phenol, $C_6H_5OH$ (p 791), and of phenol in water increase with temperature, until at 66·5° the two layers have the same composition, and are therefore completely miscible with one another This temperature of complete miscibility is described as the CRITICAL SOLUTION TEMPERATURE

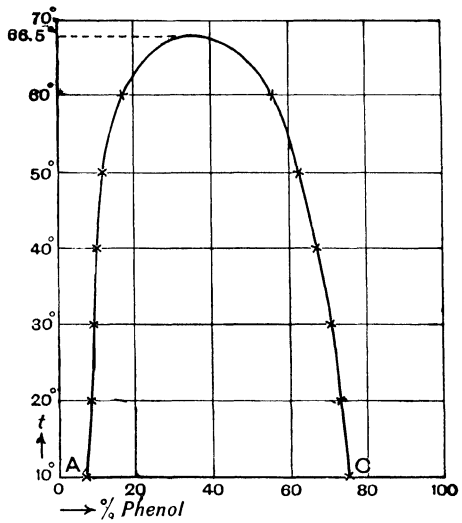



FIG 133 MISCIBILITY OF PHENOL AND WATER

**Vapour-pressure of homogeneous binary mixtures of liquids.**—The vapour-pressure-composition curves of binary mixtures of completely miscible liquids fall into three classes, (i), (ii) and (iii), which are discussed below

(i) In the first type of curve, the vapour-pressure of the mixture varies progressively from that of one liquid to that of the other liquid Mixtures of benzene and toluene, or of ether and aniline, give curves of this kind The diagram, Fig 134 (*a*), represents the behaviour of an ideal mixture of liquids in which (in accordance with Raoult's Law of Vapour Pressures, p 516) the partial vapour-pressure of each component is proportional to its molecular concentration in the mixture The partial vapour-pressure of the component *A* is therefore represented by a straight line *PS* falling from the vapour-pressure of *A* at *P* to a zero value at *S* In the same way, the partial vapour-pressure of the component *B* is represented by a straight line *QR* The total vapour-pressure of the mixture, which is equal to the sum of these two partial pressures, is therefore represented by the straight line *PR*

The molecular composition of the vapour from such a mixture is proportional to the partial pressures of the two components In the particular case shown in Fig 134 (*a*), these are proportional to the vapour-pressure of the pure components multiplied by their concentrations in the mixture The vapour is therefore richer than the liquid in the component of higher vapour-pressure , and the mixture can be separated by distillation into fractions which are richer and poorer in this component than the original liquid mixture By repeated distillation (or by distillation through a still-head) both components of such a mixture can be isolated in a pure state.

Precisely similar results follow if the lines $PS$, $QR$, and $PR$ are not straight but curved, provided that the line $PR$, which represents the total vapour-pressure of the mixture, neither rises to a maximum nor falls to a minimum between $P$ and $R$

The fact that liquid mixtures of this class can be separated by distillation should be clear from Fig 134 (*b*), in which the molecular composition of the liquid and its vapour are plotted against the temperature at the boiling-point (vertical axis) The lower curve represents the composition of the liquid, and the upper one that of the vapour When a liquid of composition $l_1$ starts to boil at $t$ it gives a vapour of composition $v_1$, which is clearly richer than $l_1$ in the more volatile constituent $A$.

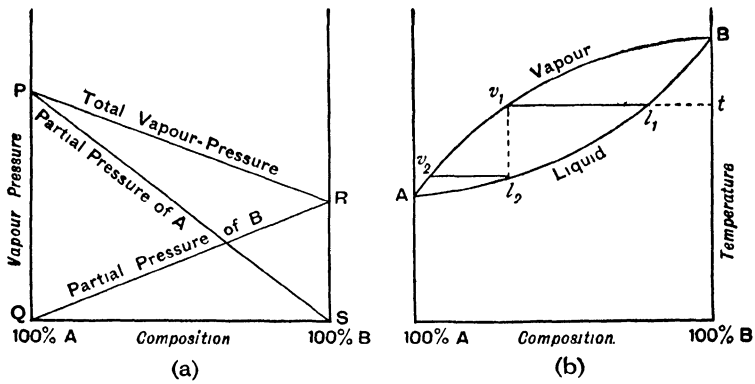



FIG 134 (*a*) VAPOUR-PRESSURE AND (*b*) BOILING-POINT GRAPHS FOR MIXTURES OF LIQUIDS OBEYING RAOULT'S LAW

(Note that the horizontal line $v_1l_1$ is known as the "tie line," and that the composition of the vapour in equilibrium with any other liquid mixture is obtained by drawing the corresponding tie line) On distillation, the liquid becomes progressively richer in the less volatile constituent, and the boiling-point therefore rises towards $B$ Now if the vapour of composition $v_1$ is condensed it will give liquid $l_2$, of the same composition, but when the latter is heated the new vapour is of composition $v_2$, which is now much richer in $A$ than the original liquid $l_1$ By continuing this process of vapourising and condensing a sufficient number of times, pure liquid $A$ would be obtained, but in actual practice the same thing is effected in one operation by using a fractionating column The vapour passing up the column is gradually cooled with the result that it is progressively condensed, the liquid condensing is richer in the less volatile constituent $B$ than is the vapour, and hence the proportion of $A$ in the latter rises until at the top of the column, under ideal conditions, the vapour consists solely of this constituent Conversely, the liquid in the flask becomes progressively richer in the less volatile constituent, and hence the boiling-point rises until it reaches that of pure $B$ Distillation under these conditions gives first of all, therefore, a fraction consisting of

pure $A$, then a small middle fraction (the size depending upon the difference in the boiling-points of $A$ and $B$—the bigger the difference the smaller the middle fraction is) consisting of $B$ contaminated with remnants of $A$, and finally a fraction consisting of pure $B$

(ii) The second class of liquid mixtures is that in which the vapour-pressure composition curve exhibits a minimum as in Fig 135 (*a*) Unlike the former class, it is impossible to separate these mixtures by

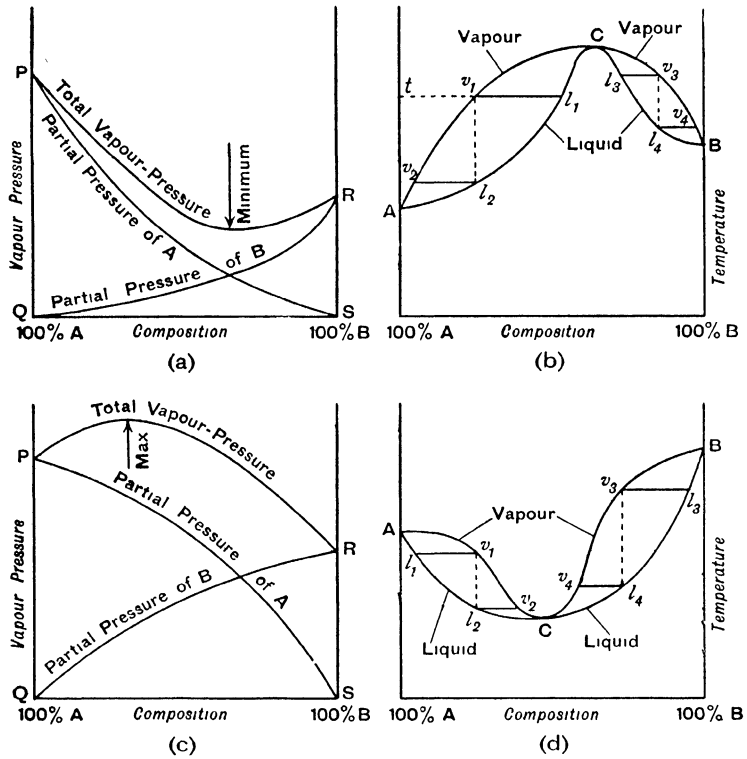



FIG 135 MIXTURES WITH (*a*) MINIMUM VAPOUR-PRESSURE, (*b*) MAXIMUM BOILING-POINT, (*c*) MAXIMUM VAPOUR-PRESSURE AND (*d*) MINIMUM BOILING-POINT

distillation into the fractions consisting of pure $A$ and pure $B$, instead a fraction consisting of either pure $A$ or pure $B$ will be obtained first of all, and then a mixture of MAXIMUM BOILING-POINT, which has a composition corresponding with the minimum vapour-pressure point on the graph (Fig 135 (*a*))

The effect of distillation on this class of liquid mixture is made clear by considering Fig 135 (*b*), in which the composition of the liquid and its vapour is plotted against the temperature at the boiling-point If liquid

of composition $l_1$ is heated it starts to boil at $t$ and gives off vapour of composition $v_1$, which is clearly richer in component $A$ than the parent liquid Condensation of the vapour $v_1$ will give a liquid of composition $l_2$, which, when heated, will give vapour of composition $v_2$, and so on, until pure $A$ is obtained When, therefore, the liquid $l_1$ is distilled with a fractionating column, pure $A$ will distil over and the composition of the liquid in the flask will get progressively poorer in $A$ until the point $C$ is reached At this MAXIMUM BOILING-POINT the liquid has precisely the same composition as the vapour which is in equilibrium with it, and hence it distils over without any further separation into $A$ and $B$

Similar reasoning can be applied to a mixture which has a composition corresponding to $l_3$—the vapour, $v_3$, condenses to liquid $l_4$, which gives vapour $v_4$, etc Distillation with a column will give pure $B$, so that the composition of the liquid in the flask passes towards $C$, and when $C$ is reached no further separation can be effected Incidentally, it is important to realise that it is the composition of the original mixture (*i e* whether it is to the right or left of $C$) and not the relative volatility of $A$ and $B$ that decides which of them will be the first to distil before the constant-boiling mixture, *e g* liquid $l_2$ gives $A$, but liquid $l_3$ gives $B$, even though $B$ is a less volatile liquid than $A$

Examples of pairs of liquids giving MIXTURES OF MAXIMUM BOILING-POINT and minimum vapour-pressure are set out in Table 53

TABLE 53 —MIXTURES OF MAXIMUM BOILING-POINT

| | | Composition | Boiling-point |
|---|---|---|---|
| Sulphuric acid | + water | 98 7% $H_2SO_4$ | 338° |
| Nitric acid | + water | 68% $HNO_3$ | 120 5° |
| Hydrofluoric acid | + water | 37% HF | 120° |
| Hydrochloric acid | + water | 20 24% HCl | 110° |
| Hydrobromic acid | + water | 48% HBr | 125° |
| Hydriodic acid | + water | 58% HI | 127° |

It is noteworthy that these pairs of liquids all liberate heat when mixed Their molecules have, therefore, considerable affinity for one another, and for this reason give rise to mixtures of high boiling-point and low vapour-pressure

(iii) The third class of liquid mixtures gives a vapour-pressure composition curve which exhibits a maximum (Fig 135 (*c*)) The mixture which has this maximum vapour-pressure will have a minimum boiling-point, $C$ (Fig 135 (*d*)), and therefore distil over first and leave either pure $A$ or pure $B$ in the flask, depending (as in the former case) on the composition of the original mixture Thus, liquid of composition $l_1$ (Fig 135 (*d*)) gives vapour of composition $v_1$, which on condensation gives $l_2$, and this is in equilibrium with vapour of composition $v_2$—further fractionation eventually gives $C$, the mixture with a MINIMUM BOILING-POINT, whilst the liquid remaining in the flask is pure $A$ Similar reasoning, applied to the liquid mixture $l_3$, on the other side of $C$, shows that $B$ will remain in the flask when the constant-boiling mixture has been expelled

Examples of constant-boiling MIXTURES OF MINIMUM BOILING-POINT and maximum vapour-pressure are set out in Table 54

TABLE 54 —MIXTURES OF MINIMUM BOILING-POINT

| | Composition | Boiling-point |
|---|---|---|
| Pyridine + water - - - - | 59% $C_5H_5N$ | 92° |
| Alcohol + water - - - - | 95 59% $C_2H_5OH$ | 78 13° |

It was formerly thought that constant-boiling mixtures such as the above were chemical compounds, but this is obviously incorrect, since their composition is changed by altering the pressure of distillation Thus the concentration of HCl falls from 20 24 to 18% when the pressure is raised from 760 to 2500 mm. This does not exclude the possibility that unstable compounds may be present in equilibrium with their components, *e g* HCl, $n H_2O \rightleftharpoons HCl + n H_2O$ This equilibrium would be affected by the temperature and therefore by the pressure of distillation, so that the composition of the distillate would also vary

**Vapour-pressure of partially miscible liquids.**—The vapour-pressure of a mixture of two liquids which are soluble in one another only to a limited extent, *e g* ether and water at 20°, gives a different type of diagram, (Fig 135 (*e*)), when plotted against the composition of the mixtures As ether is added to water, the vapour-pressure of the solution increases, as indicated by the line *OP*, until the water is saturated with ether (about 7%), when an additional upper layer of ether saturated with water appears The vapour-pressure of the system at a given temperature is found to be constant over a range of compositions (see phase rule, p 532) as represented by the line *PQ* The addition of more ether then alters the relative amounts of the two layers, but it does not alter the vapour-pressure until the point *Q* is reached At this point, enough ether has been added to dissolve all the water, giving rise to an unsaturated solution of water in ether The vapour-pressure curve then rises from the value for a saturated solution of ether in water (or of water in ether) to the vapour-pressure of pure ether at *R*

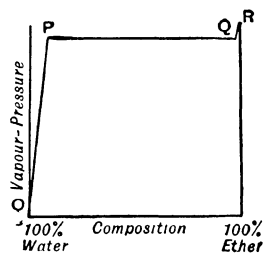



FIG 135 (*e*) VAPOUR-PRESSURE OF PARTIALLY MISCIBLE LIQUIDS

Two mutually saturated solutions which are in equilibrium with one another are termed CONJUGATE SOLUTIONS The composition of these conjugate solutions is given by the points *P* and *Q* Since they are in equilibrium with one another, their vapour-pressures must be equal, and this condition applies also to the partial vapour-pressures of each component, otherwise ether or water would pass from one layer to the other The vapour-pressure of two conjugate solutions is always *less* than the sum of the vapour-pressures of the pure components, and in the case of ether and water (though not in all other cases) it is less than the vapour-pressure of the more volatile constituent, namely, the ether

**Vapour-pressure of immiscible liquids. Steam-distillation.**—If two liquids, $A$ and $B$, are completely insoluble in one another, they cannot affect one another's partial vapour-pressures, and hence, irrespective of the relative quantities of $A$ and $B$, the vapour-pressure of the mixture is the sum of the individual vapour-pressures that $A$ and $B$ exert when they are alone In practice, however, liquids are never quite insoluble in one another, although there are many pairs of liquids whose mutual solubility is so small that it may be ignored

Let us suppose that two immiscible liquids have vapour-pressures $p_1$ and $p_2$ at the boiling-point of the mixture, and that the relative weights of the molecules are $M_1$ and $M_2$ The relative weights of the two liquids in the vapour coming off the mixture will be $n_1M_1$ and $n_2M_2$ respectively, where $n_1$ and $n_2$ are the number of molecules of each in the vapour. Since the ratio $n_1/n_2$ is equal to $p_1/p_2$, it follows that

$$\frac{\textit{weight of first liquid in distillate}}{\textit{weight of second liquid in distillate}} = \frac{p_1M_1}{p_2M_2}$$

The above principle finds an important application in the use that is made of steam distillation to separate and concentrate liquids such as aniline, p 797, from aqueous solutions The small molecular weight of steam, and the relatively high boiling-point of water, often make the process surprisingly efficient, as can be seen from the following data for the system bromobenzene and water The vapour-pressures of the pure liquids are set out in Table 55, and their sum is given in the last column

TABLE 55.—VAPOUR-PRESSURES OF WATER AND BROMOBENZENE

| Temperature | Vapour-pressure of | | Mixture |
|---|---|---|---|
| | Water | Bromobenzene | |
| 80° | $p_1 = 356$ mm | $p_2 = 66$ mm | $p_1 + p_2 = 422$ |
| 85° | 434 | 79 | 513 |
| 90° | 526 | 98 | 624 |
| 95° | 634 | 117 | 751 |
| 100° | 760 | 141 | 901 |

By graphical interpolation it is found that the sum of the vapour-pressure rises to 760 mm at 95 2°, the mixture therefore boils at 95 2° under atmospheric pressure At this temperature $p_1 = 641$ and $p_2 = 119$ mm The molecular weights of the vapours are 18 and 157 respectively The ratio by weight of bromobenzene to water in the distillate is therefore

$$\frac{157 \times 119}{18 \times 641} = 1\ 62.$$

Although, therefore, the vapour-pressure of bromobenzene is much lower than that of water, its greater molecular weight has the effect of increasing

the relative weight of this compound in the vapour to such an extent that the distillate actually contains considerably more bromobenzene than water If the distillation were carried out at 450 mm , the boiling-point of the mixture would be 81 7°, $p_1 = 381$ and $p_2 = 69$ mm The ratio of bromobenzene to water would then be $\frac{69 \times 157}{381 \times 18} = 1\ 58$, and at lower pressures still less In general, the rate at which the less volatile substance distils in steam increases with increase of pressure , in certain technical processes distillation is therefore carried out under pressure with super-heated steam, in order to take advantage of this behaviour

**Solutions of solids in liquids** —(*a*) *Conditions governing solubility* — The solubility of a solid in a liquid depends upon (i) the nature of the solute and solvent, (ii) the temperature, and (iii), to a minor extent, the degree of subdivision of the solute

(i) The solubility of solids in liquids is determined mainly by the factors which lead to miscibility or non-miscibility of liquids Non-polar molecules are held together only by weak cohesive forces in solids such as naphthalene or paraffin wax The crystals are therefore relatively soft and easily melted, and often dissolve freely in non-polar solvents, especially when these are of similar chemical character Polar solvents, on the other hand, which refuse to mix with a non-polar liquid, are unlikely to dissolve the same substances in the solid state Thus benzene is a good solvent for naphthalene, whereas water is a very bad solvent for all hydrocarbons On the other hand, water is an excellent solvent for ionised salts such as sodium chloride, $Na^+Cl^-$ Dissolution then depends on the attraction of the *positive ions* for the negative end of the water dipoles and of the *negative ions* for the positive end of the water dipoles The *sodium ions* thus become surrounded by a watery atmosphere with the oxygen atoms facing towards the centre, and the *chloride ions* by a watery atmosphere with the hydrogen atoms facing inwards The formation of these watery aggregates breaks up the ionic aggregate of the solid salt and brings it into solution, whereas the larger ions of silver iodide exert too small an attraction for the dipoles of water to enable them to dissolve in it

The solubility of a solid in different types of solvent can be used as a rough test of its polar qualities Thus mercuric chloride, $HgCl_2$, unlike most other salts, would appear to be a covalent compound, because it is soluble in ether, a solvent in which ionised salts do not usually dissolve This is in harmony with measurements of conductivity, which show that it is only very feebly ionised even in dilute aqueous solution It must be remembered, however, that the polar character of the molecules of solute and solvent is not the only factor which determines their miscibility, although it is a very important one

(ii) The solubility of solids in liquids generally increases with the temperature Le Chatelier's principle (p 558) therefore tells us that near the saturation point most solids dissolve with absorption of heat The solubility curves of a few salts in water are given in Fig 22 (p 109) It will be seen that the actual effect of temperature varies enormously from salt to salt, *e.g.* the solubility of common salt varies very little with the

temperature, since this salt dissolves with very little absorption of heat ( − 1281 cal per gram mol ), whilst that of potassium nitrate varies very rapidly, corresponding with its large negative heat of solution ( − 8459 cal ) The solubilities of $Na_2CO_3,10H_2O$ and $Na_2SO_4,10H_2O$ (Fig 136) also increase rapidly with rising temperature, since the two decahydrates have large negative heats of solution ( − 16,150 and − 18,900 cal ), but the solubilities of the monohydrate, $Na_2CO_3,H_2O$, and of the anhydrous sulphate, $Na_2SO_4$, decrease with rising temperature, since their heats of solution are *positive* ( + 2250 and + 5500 cal ) A maximum of solubility occurs at 33° where the curves for $Na_2SO_4$ and for $Na_2SO_4,10H_2O$ intersect at the transition-temperature (p 536), but in the case of sodium

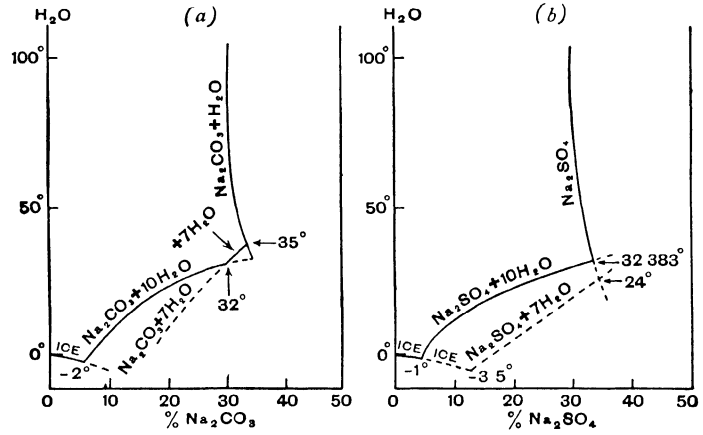



FIG 136 —EQUILIBRIUM-DIAGRAMS FOR
(*a*) SODIUM CARBONATE AND WATER (*b*) SODIUM SULPHATE AND WATER

carbonate the heptahydrate is stable over a narrow range and the solubility curve shows a kink at 32° and a maximum at 35° The broken lines represent the solubility of salts at temperatures where they are not the stable form, as is always the case, the unstable form has the greater solubility. The solution is therefore SUPERSATURATED, and the system can only persist in the absence of nuclei of the stable form

(iii) The solubility of a solid is generally increased by subdivision, but this effect is almost negligible, except in the case of very sparingly soluble substances Thus the solubility of precipitated yellow mercuric oxide (p. 339) is said to be 10% greater than that of the coarse red variety

(*b*) *The determination of solubilities* —A saturated solution of the solid is first prepared, either by stirring an excess of the solid with the solvent for about an hour in a thermostat, or by heating to obtain a nearly saturated solution at a higher temperature and then cooling down in the presence of excess of solid A given weight of the saturated solution is then taken, and the quantity of solute determined by evaporating to dryness on a water bath. This method cannot always be employed,

because the pure anhydrous solute is sometimes not obtained on evaporation, *e g* magnesium chloride is partially hydrolysed In cases such as these a given weight of the saturated solution is diluted to a known volume, and the quantity of solute estimated by a chemical method, *e g* magnesium chloride could be estimated by means of standard silver nitrate

When a solute is very sparingly soluble, the solubility is often determined by measurements of conductivity or of electromotive force Thus, in Expt 124 (p 611), the solubility of barium oxalate is deduced from the conductivity of a saturated solution of the salt

A quick, but rough, determination of the solubility may be obtained by heating a given weight of the solid with a given weight of solvent, and noting the temperature at which the solid disappears on heating and reappears on cooling The mean of these two temperatures will give a very fair result, if the liquid is stirred continuously and the heating or cooling is carried out gradually

**Solutions of solids in solids.**—Isomorphous solids (p 22) will mix in any proportion to give a product which is physically homogeneous Thus, if a mixture of potash alum (white) and chrome alum (purple) is crystallised from water, only one type of crystal is formed, its colour and composition being intermediate between those of the two alums Some alloys belong to this class, *e g* nickel and copper are miscible in all proportions, and their alloys form homogeneous crystals like those of a pure metal, but the majority of metals are either miscible only to a limited extent, or not miscible at all, so that their alloys are heterogeneous in character.

EXPT 96 **Separation and analysis of air dissolved in water**

By means of a water-jet pump, draw air through about 2 litres of distilled water for half an hour, in order to saturate the water with oxygen and nitrogen Fill a round-bottomed 1500 c c flask with this water Fit the flask with a rubber stopper and delivery tube, leading to a graduated eudiometer, filled with mercury and standing in a suitable trough The delivery tube must also be filled with water Heat the flask slowly at first, and then bring the water to the boil Collect the expelled gases in the eudiometer, and transfer the eudiometer to a deep jar of water Measure the volume of gas when the level of water is the same inside and outside the tube (Any mercury left in the eudiometer will fall to the bottom of the jar ) The temperature of the water and the height of the barometer should be read at the same time

Push up into the gas a wire carrying a pellet of phosphorus and leave it for 48 hours , then remove the phosphorus and read the volume of the nitrogen which remains, noting the temperature and barometric height as before Calculate from these measurements the percentage by volume of oxygen in the dissolved gas, and compare your results with the values calculated from the absorption coefficients (p 497)

EXPT. 97. **Absorption coefficient of oxygen in water.**

The cylinder *A* (Fig 132, p 498) is filled with distilled water (which has been boiled to expel dissolved air) and attached to a short piece of rubber

tubing This is filled with oxygen through the tap $T$, and its open e is fastened to one of the exits of the calibrated limb, $B$, which is f of mercury Oxygen is passed into $B$ by lowering the open limb, $C$, a opening the taps, $T$ and $T'$, its volume (about 40 c c ) at room temperatı and pressure is read on the scale The taps are now turned so that $A$ and are connected directly to one another, and, to facilitate the absorption oxygen by providing a larger surface of contact, a known volume of wa (20 c c ) is run out of $A$ The water is shaken from time to time, and t mercury levels in $B$ and $C$ are kept approximately equal so that the so bility is measured under atmospheric pressure After about 24 hours t absorption will be complete The volume of oxygen in $B$ is read from t scale and the volume of water in $A$ is measured The absorption coefficie is then calculated as the ratio of the volume of oxygen dissolved to t volume of water used to dissolve it

EXPT 98 **Steam-distillation**

Place 100 c c of chlorobenzene and 150 c c of water in a 500 c c d tilling flask, fitted with a thermometer and a condenser Distil the mixtu collecting the distillate 50 c c at a time in graduated cylinders Read t temperature at which each fraction distils After a few minutes read t volumes of the chlorobenzene (lower layer) and water in each fractic Taking the density of chlorobenzene as 1 11, calculate the ratio by weig of chlorobenzene to water Compare this with the value predicted fr the vapour-pressures at the temperature of distillation, as recorded Table 44 (p 482)

# CHAPTER XXXVII

## OSMOTIC PRESSURE

**Osmosis.**—It has long been known that the cells of living plants and animals are usually surrounded by a membrane through which water can pass readily Thus, when red blood cells are placed in water they rapidly swell and burst, owing to the passage of water through their outer membrane into the cell On the other hand, if the red corpuscles are placed in a strong solution of salt, water passes out of the cells into the solution, with the result that the corpuscles lose their characteristic disc-like shape and shrivel up In the same way, if a solution of sugar is placed in a bag of parchment paper and the bag is immersed in water as in Expt 99, water passes spontaneously through the parchment to the sugar solution inside the bag This spontaneous flow of liquids through a membrane is termed OSMOSIS and is obviously of great importance in the study of living cells A close study of the phenomenon of osmosis has resulted in the discovery of a number of rules, which have led to a great advance in our knowledge of the nature of solutions

(i) Osmosis is observed only when the membrane is more permeable to the solvent (usually water) than to the dissolved substance Thus, if the membrane is equally permeable to both constituents of a solution, mixing may occur through the membrane, but osmosis will be reduced because a flow of liquid will take place in both directions When a bag of parchment paper containing a sugar solution is immersed in water, very little sugar escapes from the bag, although water passes into it freely , there is therefore a very marked osmosis A membrane which allows the solvent but not the solute to pass is termed a SEMIPERMEABLE MEMBRANE Parchment paper is not a perfect semipermeable membrane for sugar and water, since it allows a little sugar to escape , but copper ferrocyanide, $Cu_2FeC_6N_6$, inhibits completely the passage of sugar and of some other substances, and has therefore been very largely used in investigations of the osmotic properties of solutions (Expt 100)

(ii) The flow through the membrane takes place in such a direction as to equalise the concentrations of the solutions on either side of it Thus, if an aqueous solution is placed on one side of a membrane, and pure water on the other side, water always passes into the solution so as to make it more dilute This behaviour is closely related to the DIFFUSION of a substance in solution, *e g* if a layer of a strong solution of a coloured salt is introduced carefully below a column of water, it will be seen after some hours that the boundary of the solution shades off through a series of intermediate tints to the colourless layer of water, because the salt has diffused progressively into it

Graham found that although different substances diffused at very different rates, yet the direction of the diffusion was always from regions of high concentration to regions of lower concentration, so that *the concentrations throughout the solution tended to become equal* This is precisely what is found in the phenomenon of osmosis The salt cannot diffuse, since it is restrained by the semipermeable membrane , but dilution is effected by the transit of water through the membrane to the stronger solution

In agreement with this conception of osmosis it is found that, when a membrane separates two solutions of the same substance, the osmotic flow of water from the weaker to the stronger solution ceases *when the solutions have the same concentration* When two solutions containing different substances are used, the concentrations at which osmosis ceases will not be identical, but can be determined by experiment A pair of solutions which produce no flow through a semipermeable membrane are said to be " isotonic " and are described as ISOTONIC SOLUTIONS It is also found that *solutions which are isotonic with a given solution are isotonic with one another* This is sometimes called the LAW OF ISOTONIC SOLUTIONS, and provides a convenient method for comparing the osmotic pressures of different substances Thus red blood corpuscles do not change in appearance when placed in 0 85% sodium chloride solution and observed under the microscope In weaker solutions they swell and burst, whilst in stronger solutions they shrivel up The 0 85% solution of salt is therefore isotonic with the contents of the red cells , it is known in medicine and surgery as a " normal saline solution " By making similar experiments with other substances, we can determine the concentrations at which they are isotonic with the cell contents, and therefore with 0 85% sodium chloride solution or with each other

**Osmotic pressure.**—A membrane of copper ferrocyanide is so fragile that it can support only a very minute pressure , but by precipitating copper ferrocyanide in the pores of a vessel of porous earthenware, Pfeffer obtained a membrane which could support considerable pressures He was then able to show that the osmotic flow could be stopped by applying a pressure to the solution When a small pressure is applied to the solution, the flow slackens, but does not cease , but when a high pressure is applied, the direction of flow can actually be reversed For a given solution there is one pressure which just causes osmosis to cease and this is termed the OSMOTIC PRESSURE of the solution

**The measurement of osmotic pressure.**—(*a*) *Pfeffer* —The osmotic pressure of a solution can be determined by applying a measured pressure to the solution by mechanical means, and observing the direction of osmosis This was the method adopted by some of the later workers, but Pfeffer (1877) used the simpler arrangement of allowing water to pass into a closed cell, and thus to raise the pressure spontaneously until the equilibrium pressure was reached

Pfeffer's apparatus is shown in Fig 137 The membrane is prepared by filling a porous pot with a dilute solution of copper sulphate and immersing it for a few days in a dilute solution of potassium ferrocyanide

The solutions meet in the pores of the pot and interact to form a thin film of copper ferrocyanide, which clogs the pores.

$$2CuSO_4 + K_4FeC_6N_6 = Cu_2FeC_6N_6 + 2K_2SO_4$$

The pot is well washed with distilled water and then clamped to a pressure gauge containing nitrogen in a calibrated tube over mercury The whole of the space between the pot and the mercury in the gauge is filled with solution, any excess being expelled through the bent glass tube at the top of the headpiece, which is finally sealed off When the pot is immersed in water, the pressure inside it rises slowly, and (if the membrane is satisfactory) a constant pressure is finally reached, which is the osmotic pressure of the solution The magnitude of this pressure can be deduced from the volume of the nitrogen in the left-hand limb

(*b*) *Morse and Frazer* —The preparation of a good membrane is a matter of considerable difficulty, and many failures are experienced Morse and Frazer found that it was necessary to manufacture special pots from suitable clays, in order to secure fine and even pores, which would give the membrane suitable support and enable it to withstand pressures up to 300 atmospheres After removing the air by soaking the pots in water and evacuating, a semipermeable membrane was deposited in the pores by electrolysis This was done by placing a tenth-molecular solution of copper sulphate in the cell, and immersing it in a vessel containing a tenth-molecular solution of potassium ferrocyanide An electric current was passed from a flat platinum anode inside the cell to a cylindrical platinum cathode surrounding it, in order to facilitate the diffusion of the two salts into the pores, where they met and formed the membrane When the electrical resistance of the cell reached a maximum, the current was stopped, the cell was placed in distilled water for some time, and then tested with a solution of cane-sugar The treatment was then repeated, if necessary during a period of several months, until a constant osmotic pressure was observed, showing that the membrane was free from holes

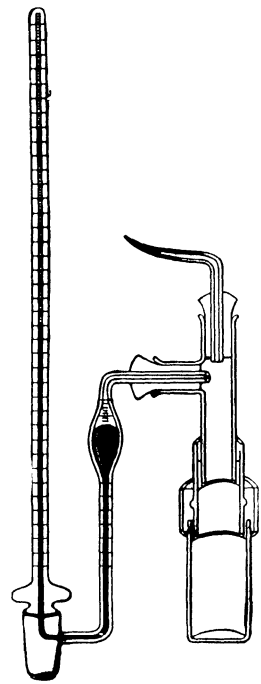


FIG 137 PFEFFER'S APPARATUS FOR THE MEASUREMENT OF OSMOTIC PRESSURE

Morse and Frazer measured the pressures with a gauge similar to that used by Pfeffer. Table 56 contains some of their data for aqueous solutions of cane-sugar It will be seen that the osmotic pressure increases with concentration and with rising temperature, and that the osmotic pressures of the solutions are large Thus, a solution containing 1 gram-molecule ($C_{12}H_{22}O_{11} = 342$) of cane-sugar in 1000 grams of water has an osmotic pressure at the ordinary temperature of more than 25 atmospheres.

TABLE 56 —OSMOTIC PRESSURES OF CANE-SUGAR SOLUTIONS (Morse and Frazer)

| Concentration (Gram-mols per 1000 grams of water) | Osmotic pressure in atmospheres | | | |
|---|---|---|---|---|
| | 0° C | 10° C | 20° C | 25° C |
| 0 1 | 2 462 | 2 498 | 2 590 | 2 634 |
| 0 2 | 4 722 | 4 893 | 5 064 | 5 148 |
| 0 3 | 7 085 | 7 334 | 7 605 | 7 729 |
| 0 4 | 9 442 | 9 790 | 10 137 | 10 296 |
| 0 5 | 11 895 | 12 297 | 12 748 | 12 943 |
| 0 6 | 14 381 | 14 855 | 15 388 | 15 624 |
| 0 8 | 19 476 | 20 161 | 20 905 | 21 252 |
| 1 0 | 24 825 | 25 693 | 26 638 | 27 053 |

(*c*) *Berkeley and Hartley* —Osmotic pressures up to 150 atmospheres were recorded by the Earl of Berkeley and Mr E G Hartley, who used the method of applying to the solution a pressure which was just sufficient

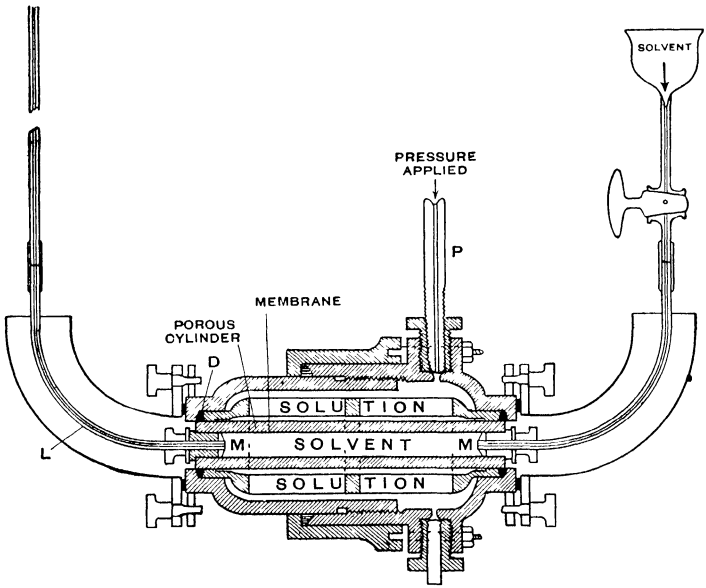



FIG 138 BERKELEY AND HARTLEY'S APPARATUS FOR THE MEASUREMENT OF OSMOTIC PRESSURE

to stop osmosis Their apparatus is shown in diagrammatic form in Fig. 138 The solution was contained in an annular space around a porous cylinder on which a membrane of copper ferrocyanide was deposited Hydraulic pressure was applied to the solution through a side tube and measured by a gauge The inside of the porous vessel contained

water, and osmosis to or from the solution could be detected by the movement of the water-level in the capillary tube shown on the left-hand side of the figure Two pressures were found, of which the lower just allowed a slow flow of water into the solution, whilst the higher caused a slow flow of water from the solution The mean of these two pressures was taken as the osmotic pressure of the solution

Table 57 contains some of the results of Berkeley and Hartley for strong solutions of cane-sugar, together with values interpolated from data obtained by Frazer and Myrick by Morse's method The results obtained by the two methods of measurement are in good accord , the osmotic pressures of these solutions are therefore known with considerable accuracy

TABLE 57 —OSMOTIC PRESSURES OF CONCENTRATED SOLUTIONS

| Concentration (Grams of sugar in 1 litre of solution) | Osmotic pressure in atmospheres at 0° | |
|---|---|---|
| | B and H | F and M |
| 180 1 | 15 48 | 15 59 |
| 300 2 | 29 72 | 29 78 |
| 420 3 | 48 81 | 47 88 |
| 540 4 | 74 94 | 73 06 |
| 660 5 | 111 87 | 109 10 |
| 750 6 | 148 46 | 148 80 |

**The laws of osmotic pressure.**—Pfeffer's experiments were carried out for botanical purposes, and their theoretical importance was not realised until van 't Hoff used them ten years later to demonstrate the close analogy which exists between osmotic pressure and gas pressure This parallelism can be illustrated better, however, by using the later and more accurate measurements of Berkeley and Hartley

(*a*) *Influence of concentration* —Pfeffer found that the osmotic pressure of a solution increased with the concentration of the solute, but van 't Hoff showed that osmotic pressure was directly proportional to the molecular concentration of the solute (compare Boyle's law)

Table 58 shows that Boyle's law, $PV = \text{const}$ , can be extended to solutions by using the symbol $P$ to represent the osmotic pressure in atmospheres and $V$ to represent the volume in litres containing one gram-molecule of the dissolved substance, *e g* 342 grams of cane-sugar

TABLE 58 —OSMOTIC PRESSURE OF AQUEOUS SOLUTIONS OF CANE-SUGAR AT 0° (Berkeley and Hartley )

| Concentration | Osmotic pressure $P$ | Volume $V$ | Product $PV$. |
|---|---|---|---|
| 2 02 gm /litre | 0 134 atm | 169 3 litres | 22 7 |
| 10 0 | 0 66 | 34 2 | 22 6 |
| 20 0 | 1 32 | 17 1 | 22 6 |
| 45 0 | 2 97 | 7 60 | 22 6 |
| 93 75 | 6 18 | 3 65 | 22 5 |

(*b*) *Influence of temperature* —Van 't Hoff showed further that the osmotic pressure of a solution varies with temperature in precisely the same way as the pressure of a gas at constant volume This conclusion is verified in Table 59 from the data of Morse and Frazer

TABLE 59 —VARIATION OF OSMOTIC PRESSURE WITH TEMPERATURE
(Morse and Frazer )

| | | | | |
|---|---|---|---|---|
| $t°$ C - - | 0° | 10° | 20° | 25° |
| $T°$ abs - | 273 | 283 | 293 | 298 |
| $P$ - - | 7 085 | 7 334 | 7 605 | 7 729 |
| $P/T$ - - | 0 02594 | 0 02591 | 0 02595 | 0 02594 |

These data show that the osmotic pressure of a solution containing 0 3 gram-molecule of sugar per 1000 grams of water is accurately proportional to the absolute temperature, since the ratio $P/T$ is constant throughout

(*c*) *Value of the constant* $PV/T$ Since the osmotic pressure is proportional to the concentration of the solution and to the temperature, its magnitude can be expressed by an equation, precisely similar to that used for gases, namely,

$$PV = R'T,$$

where $P$ and $V$ have the meanings given above and $R'$ is a constant Van 't Hoff showed that the constant $R'$ of this osmotic equation has the same value as the $R$ of the gas equation, which for ideal gases is equal to 0 0821 (p 455) in litre-atmospheres We can calculate $R'$ for the osmotic equation from the data in Table 51 The mean value of $PV$ is 22 6 , dividing this by $T = 273$, we find $R' = 0\ 0828$ in good agreement with the value found for gases

These relations may all be summed up in the following law

> *The osmotic pressure of a dilute solution is equal to the pressure which the dissolved substance would exert if it were a gas at the same temperature, and occupied the same volume as the solution*

The Boyle-Charles gas equation, $PV = RT$, may therefore be used to represent osmotic pressures without any change in the magnitude of the fundamental constant $R$

Although this is true for non-electrolytes, electrolytes have been shown (usually by indirect methods) to give higher osmotic pressures than those calculated from the gas equation Van 't Hoff allowed for this abnormality by inserting a factor, $i$, in the osmotic equation, thus $PV = iRT$ The interpretation of this factor in terms of Arrhenius' Theory of Electrolytic Dissociation is discussed in Chap XLIV

**Molecular weights of dissolved substances** —The identity of the osmotic constant of cane-sugar with the gas constant suggests at once that we are dealing with a " molecular " property, which depends on the number of molecules of the solute and not on their nature In other words, we should expect that the osmotic pressures of solutions of equal molecular concentrations would be equal, *i e* that Avogadro's hypothesis could be applied to solutions as well as to gases In general, this is found to be true for dilute solutions, provided that they are not electrolytes. Thus Morse and

Frazer's data for dilute solutions of glucose give for the osmotic constant the normal value $R' = 0.081$, just as in the case of cane-sugar. It can also be shown by indirect methods that the osmotic pressure is independent of the nature of the solvent, as indeed it must be in order to be identical with the gas constant.

This discovery is of great practical importance, since it enables us to determine the molecular weight *in solution* of many substances, such as the sugars, which decompose on heating, and cannot therefore be converted into vapour for the purpose of determining their molecular weights by measurements of vapour-density. For such substances the measurement of osmotic pressure gives us an independent method of finding the molecular weight.

As an example of the calculation of a molecular weight from direct measurements of osmotic pressure we may take an observation of Morse and Frazer on glucose. A solution containing 18 grams per litre had an osmotic pressure of 2.39 atmospheres at 23°. If $M$ is the molecular weight of glucose, $V = M/18$, $P = 2.39$ and $T = 296$. Since $R = PV/T$, we have

$$\frac{2.39 \times M}{18 \times 296} = 0.0821,$$

or

$$M = \frac{0.0821 \times 18 \times 296}{2.39} = 183.$$

The formula $C_6H_{12}O_6$ gives $M = 180$. The equality of osmotic pressures and gas pressures is true, however, only for dilute solutions. As the solutions become more concentrated, the osmotic pressure increases more rapidly than the ideal gas pressure and the product $PV$ increases, just as it does in the case of gases at high pressures (Chap. XXXIV).

**Method of action of semipermeable membranes.**—Some of the earlier investigators thought that the semipermeable membrane acted like a sieve, *i.e.* that it had pores which were small enough to let the water molecules pass but retained the larger molecules of sugar. This view was supported by the fact that an osmotic pressure can be produced by immersing a mixture of propyl alcohol and water either in propyl alcohol or in water. It was suggested that the solution contained hydrated molecules of propyl alcohol, which were too large to pass through the membrane.

Another view is that the solvent dissolves in the membrane and can therefore pass through it by diffusion in either direction, whilst the solute is insoluble in the membrane and cannot therefore pass through it. This view, which is little more than a restatement in other words of the fact that the membrane is semipermeable, is supported by Expt. 102 (p. 515), in which a layer of phenol acts as a semipermeable membrane for an aqueous solution of calcium nitrate, presumably because water is soluble in phenol, whilst calcium nitrate is insoluble.

On this basis, osmosis and osmotic pressure must be attributed to a disturbance by the solute of the equilibrium between the solvent in the membrane and in the liquid layers on either side of it. Exactly as in the case of vapour-pressure, we suppose that the number of molecules of water which *escape* from the membrane into the medium in a given time is the

same on both sides, but that the number of molecules which *enter* the membrane from the medium is, under similar conditions, greater for the pure solvent than for the solution (just as its rate of evaporation would be greater), because the surface of the solution is partially blocked by molecules of the solute, which are insoluble in the membrane and cannot therefore cross the boundary We must then suppose that numerical equality is restored by increasing the *pressure* at the boundary between the solution and the membrane Since osmotic pressure is a " molecular " property, depending only on the number and not on the nature of the molecules of solute, this blocking effect must also be independent of the nature of the solute, and cannot therefore be attributed to van der Waals' forces between the molecules of the solvent and the solute

EXPT 90 **Osmosis through parchment paper**

Fit a diffusion-thimble of parchment paper (Sleicher and Schull's No 579 is suitable) with a rubber stopper carrying a narrow glass tube, which at the inner end is level with the cork Fill the thimble with a strong solution of cane-sugar, insert the stopper, so that no air-bubble is present, and immerse the thimble in water Attach a paper scale, *e g* a strip of squared paper, to the tube, and read the level of the liquid in the tube In the course of half an hour it should rise by one or two centimetres, showing that water is passing inward through the membrane to the sugar solution

EXPT 100 **Preparation of a semipermeable membrane of copper ferrocyanide**

(*a*) Prepare solutions of 6 25 grams of copper sulphate in 250 c c of water, and of 5 5 grams of potassium ferrocyanide in 250 c c Mix a few cubic centimetres of the two solutions in a test tube, and note the chocolate-brown precipitate of copper ferrocyanide, $Cu_2Fe(CN)_6$

(*b*) Half-fill a boiling tube with the ferrocyanide solution Draw out the end of a tap-funnel to a fine point and fill the funnel and stem completely with the copper sulphate solution Lower the stem of the funnel to the bottom of the boiling tube, allow the liquid to rest for a few minutes in order to become completely quiescent, then open the tap and allow the copper sulphate to flow in slowly, so as to form a distinct layer at the bottom of the tube Close the tap and observe the interface The boundary will be seen to be covered with a thin membrane of copper ferrocyanide, which does not grow thicker since neither of the two salts can pass through it On standing, the membrane will gradually bulge downwards, since the ferrocyanide solution has the greater osmotic pressure and will therefore abstract water from the copper sulphate solution below it

(*c*) Half-fill another tube with the copper sulphate solution Dissolve 10 grams of sugar in 50 c c of the ferrocyanide solution, and allow a few drops of this solution to fall from a pipette to the bottom of the copper sulphate solution The drops will be seen to grow by absorption of water As they do so, the membrane bursts and heals itself by fresh deposits of copper ferrocyanide. When the drops have absorbed enough water to make them less dense than the copper sulphate solution, they will rise, still surrounded by the membrane, and float to the surface

**Expt 101 Measurement of osmotic pressure.**

Procure a glass filter with a fused-in glass mat as shown in Fig 139 Moisten the mat thoroughly by sucking water through it Invert the cup and fill the tube with the copper sulphate solution used in the previous experiment, then close the end *A* with a rubber stopper, taking care not to enclose an air bubble Fill *B* with the potassium ferrocyanide solution used in the same experiment Allow three days for the membrane to form and then wash the apparatus thoroughly with water Fill the lower part with a 1% solution of cane-sugar, and insert the stopper, *A*, carrying the bent capillary tube, *C*, on which a paper scale should be mounted The sugar-solution should then fill completely the space below the mat and the capillary tube up to the scale

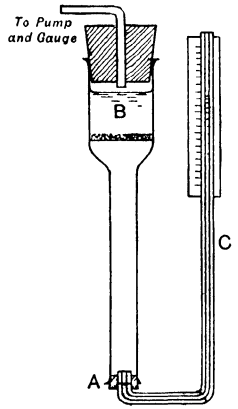



Fig 139 Apparatus for measurement of Osmotic Pressure

Fill the cup, *B*, with water and close the top with a rubber stopper carrying a tube connected to an empty bottle, gauge and water-jet pump Maintain a difference of pressure of about 700 mm between *B* and the open end of *C*, and read the level of the solution in *C* every five minutes for twenty minutes A steady rate of flow of water from *C* to *B* should be recorded Repeat the observations with a difference of pressure of 600, 500 and 400 mm The direction of flow should reverse between 600 and 500 mm Plot the rate of flow against the pressure, and read off the point of zero flow The pressure at which this occurs is the osmotic pressure of the sugar-solution The experiment is, however, a difficult one to carry out, and should not be attempted unless ample time is available

Expt 102 **Preparation of a liquid semipermeable membrane**

Prepare two mutually saturated solutions by shaking phenol and water together in a separating funnel, and running off the lower layer of phenol, after allowing time for the two layers to separate Saturate a concentrated solution of calcium nitrate (50 grams in 100 c c) with phenol in a similar manner Half-fill a boiling tube with the phenol-saturated solution of calcium nitrate Pour on to this a layer, about 5 mm thick, of phenol saturated with water By means of a tap-funnel with a capillary tip, place above this a layer, 3 to 4 cm thick, of water saturated with phenol, and then mark the position of the layer of phenol with a rubber band After a few hours the phenol will be displaced upwards owing to the passage of water into the solution of calcium nitrate.

# CHAPTER XXXVIII

## MOLECULAR WEIGHTS IN SOLUTION

**Lowering of vapour-pressure.**—It has been shown in the previous chapter that the molecular weight of a dissolved substance can be calculated from the osmotic pressure of its solutions. Unfortunately, the measurement of osmotic pressures is a difficult operation, which cannot be carried out as an ordinary laboratory process. Accurate results have therefore been obtained only for a few substances, and for these only in aqueous solutions. This method is therefore of little value for the determination of molecular weights. There are, however, a number of other properties of a solution which are related to its osmotic pressure and which can be determined with moderate ease. Thus, when a non-volatile solute is added to a volatile liquid, the vapour-pressure is lowered to an extent which depends on the osmotic pressure that is developed, the boiling-point of the solution is therefore higher than that of the pure solvent, whilst its freezing-point is usually lower. All these properties can be used under certain conditions in order to determine the molecular weights of dissolved substances.

The earliest experiments on the vapour-pressure of solutions were made by the "barometer" method (Expt. 93), although more accurate and convenient methods have since been discovered. Suppose the pure liquid has a vapour-pressure $p$, and that a solution of known concentration has a vapour-pressure $p - \Delta p$, where $\Delta p$ is the lowering of vapour-pressure. It was shown as early as 1848 by von Babo that, although the value of $p$ increases rapidly with the temperature, the ratio $\Delta p/p$ is the same at all temperatures for a given dilute solution. This ratio is termed the RELATIVE LOWERING OF THE VAPOUR-PRESSURE.

**Raoult's law.**—From a study of the lowering of the vapour-pressure of ether by known concentrations of organic substances, Raoult was able to show that the relative lowering was proportional to the molecular concentration of the solute. Further, when other organic solvents were used, he was able to establish the important rule that

> *The relative lowering of the vapour-pressure of a solution is equal to the ratio of the number of molecules of solute to the total number of molecules in the solution*, or

$$\frac{\Delta p}{p} = \frac{n}{N+n}, \quad \ldots\ldots\ldots \quad (1)$$

where $n$ = number of gram-molecules of dissolved substance,

$N$ = number of gram-molecules of solvent.

Table 60 gives some of Raoult's results for the relative lowering of vapour-pressure of solutions containing 1 gram-molecule of the solute in

100 gram-molecules of solvent, *i e* $n/(N+n) = 0.0099$ It will be seen that the relative lowering of the vapour-pressure $\Delta p/p$ varies from 0 0096 to 0 0108 and in every case is nearly equal to $n/(N+n)$

TABLE 60 —LOWERING OF VAPOUR-PRESSURE OF DIFFERENT SOLVENTS (Raoult)

| Solvent | $\Delta p/p$ | Solvent | $\Delta p/p$ |
|---|---|---|---|
| Water | 0 0102 | Chloroform | 0 0105 |
| Phosphorus trichloride | 0 0108 | Benzene | 0 0106 |
| Carbon disulphide | 0 0105 | Ether | 0 0096 |
| Carbon tetrachloride | 0 0105 | Acetone | 0 0101 |

**Relation between vapour-pressure and osmotic pressure** —The theoretical importance of Raoult's law was demonstrated in 1887 by van 't Hoff, who showed from thermodynamical considerations that the lowering of the vapour-pressure of a dilute solution was related directly to its osmotic pressure by the expression

$$\frac{\Delta p}{p} = \frac{PM}{sRT}\ ,$$

where $P$ = osmotic pressure, $M$ = molecular weight of solvent, $s$ = density of solvent A simple method of deducing this relation between osmotic pressure and the lowering of vapour-pressure is to consider the conditions under which equilibrium may be attained when the solution is enclosed in a vessel provided with a semipermeable membrane $A$, and immersed at constant temperature in a bath of the pure solvent as in Fig 140, where the large outer vessel is supposed to be evacuated

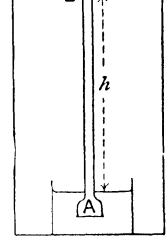



FIG 140 APPARATUS TO ILLUSTRATE THE RELATION BETWEEN VAPOUR-PRESSURE AND OSMOTIC PRESSURE

Let us consider what the vapour-pressures must be in different parts of the system when osmotic equilibrium has been reached, *i e* when the pressure of the column of solution in the tube attached to $A$ is equal to the osmotic pressure First of all, the vapour-pressure $p'$ of the solution at $B$ must be equal to the pressure of water-vapour in the surrounding space at $B$ Thus, if $p'$ were less than the pressure of water-vapour at $B$, water would condense at $B$, this would dilute the solution, so that water would pass out through the semipermeable membrane at $A$, with the result that there would be a continuous flow of water from $B$ to $A$, and consequently the system would not be in equilibrium

Conversely, if $p'$ were greater than the pressure of water-vapour at $B$, water would evaporate from the surface of the solution at $B$, this would

* *N B* —When using this equation express $P$ in dynes and $R$ in ergs (p 456) Try question 3, p 831

increase the concentration of the solution, so that water would be drawn in through the semipermeable membrane, and there would be a continuous flow up the tube from $A$ to $B$. Only when the vapour-pressure of the solution is equal to the pressure of water-vapour at $B$ is there no flow of water through the tube, and only then is the system in equilibrium.

The pressure of water-vapour at $B$ is not equal, however, to the vapour-pressure of pure water $p$, at the surface of the bath at $A$, for, just as the pressure of the atmosphere diminishes as a mountain is ascended, so the pressure of water-vapour in the vessel falls off slightly at higher levels. The difference in the pressures of water-vapour at $A$ and $B$ must be equal to the hydrostatic pressure of a column of vapour of height $h$ equal to the height of the column of liquid within the tube which measures the osmotic pressure, *i e*

$$p - p' = \Delta p = hd,$$

where $d$ is the density of the vapour.

Let $M$ be the molecular weight of the solvent, then the volume occupied by $M$ grams of vapour at a pressure $p$ and at the absolute temperature $T$ is $V = RT/p$. The density of the vapour is therefore

$$d = \frac{M}{V} = \frac{Mp}{RT} \qquad (2)$$

Since the density of a dilute solution can be taken as equal to that of the pure solvent $s$, the osmotic pressure $P$ of the solution is given by the equation

$$P = hs \quad \text{or} \quad h = \frac{P}{s} \qquad (3)$$

Now we have seen that $\Delta p = hd$, so that, putting in the values of $h$ and $d$ given by (2) and (3),

$$\Delta p = \frac{P}{s}\frac{Mp}{RT} \quad \text{or} \quad \frac{\Delta p}{p} = \frac{MP}{sRT} \qquad (4)$$

This equation gives the relation between the osmotic pressure of the solution and the relative depression of the vapour-pressure.

To calculate the osmotic pressure we have from the gas laws,

$$P = n\frac{RT}{V'},$$

where $V'$ is the volume of the solvent which contains 1 gram-molecule of the solute, or, since $V' = \frac{NM}{s}$, $P = \frac{nsRT}{NM}$.

Putting this in (4), we have

$$\frac{\Delta p}{p} = \frac{M}{sRT}\frac{nsRT}{NM} = \frac{n}{N}, \qquad \ldots \quad (5)$$

which is identical with Raoult's equation (1) when the solution is dilute, because then $N + n$ is nearly the same as $N$.

**Ideal solutions.**—In deducing Raoult's law from van 't Hoff's theory of osmotic pressure, we have assumed (1) that the *density* of the vapour

varies only to a negligible extent throughout the column, although the variations of *pressure* are of fundamental importance, and (ii) that the density of the solution is equal to that of the pure solvent, (iii) that the osmotic pressure obeys the gas laws These assumptions are nearly true for dilute solutions when $\Delta p$ is small compared with $p$, but they are no longer valid for stronger solutions This method of deduction is therefore very limited in its scope On the other hand, Raoult's law, unlike van 't Hoff's application of the gas laws to osmotic pressures, can be applied just as readily to strong as to weak solutions, and therefore provides a very valuable criterion for detecting the existence of ideal solutions, and for measuring the extent to which the properties of other solutions deviate from the ideal An IDEAL SOLUTION can in fact be defined as *a solution which obeys Raoult's law over the whole range of concentrations from* 0 *to* 100%, *and* (it is generally added) *over a considerable range of temperatures*

**Static and dynamic methods for measuring vapour-pressures** —The experimental methods used in measuring vapour-pressures may be divided into two groups, which are termed " static " and " dynamic " methods In the " static " methods, the vapour-pressure of the solvent or solution is balanced against a column of liquid, whilst in the " dynamic " methods a stream of gas is passed through the liquid, and its vapour-pressure is deduced from the rate of evaporation

(*a*) *Static method* —The barometer method (Expt 93) is a typical static method but cannot usually be applied for the determination of molecular weights, since the depressions of vapour-pressure are too small to be measured with accuracy A number of methods have been devised in which the *difference* in vapour-pressure between the pure solvent and the solution is balanced against a column of the solvent and so can be measured with fair accuracy The method of Menzies (Expt 103) is of this type

(*b*) *Dynamic methods* —In the " dynamic " method a stream of air is bubbled successively through (i) the solution, (ii) the pure solvent, and (iii) an absorbing agent which retains the vapour of the solvent The air, and all the vessels, must be kept at the same temperature , and the rate of bubbling must be slow enough to ensure that the gas is saturated with vapour in each vessel It can then be assumed that the vapour-pressure of the solutions is proportional to the loss in weight of (i), whilst the vapour-pressure of the pure solvent is proportional to the gain in weight of (iii) The depression of the vapour-pressure is proportional to the loss in weight of (ii), so that

$$\frac{\Delta p}{p} = \frac{\text{loss in weight of (ii)}}{\text{gain in weight of (iii)}},$$

the change in the weight of (i) being used only as a check The experimental details for the application of this method to aqueous solutions are described in Expt 104

**Elevation of the boiling-point.**—Since the boiling-point is the temperature at which the vapour-pressure is equal to atmospheric pressure, it is obvious that a solution, of which the vapour-pressure has been lowered by

the addition of a non-volatile solute, must boil at a higher temperature than the solvent This elevation of the boiling-point was studied by Raoult, and later by Beckmann, who improved the experimental methods and obtained results of considerable accuracy The apparatus developed by Beckmann is shown in Fig 141

The " Beckmann thermometer," which passes through the neck of the vessel, $A$, is designed for measuring small differences of temperature at various points of the thermometric scale It has a scale of 6°, which is graduated to 0 01° , but the quantity of mercury in the bulb can be adjusted for use with solvents of widely different boiling-points by causing it to overflow into an auxiliary bulb or reservoir at the top of the thermometer The mercury in the reservoir can be recovered by heating the thermometer until the thread reaches up and touches the surplus mercury, which can then be drawn back into the bulb as the thread retreats

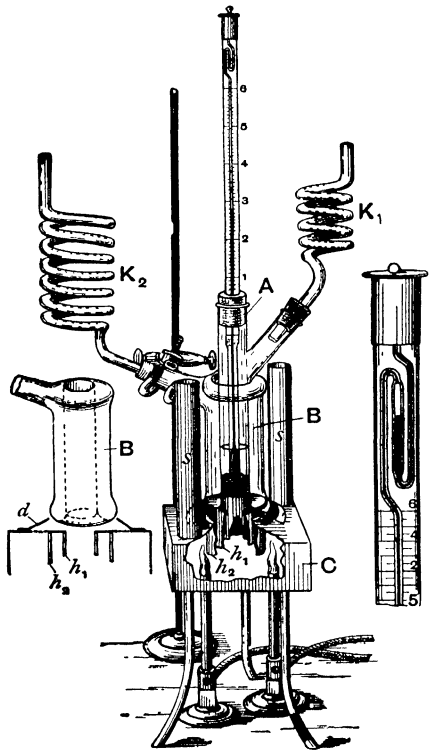



FIG 141 BECKMANN'S BOILING-POINT APPARATUS

The principal difficulty in determining the boiling-point with accuracy is to eliminate superheating of the liquid, by getting a steady and quiet evolution of bubbles For this purpose the boiling-tube, $A$, of Beckmann's apparatus, which carries the Beckmann thermometer and an air-condenser, $K_1$, is surrounded by a vapour-jacket, $B$, with an air-condenser, $K_2$, in which the pure solvent is boiled and condensed A platinum peg passes through the bottom of the tube, $A$, to conduct heat to the liquid , and the bubbles which rise from it are broken up by a layer of glass or agate beads, in order to produce good stirring and steady boiling Even with these precautions considerable skill and experience are required to get good results with this apparatus

A more effective method of preventing superheating is to raise the solution to the boiling-point by blowing into it a stream of vapour of the solvent This method is used in Landsberger's apparatus, which is shown in Fig 142 In this apparatus, vapour from the flask, $A$, passes

into the solvent in the graduated vessel, *B*, and condenses there, its latent heat of evaporation raising the liquid to boiling-point, which is read from the thermometer The surplus escapes through the orifice, *C*, and is condensed by the condenser, *D* A weighed quantity of solute is then added and the boiling-point redetermined The volume of the solution is read from the scale, after first removing the thermometer and delivery tube The experiment is usually repeated once or twice with further quantities of solute

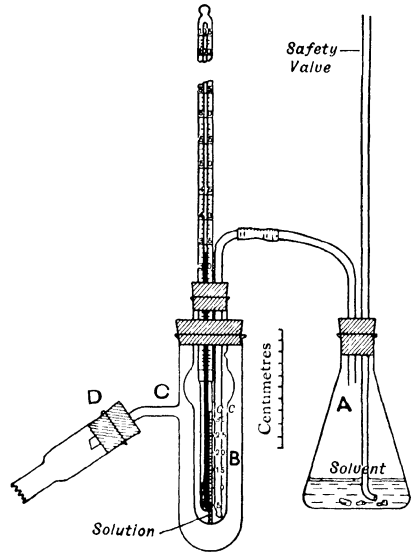



FIG 142 LANDSBERGER'S BOILING-POINT APPARATUS

A still better method has been devised by Cottrell, in which the bulb of the thermometer is raised above the surface of the solution and is continually bathed by a stream of the solution forced up a bent tube by bubbles of vapour A simple form of Cottrell's apparatus is described in Expt 105*b*

**Laws of elevation of boiling-point.**—A study of the boiling-points of solutions by the methods described has shown that

(*a*) the rise of boiling-point $\Delta T$ is proportional to the concentration, provided that the solutions are dilute ,

(*b*) for a given solvent, the same rise of boiling-point is produced by dissolving 1 gram-molecule of any substance in a fixed quantity of solvent

These relations may be expressed by the formula

$$\frac{M\,\Delta T}{c} = K,$$

where $M$ is the molecular weight of the dissolved substance, $\Delta T$ the rise in boiling-point, and $c$ the weight of substance dissolved in 1000 grams of solvent The constant $K$ is termed the MOLECULAR ELEVATION OF THE BOILING-POINT or the EBULLIOSCOPIC CONSTANT of the solvent It represents the rise of boiling-point which would be produced by dissolving 1 gram-molecule of a solute in 1000 grams of the solvent if the ratio observed in dilute solutions were maintained It is sometimes more convenient to measure the *volume* of the solvent (as in Landsberger's method), than its weight The concentration is then expressed in grams per 1000 c c , and the molecular elevation of the boiling-point is indicated by the symbol $K'$. Obviously $K' = K/d$, where $d$ is the density of the solvent at its

boiling-point Table 61 gives the values of $K$ and $K'$ found experimentally for a number of common solvents.

TABLE 61.—MOLECULAR ELEVATION OF THE BOILING-POINT

$K$ = rise in B P for 1 gram-molecule per 1000 grams of solvent

$K'$ = " " " " " C C " "

| Solvent | $K$ | $K'$ | $\frac{0.002T^2}{l}$ |
|---|---|---|---|
| Water - - - | 0 52° | 0 54° | 0 515° |
| Ether - - - | 2 11 | 3 03 | 2 09 |
| Chloroform - - | 3 88 | 2 77 | 3 80 |
| Ethyl alcohol - - | 1 15 | 1 56 | 1 19 |
| Acetone - - - | 1 72 | 2 22 | 1 72 |
| Benzene - - - | 2 57 | 3 15 | 2 61 |

**Relationship between molecular elevation and latent heat of vaporisation.**—Van 't Hoff showed by thermodynamical arguments that the elevation of the boiling-point depends on the osmotic pressure of the solution, and that the constant $K$ can be predicted from the physical properties of the solvent by the formula

$$K = \frac{0.002T^2}{l}$$

Here $T$ is the boiling-point on the absolute scale and $l$ the latent heat of evaporation per gram of solvent The fourth column in Table 61 gives the values of $K$ calculated from measurements of the latent heat It will be seen that they are in good agreement with the values found experimentally

**Depression of the freezing-point.**—The freezing-point of a substance is generally lowered by the presence of a foreign substance This effect was studied quantitatively by Raoult, who found that the laws for the depression of the freezing-point were the same as for the elevation of the boiling-point Thus, the lowering of the freezing-point is proportional to the concentration of the dissolved substance, and the depression is the same for one gram-molecule of a large number of solutes dissolved in 1000 grams of a given solvent Thus,

$$K = \frac{M\,\Delta t}{c},$$

where $K$ is described as the MOLECULAR DEPRESSION OF THE FREEZING-POINT or the CRYOSCOPIC CONSTANT of the solvent, $M$ is the molecular weight of the solute, and $\Delta t$ the depression of the freezing-point brought about by a concentration of $c$ grams of solute in 1000 grams of solvent Table 62 gives the values found experimentally for this constant, together with values calculated (in the same manner as in the case of the

* Raoult's constant $K$ was defined using $c$ as the concentration per 100 gm of solvent The values of $K$ recorded in the literature are therefore often 10 times as large as the numbers given in Tables 61 and 62.

boiling-point constant) from the latent heat of fusion of the solvent, by means of the formula

$$K = \frac{0.002T^2}{L},$$

where $T$ is the freezing-point on the absolute scale and $L$ is the *latent heat of fusion* of 1 gram of the solvent The table shows that this formula gives results in good agreement with those found by direct measurement

TABLE 62 —MOLECULAR DEPRESSION OF THE FREEZING-POINT '

| Solvent | F P | $K$ | $\frac{0.002T^2}{L}$ |
|---|---|---|---|
| Water - - - | 0° | 1 85° | 1 86° |
| Benzene - - - | 5 5 | 5 12 | 5 07 |
| Acetic acid - - | 17 | 3 9 | 3 82 |
| Phenol - - - | 39 | 5 3 | 5 05 |
| Naphthalene - - | 80 | 6 9 | 6 95 |
| Camphor - - - | 175 | 40 0 | — |

**Experimental methods.**—Beckmann's apparatus for use with solvents of low melting-point is shown in Fig 143 The pure solvent in known amount is placed in the inner tube, *A*, which is separated by a narrow air-jacket, *B*, from the cooling bath, *C* The presence of this air-jacket ensures a uniform temperature round the inner tube, *A*, which otherwise might be subjected to different temperatures in different parts The solvent is allowed to supercool a little below its freezing-point and is then stirred vigorously to start crystallisation As crystals separate, the temperature rises and remains steady at the freezing-point A weighed pellet of solute is added by the side tube, and dissolved by removing *A* and warming in a suitable bath The freezing-point is then redetermined, care being taken to minimise the supercooling by stirring vigorously, since otherwise a considerable amount of solvent crystallises out and the concentration of the solution becomes greater than that calculated from the weights of solvent and solute

The freezing bath in *C* should be at a temperature which is about 5° lower than that of the freezing-point of the solvent in *A*, since a larger difference in temperature produces too rapid cooling for an accurate determination of freezing-point For water as solvent, ice and salt should be placed in *C*, for acetic acid or benzene, ice and water , for phenol,

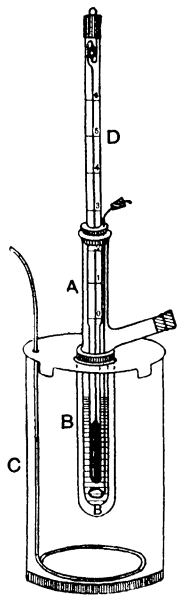



FIG 143 BECKMANN'S FREEZING-POINT APPARATUS

* See footnote, p 522.

cold water, etc When a solvent with a small molecular depression is used, a Beckmann thermometer is required to give accurate readings, with naphthalene, however, quite good results can be obtained with a thermometer divided in 0 1°

**Limitations of the methods for determining molecular weights in solution** —The methods described in this chapter allow of the determination of the molecular weights of a large number of substances which cannot be vaporised without decomposition, but which can be dissolved in suitable solvents These methods are therefore used constantly in organic chemistry, in order to determine the molecular formula of a compound after its empirical formula has been found by analysis For this purpose a rough value of the molecular weight is usually sufficient Most of the methods described will give numbers within 5% or less of the true value

Measurements of freezing-points are, however, generally preferred to measurements of vapour-pressure or boiling-point, since they are more easily made and are generally more accurate Thus Beckmann's freezing-point apparatus is capable of giving results which are often within 1% of the theoretical value

The experimental conditions which must be observed in order to ensure accurate results have already been indicated, *e g* the use of sufficiently sensitive thermometers, the avoidance of superheating in the boiling-point method, or of too great a supercooling in the freezing-point method, etc Moreover, scrupulous care must be taken to ensure that the apparatus is clean and dry and that the materials used are as pure as possible There are, however, a number of theoretical conditions which are equally important Thus we have seen that the simple formulae only hold accurately for very dilute solutions More complex formulae can be developed to deal with more concentrated solutions, but, if errors up to 5% in the molecular weight may be tolerated, the simple formulae may be used for solutions containing up to half a gram-molecule of solute per 1000 grams of solvent

A second condition is that the solute must remain entirely in the solution, and not escape from it into the vapour or solid phase, since this would give rise to just the same sort of errors as the use of a leaky membrane in the measurement of osmotic pressure When using the boiling-point and vapour-pressure methods this means that the solute must be non-volatile, or in practice that the boiling-point of the solute should be at least 100° higher than that of the solvent

In the freezing-point method this condition means that the solvent and solute must not form solid solutions (p 545), but that the crystals which separate must consist of pure solvent only In some cases, where solid solutions are formed, there is a *rise* in freezing-point on adding the solute instead of a depression An example of this, in solutions of $\beta$-naphthol in naphthalene, is given in Expt 106*b* Fortunately, in organic chemistry, it is usually only compounds of similar constitution which form solid solutions, so that by choosing a suitable solvent, or by using several solvents of different chemical character, this source of error can be avoided.

**Abnormal molecular weights.**—(*a*) *Association* —Many substances give molecular weights in solution which are greater than those corresponding to the usual formula Thus acetic acid in benzene has a molecular weight of nearly 120 instead of 60, as calculated from the formula $CH_3$ CO OH Chloracetic acid in naphthalene behaves similarly (Expt 106*b*) In these cases the molecular weight often varies with the solvent, and with the concentration of the solution Thus, observations of the freezing-point of solutions of acetic acid in water give a normal molecular weight of 60 for the acid In general, we may suppose that there is an equilibrium between complex and simple molecules of the acid, *e g*

$$(CH_3 \quad CO \quad OH)_2 \rightleftharpoons 2CH_3 \quad CO \quad OH,$$

and that this equilibrium is influenced by the solvent, concentration and temperature This view is supported by the fact that the vapour-density of acetic acid in the neighbourhood of the boiling-point is much greater than the normal value, *i e* even the vapour appears to be associated

Substances which behave in this manner are said to be " associated ' in solution In general, acids, hydroxy-compounds and amines exhibit this phenomenon These are precisely the substances which have anomalous physical properties in the liquid state (p 77)

(*b*) *Dissociation* *—In contrast to the associated compounds described above, most salts in aqueous solution give values for the molecular weight which are lower than those deduced from the formulae of the salts This is accounted for by their dissociation into ions, *e g*

$$KCl \rightleftharpoons K^+ + Cl'$$

Thus, at extreme dilutions the apparent molecular weight of potassium chloride is only half of that calculated from the formula KCl The theory of electrolytic dissociation which is used to explain these results is discussed more fully in Chap XLIV

It is interesting to note that similar abnormalities are found amongst vapour-densities although these are not caused by ionisation Thus, at 400° C and 760 mm pressure, the vapour of ammonium chloride has only half the density expected for the formula $NH_4Cl$, and this is explained by assuming that it is completely broken up into $NH_3 + HCl$

EXPT 103 **Determination of lowering of vapour-pressure by Menzies' method.**

The apparatus is shown in Fig 144 The outer bulb, *E*, contains the solvent The inner tube, *C*, contains the solution and is graduated in cubic centimetres The lowering of the vapour-pressure $\Delta p$ is measured by the depression of the level of the liquid in the inner tube *D*, which is etched with a millimetre scale

Connect to a condenser, *B*, half-fill the outer bulb, *E*, with pure acetone, and boil vigorously for a few minutes to remove dissolved gases Fill the inner vessel, *C*, about two-thirds full of this boiled-out liquid and then

* When a decomposition is reversible it is described as DISSOCIATION , if it is brought about by heat it is called THERMAL DISSOCIATION to distinguish it from ELECTROLYTIC OR IONIC DISSOCIATION

determine the zero reading in the following manner With the liquid in the bulb boiling steadily, remove the stopper, *A*, and partly close the screw-clip leading to *B* Vapour will then blow through the solvent in the inner vessel

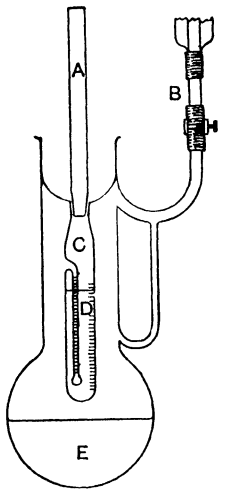



FIG 144 MENZIES' APPARATUS FOR MEASURING THE LOWERING OF VAPOUR-PRESSURE

After a minute or two, place *A* loosely in position until it is warmed up, then insert *A* and open *B* at once to its full extent Keep the liquid boiling steadily in the outer bulb and read the level on the graduated tube, shaking the apparatus occasionally In 5 to 10 minutes the level of liquid in the inner tube should be steady, and a little higher than the surrounding liquid owing to capillary rise

Repeat these operations until a constant value is found Add a weighed pellet of *p*-nitrotoluene (about 0 3 gram) to *C*, and repeat the blowing-through as described above Since the solution has a lower vapour-pressure than the solvent, the meniscus will come to rest below the level of the liquid in the inner tube The difference between the reading for the solution and for the pure solvent gives the lowering of the vapour-pressure in millimetres of the solution Read also the final volume of the solution

Since the density of acetone at its boiling-point is 0 7518, and the density of mercury is 13 6, $\Delta p = x \times 0\ 7518 - 13\ 6$ mm Hg, where $x$ is the lowering observed in millimetres of acetone

If $m$ grams of pure nitrotoluene are dissolved in $V$ c c of acetone, then $n = m/M$, where $M$ is the molecular weight to be found. Also

$$N = \frac{V \times 0\ 7518}{58}$$

But $\Delta p/p = n/N$ approximately and $p = 760$, so that

$$\frac{x \times 0\ 7518}{13\ 6 \times 760} = \frac{m \times 58}{M \times V \times 0\ 7518},$$

or

$$M = \frac{m \times 58 \times 13\ 6 \times 760}{xV \times (0\ 7518)^2} = 1{,}061{,}000\ \frac{m}{xV}$$

EXPT 104 **Determination of molecular weights by lowering of vapour-pressure Dynamical method.**

For this experiment the following apparatus is required

2 gas wash-bottles
2 Liebig potash-bulbs
3 calcium chloride U-tubes

The wash-bottles are filled with a 5% solution of cane-sugar ; the Liebig bulbs are filled with water and weighed accurately, and the weight of two

of the calcium chloride tubes is also determined, the third is merely a guard tube The apparatus is connected together in the following order, using tightly-fitting pressure-tubing

Wash-bottles
Liebig potash bulbs
Weighed calcium chloride tubes
Guard tube
Aspirator

The whole apparatus is immersed in a tank of water in order to maintain a constant temperature, and the inlet of the first wash-bottle is connected to a length of composition tubing, immersed in the same bath, so that the air drawn through the system by the aspirator is brought to the temperature of the bath

The aspirator is started at a speed which draws 1 or 2 bubbles per second through the bulbs, and is allowed to run for 1½ to 2 hours The Liebig bulbs and calcium chloride tubes are then removed, dried carefully and weighed If the air is passed slowly enough, it becomes saturated at the vapour-pressure of the solution in the wash-bottles, and takes up more moisture in the bulbs when it comes in contact with pure water The whole of this is absorbed in the calcium chloride tubes Hence

$$\frac{\text{Lowering of vapour-pressure}}{\text{Vapour-pressure of pure solvent}} = \frac{\Delta p}{p}$$
$$= \frac{\text{Loss in weight of Liebig bulbs}}{\text{Gain in weight of } CaCl_2 \text{ tubes}}$$

From the loss and gain in weight, and the composition of the solution, calculate the molecular weight of cane-sugar

EXPT 105 **Determination of molecular weights by elevation of the boiling-point.**

(*a*) *Landsberger's method* —Read carefully the account of this method on pp 520-521, then fit up the apparatus as shown in Fig 142, using a centigrade thermometer which is graduated in tenths of a degree Clamp the flask *A* so that it can be heated over wire gauze on a tripod stand, and place in it about 120 c c of the solvent together with a few pieces of porous pot to assist ebullition Pour 5 c c of the solvent into the tube *B* and record its steady boiling-point by passing in vapour from *A*, then add a weighed quantity of one of the solutes recommended below, and redetermine the boiling-point when the volume of the solution is about 15 c c Immediately remove the burner from under the generator and the thermometer and delivery tube from *B*, and read the volume of the solution Reassemble the apparatus, pass in more vapour and remeasure the boiling-point when the volume of the solution has increased to about 20 c c , then carefully measure the volume of the latter as before A further reading

ıt about 25 c c may then be taken The following solvents and quantities )f solute are recommended

(ı) water with urea (ı 5 gm ) or oxalic acid (3 o gm ) ,

(ıı) acetone with acetanilide (ı 5 gm ) or *p*-nitrotoluene (ı 5 gm )

Calculate the molecular weight of the solute on the assumption that one gram-molecular weight of it will raise the boiling-point of 1000 c c of water by o 54°, and 1000 c c of acetone by 2 22°

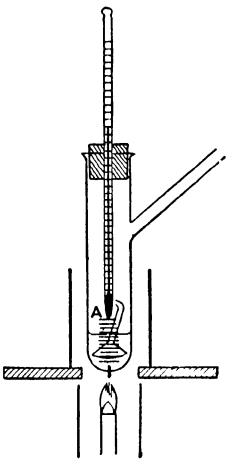



FIG 145 COTTRELL'S APPARATUS FOR MEASURING THE ELEVATION OF THE BOILING-POINT

(*b*) *Cottrell's method* —The apparatus required is shown in Fig 145 The essential feature is an inner funnel-tube, which collects the bubbles rising from a few fragments of porous pot (or better, from a platinum wire sealed through the bottom of *A*) and pumps a stream of liquid and vapour over the bulb of a thermometer supported one or two centimetres above the surface of the liquid The vessel *A* is calibrated in cubic centimetres with the funnel in position

Fit a thermometer, reading to o ı° or o 05° over the range from 50° to 100°, in the cork closing *A* Place 12-15 c c of pure acetone in *A* and boil, using screens (as indicated in the figure) to shield the tube and burner from draughts It will be found that above a certain rate of boiling the thermometer attains a steady temperature Stop the flame and, as soon as bubbling ceases, read the volume This gives the volume of solvent in the ube, and ignores that present in the condenser attached to the side arm Remove the cork and drop in rapidly about o 5 gram of *p*-nitrotoluene or ıcetanilide Boil the solution and read the thermometer at intervals until t is again steady Calculate the molecular weight as in Landsberger's nethod

EXPT 106 **Determination of molecular weights by the freezing-point method.**

(*a*) *Camphor in benzene* —The tube *A* (Fig 143) is removed and weighed* vithout the thermometer and stirrer, and then reweighed with about 20 gm of pure " Analar " benzene If the latter is not available, the pure ıquid can be obtained by freezing thiophene-free benzene, decanting the supernatant liquid when two-thirds of the benzene has solidified, and melting the crystalline residue The freezing-point of this specimen is then letermined as indicated on p 523 About o 4 gram of camphor is then ıdded, and the freezing-point is redetermined Three or four other readings are taken after adding further quantities of camphor The molecular

*Alternatively, 25 c c of benzene may be measured out with a clean dry )ipette ($K = 5\ 79°$ per 1000 c c ), this is much quicker than the weighing nethod

weight is calculated by substituting the experimental values in the equation.

$$M = \frac{Kc}{\Delta t},$$

where $K$ = molecular depression of the freezing-point = 5·12° for benzene,
$c$ = grams of camphor per 1000 grams of benzene,
$\Delta t$ = observed depression of the freezing-point

(*b*) *Solutions in naphthalene*.—Fit a stout boiling tube with a cork carrying a thermometer (50° to 100° in 0·1° or 0·05°) and a stirrer of thin glass rod. Mount the tube by means of a cork in the neck of a wide-mouthed bottle, which thus forms an air-jacket round the tube. Weigh out 10 grams of naphthalene, and place it in the tube. Remove the latter from its jacket, and then heat in a bath of boiling water.

(i) Fix the thermometer and stirrer in position, and, when all the naphthalene is melted, remove from the bath, dry the outside of the tube rapidly and insert in the bottle. Stir steadily and watch the thermometer. It will fall at first a little below the freezing-point, but will rise as crystals begin to separate and finally reach a maximum. The maximum reading is taken as the freezing-point of the pure solvent. Make two determinations in this way, reading the temperature to the nearest 0·01°.

(ii) Add a weighed pellet of *p*-nitrotoluene (about 0·7 gram) and repeat the determination of the freezing-point. A second determination should be made on the same mixture, stirring when the temperature falls 0·1° below the value first found, in order to avoid excessive supercooling. If desired, a second weighed pellet can be added and the determination repeated.

(iii) Starting with fresh solvent for each substance, make similar observations with camphor, monochloracetic acid, and β-naphthol.

(iv) The melting-point of naphthalene is 80°, and its latent heat of fusion is 35·6 cal. per gram. Use these figures in order to calculate the molecular depression of the freezing-point, and compare it with the value found experimentally in (ii).

# CHAPTER XXXIX

## THE PHASE RULE

**Equilibrium between ice, water and steam.**—(*a*) *Vapour-pressure curve*, —It has been stated in Chap XXXIV (p 482) that the vapour-pressure of a liquid increases rapidly as the temperature rises Thus, if we plot the vapour-pressure of water against temperature, we obtain the curve which is represented diagrammatically by the line *OC* in Fig 146 (The pressures are not drawn to scale in this diagram ) This curve shows a series of pressures and temperatures at which water and its vapour can

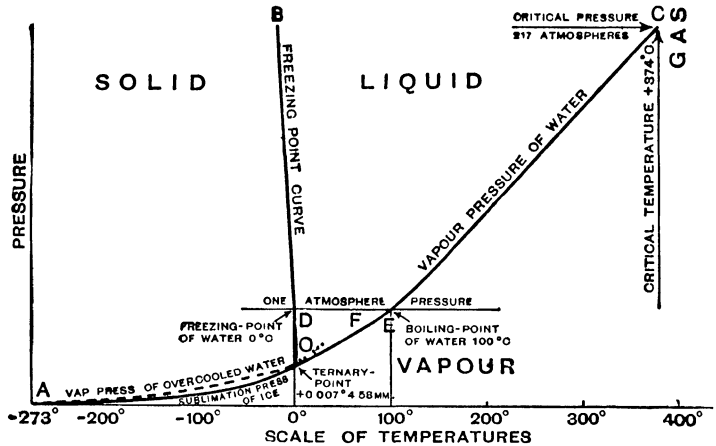



FIG 146 EQUILIBRIUM-DIAGRAM FOR WATER (NOT DRAWN TO SCALE)

co-exist, *e g* in a vessel from which all the air has been removed At higher pressures, corresponding with points *above* the line *OC*, the vapour would condense to a liquid , on the other hand, if the pressure were reduced, corresponding to points *below* the line *OC*, the whole of the liquid would boil and pass into vapour At the upper limit of temperature, the curve terminates at the critical-point *C*, since above this temperature liquid and vapour are indistinguishable, and the term vapour-pressure has then no meaning At the lower limit, the curve would normally terminate at the point *O*, at which water freezes to ice , but if the water could be prevented from freezing, the vapour-pressure curve could be continued below the freezing-point, as is indicated by the broken line *OA*, which is labelled " vapour-pressure of overcooled water "

(*b*) *The sublimation-pressure curve* —Even after freezing, however, ice has a small vapour-pressure, as is proved by the fact that snow can disappear in frosty weather, when the temperature is never high enough to melt it This vapour-pressure is described as the SUBLIMATION-PRESSURE of the solid, and, although small, can be measured It is then found that the curve representing the vapour-pressure of ice at different temperatures is not a continuation of the curve *OC*, which represents the vapour-pressure of water, but falls off more steeply as shown by the full line *OA* This line cuts the curve *OC* at *O* The point *O* therefore shows the freezing-point of water, not at atmospheric pressure, but under the vapour-pressure of melting ice This pressure is about 4 58 mm , and since the freezing-point of ice is lowered to the extent of about 1° for each additional 140 atmospheres, it will be raised slightly when the pressure is reduced from 760 to 4 58 mm The point *O* therefore represents a temperature about +0 007° C higher than the freezing-point under atmospheric pressure

(*c*) *The freezing-point curve* —Starting from *O*, we can draw a third curve *OB* on the diagram, to represent the effect of pressure on the freezing-point This curve, although very different in direction from the two vapour-pressure curves, is in some ways very similar to them, since it shows the temperature at which *ice* and *water* are in equilibrium at different pressures, just as the other curves show the conditions under which *water* and *water-vapour*, or *ice* and *water-vapour*, can co-exist Since the effect of pressure is small, the curve *OB* is nearly parallel to the vertical axis of pressure Moreover, since the freezing-point of water is *lowered* by pressure, the curve slopes upwards towards the left , but in the case of most other substances the freezing-point is *raised* by increasing the pressure, and the curve slopes upwards towards the right

**Equilibrium-diagrams.**—An **equilibrium-diagram** of the same general type as Fig 146 can be drawn for any pure substance These diagrams contain a number of *areas*, *lines*, and *points of intersection*, of which the significance may now be discussed

(*a*) *Areas* —The water-diagram of Fig 146 is divided by the curves *OA*, *OB*, *OC*, into three areas, which we can label *solid*, *liquid* and *vapour* If we bring the substance to the pressure and temperature represented by any point in the area bounded by *AOB*, it will pass completely into the *solid* state No liquid can remain since the temperature is lower than the freezing-point represented by the line *OB* , and any vapour initially present will be condensed, since the pressure is higher than the sublimation-pressure of the solid as represented by the line *OA* Similarly it will be seen that, at pressures and temperatures represented by points in the area *BOC*, we can have only *liquid*, and in the area below *AOC* only *vapour*

Note that in each case we can vary both the pressure and the temperature over a considerable range without trespassing into a different area Thus it is possible for the solid state to persist alone over a wide range of temperatures and pressures, provided that the temperature is not raised above the limit imposed by the line *OB*, or the pressure lowered below the limit imposed by the line *OA* In the same way, the liquid persists

alone throughout its own area, until we reach the boundary *OB* of the 'solid" area or *OC* of the "vapour" area

(*b*) *Boundary lines*.—The curve *OC* represents a series of temperatures and pressures at which liquid and vapour are in equilibrium If, at a point *E* on this curve, we keep the temperature constant and slightly *increase the pressure*, the vapour will all be condensed to liquid If, on the other hand, we slightly *decrease the pressure* the liquid will all evaporate or boil away to vapour Again, if we keep the pressure constant and *raise the temperature* slightly, the liquid (being above its boiling-point) will all evaporate , but if, on the other hand, we *lower the temperature* slightly, the vapour will all condense Hence, if we wish to have a system containing both liquid and vapour we cannot vary both pressure and temperature, because if we choose one of these quantities, the other is fixed by the position of the corresponding point on the curve *OC* Similarly the curve *OA* indicates that at each temperature there is only one pressure at which solid and vapour are in equilibrium with each other, whilst the line *OB* imposes a similar limitation in reference to the co-existence of liquid and solid

(*c*) *The central point*.—The point *O* has a special significance It represents the only temperature and pressure at which *solid*, *liquid* and *vapour* can co-exist If we vary either the temperature or the pressure from the rigidly determined values for this unique point, one of the three states of aggregation will disappear Thus, if the temperature be raised without altering the pressure, we shall pass into the vapour area and the solid and liquid will both change into steam Conversely, if the temperature be lowered, the vapour will condense to ice and all the water will freeze, since we shall have passed into the area which belongs exclusively to the solid It is possible, however, by varying temperature and pressure together, to move along one of the lines *OA*, *OB*, *OC* of the figure, and so to preserve *two* of the three states of aggregation

**The phase rule.**—The conclusions arrived at from a consideration of Fig 146 are set out in Table 63

TABLE 63.—EQUILIBRIUM OF PHASES

| System | Conditions for equilibrium | Number of independent variables | Method of representation on pressure-temperature diagram |
|---|---|---|---|
| Solid<br>Liquid<br>Vapour | Pressure and temperature can be varied independently | 2 | Area |
| Solid-liquid<br>Liquid-vapour<br>Solid-vapour | Pressure and temperature can be varied, but not independently | 1 | Line |
| Solid-liquid-vapour | Neither the pressure nor the temperature can be varied | 0 | Point |

The number of conditions (in this case pressure or temperature) which can be varied independently of one another without changing the type of system is shown in the third column It will be seen that the number of independent variables decreases as the system becomes more complex This is one example of a very general rule, formulated in 1874 by Willard Gibbs, which is usually termed the PHASE RULE It applies to any system which is in equilibrium, and defines the number of variables which can be chosen independently without altering the system The Phase Rule is written algebraically thus

$$F = C - P + 2$$

(i) $P$ represents the number of PHASES A phase is *a part of a system which is marked off from other parts by a boundary at which there is an abrupt change of physical properties* Thus, in the system represented by Fig 146, ice, water, and steam are separate phases

(ii) $C$ is the number of COMPONENTS This is defined as *the least number of substances in terms of which the composition of each of the phases may be defined* In the system considered there is only one component, represented by the chemical formula, $H_2O$, since all three phases can be produced from water only It would be wrong to regard hydrogen and oxygen as two components since the amount of either present determines exactly the amount of the other If, however, we were working at very high temperatures, at which water dissociates, and we put an excess of hydrogen or oxygen into the gas phase, then it would be necessary to write the number of components as two (namely hydrogen and oxygen) when applying the phase rule

(iii) $F$ is the number of DEGREES OF FREEDOM of the system, that is, *the number of factors which can be varied independently without altering the number of phases* For a one-component system, only the pressure and temperature can be varied , hence the maximum number of degrees of freedom is 2 If there are two components, we can also vary the relative proportions of each, and hence a new degree of freedom, namely concentration, appears In more complex systems each new component introduces another concentration which can be varied, and hence gives another possible degree of freedom

**Systems of one component.**—If we apply the phase rule to the system ice-water-steam, we can confirm the statements in Table 63

(i) *Bivariant systems* —Systems which possess two degrees of freedom are known as BIVARIANT SYSTEMS When there is only one component the number of phases in a bivariant system is reduced to one, for

$$F = C - P + 2,$$
$$2 = 1 - P + 2,$$
$$\therefore\ P = 1,$$

This agrees with the fact, already noticed, that when the system consists entirely of ice, or of water, or of vapour, both pressure and temperature can be varied independently

(ii) *Univariant systems* —Systems with only one degree of freedom are described as UNIVARIANT SYSTEMS When only one component is present,

univariant systems are produced whenever two phases are formed, since in this case,

$$F = C - P + 2 = 1 - 2 + 2 = 1$$

Three different univariant systems are represented in Fig 146 by the lines *OA*, *OB* and *OC*

(iii) *Non-variant systems* —Systems with no degrees of freedom are described as NON-VARIANT SYSTEMS In systems containing only one component they are formed whenever three phases appear simultaneously, since in this case,

$$F = C - P + 2 = 1 - 3 + 2 = 0$$

The point *O*, which represents the unique temperature and the unique pressure at which solid, liquid and gas are in equilibrium, is also termed a TRIPLE POINT, since three phases are there in equilibrium

**Stable, metastable and unstable equilibrium.**—The three *areas AOB*, *BOC*, *COA*, the three *lines OA*, *OB*, *OC* and the *point O*, represent all the systems which are in STABLE EQUILIBRIUM If, however, water is carefully cooled below the normal freezing-point, *e g* in the form of drops suspended in an oil of equal density, it does not solidify immediately, but may remain for a long time in the condition of a supercooled liquid Such water has a vapour-pressure represented by the broken line *OA*, which is a continuation of the curve *CO* If, however, a crystal of ice is brought into contact with the water, it freezes immediately, and, as a result, the vapour-pressure falls from a point on the broken line *OA* to a point on the full curve *OA* below it The supercooled water is said to be in a METASTABLE STATE, by which we mean that it can persist for an indefinite period of time, but is always in danger of passing over (often on very slight provocation) into some more stable condition On the other hand, if we attempt to heat ice above its normal melting-point, the solid becomes UNSTABLE and melts immediately, so that the dotted curve *OF* has never been realised experimentally

**Polymorphism** —Many substances exist in more than one crystalline form, so that two or more solid "phases" are possible Such substances are said to be DIMORPHIC, TRIMORPHIC or POLYMORPHIC, according as there are 2, 3 or many solid phases Thus, " soluble " sulphur crystallises in *four* polymorphic forms (Fig 72, p 247), the most familiar of which are RHOMBIC SULPHUR and PRISMATIC SULPHUR In the same way ammonium nitrate is known in not less than *five* polymorphic forms, which can be distinguished by their crystalline structure, density, etc , and ice under varying pressures appears in *six* different solid forms In the case of *elements* this phenomenon is generally described as ALLOTROPY, although this term is also used to include many cases of isomerism and polymerism, in which the nature of the molecules (as well as their arrangement in the crystal-lattice) is different in the different forms

**Polymorphism of sulphur.**—In general the various solid forms of a substance appear as separate solid phases The simple diagram (Fig 146) which shows the equilibrium of solid, liquid and vapour will therefore no longer represent all the possible conditions of equilibrium and a more complex diagram is necessary In the case of sulphur, two of the four crystalline forms, namely NACREOUS SULPHUR and TABULAR SULPHUR,

are only known in a metastable state, and need not therefore be considered at the present stage We must, however, allow for the possible existence of all or any of the following four phases, (i) rhombic sulphur (solid), (ii) prismatic sulphur (solid), (iii) liquid sulphur, and (iv) sulphur vapour The phase rule then enables us to lay down certain limiting conditions, and to predict what types of system may exist , but it is still necessary to make experiments in order to fix the positions and intersections of the lines on the equilibrium diagram

(*a*) First of all let us see if a system of four phases can exist Putting $P=4$, $C=1$, we find from the Phase Rule $F=-1$ Since this is an impossible value (a negative degree of freedom has no meaning), we conclude that there is no temperature and pressure at which all the four phases can be in equilibrium

(*b*) Secondly, we can choose four systems of three phases, namely

| 1 | 2 | 3 | 4 |
|---|---|---|---|
| Rhombic | Rhombic | Rhombic | Prismatic |
| Prismatic | Prismatic | Liquid | Liquid |
| Liquid | Vapour | Vapour | Vapour |

For each of these systems the Phase Rule gives $F=0$, that is, they will be represented by a point The equilibrium-diagram should therefore show four triple points

(*c*) Similarly, there are six possible systems of two phases, namely

| | | |
|---|---|---|
| 1 Rhombic<br>Prismatic | 2 Rhombic<br>Liquid | 3 Prismatic<br>Liquid |
| 4 Rhombic<br>Vapour | 5 Prismatic<br>Vapour | 6 Liquid<br>Vapour |

For each of these the Phase Rule gives $F=1$ These six univariant systems may, therefore, be represented by six lines on the diagram, since they are bivariant systems for which $F=2$

**Equilibrium-diagram for sulphur.**—It should be noted that although these systems may all exist, the schemes set out above represent the maximum number of possible systems, and all of them may not be found to exist when a particular substance is studied In the case of sulphur, however, they can all be realised experimentally, and are shown on the equilibrium-diagram in Fig 147 The area marked $S_\alpha$ shows the range of pressures and temperatures within which *rhombic sulphur* can exist, the area $S_\beta$ indicates the range of existence of *prismatic sulphur*, and the remaining areas show the range of existence of liquid and vapour The line *OP* shows the rise of the vapour-pressure of rhombic sulphur with temperature. *PQ* shows the vapour-pressure of prismatic sulphur at different

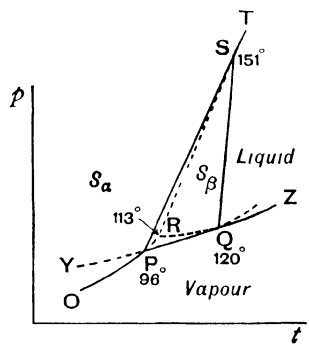



FIG 147 EQUILIBRIUM-DIAGRAM FOR SULPHUR

The diagram is not drawn to scale, and the vapour-pressures do not represent values experimentally determined

temperatures These two curves intersect at 96°, *P* This is, therefore, the only temperature at which sulphur vapour can exist in equilibrium with both prismatic and rhombic sulphur It is therefore the *triple point* for the rhombic, prismatic and vapour phases The point *P* also represents the TRANSITION TEMPERATURE for rhombic and prismatic sulphur when the external pressure is equal to their vapour-pressure, *i e* the temperature at which the two polymorphs are in stable equilibrium with one another under a given pressure Thus, if rhombic sulphur is kept a little above 96°, it is converted slowly but completely into prismatic sulphur, whilst at temperatures a little below 96° prismatic sulphur changes completely to rhombic sulphur Above 96°, therefore, rhombic sulphur is metastable and below 96° prismatic sulphur is metastable

The change from rhombic to prismatic sulphur takes place very slowly even above 96° It is therefore possible, by heating rapidly, to realise the metastable part *PR* of the vapour-pressure curve of rhombic sulphur up to the melting-point of rhombic sulphur at *R* (113°) The curve *PR* illustrates the rule that the vapour-pressure of a metastable form is always *greater* than that of the stable form of a substance at a given temperature The point *R* is a second triple point, for the three phases *rhombic sulphur*, *liquid*, and *vapour* , but since rhombic sulphur is always liable to change into prismatic sulphur at this temperature, it is a metastable triple point, which can only be realised precariously, when the conditions happen to be favourable The vapour-pressure curve of prismatic sulphur ends at its melting-point *Q* (120°) , this is the third triple point, and shows the conditions under which *prismatic sulphur*, *liquid* and *vapour* are in stable equilibrium with one another

The curve *PS* shows the change of the transition temperature with pressure, and the curve *QS* the change in the melting-point of prismatic sulphur with pressure Both changes are influenced by pressure (like the melting-point of ice, p 531), because they are accompanied by alterations of volume The two curves intersect at *S* (151°), which is a fourth triple point, since it shows the conditions under which *rhombic*, *prismatic* and *liquid* sulphur are in stable equilibrium with one another, without any vapour-phase Above *S* only two phases can exist, viz rhombic sulphur and liquid , the conditions for their equilibrium are given by the curve *ST*

**Enantiotropic and monotropic substances** —Rhombic and prismatic sulphur can be changed into one another reversibly by suitable alterations in the physical conditions Thus at atmospheric pressure rhombic sulphur changes into prismatic sulphur when the temperature is raised above 96°, whilst the reverse change takes place belo *r* 96° Dimorphous solids such as these are called ENANTIOTROPIC, in order to indicate that the change of state can be effected *in either direction* In other cases one or more of the polymorphic forms is metastable under all conditions, *e g* nacreous and tabular sulphur (p 247) are metastable at all temperatures, and change non-reversibly into rhombic or prismatic sulphur, according as the temperature is below or above 96° Solids of this type are described as MONOTROPIC, in order to indicate that the change of state can be effected *in one direction only*. White phosphorus is also mono-

tropic because it changes spontaneously, or in presence of a trace of iodine, into red (or metallic) phosphorus and can then be reproduced only by the drastic process of distillation

**Determination of transition-points** —Transition-points may be determined by making use of the changes in physical properties (such as *colour*, *density* and *solubility*) which occur when one crystalline form of a substance changes into another Thus, the temperature at which red cuprous mercuric iodide passes into the black variety can be observed by heating some of the solid in a melting-point tube in a bath of water

When there is a difference of density between the two forms, as in the case of rhombic and prismatic sulphur, a dilatometric method can be used The dilatometer (Fig 148) resembles a thermometer, of which the bulb is partly filled with the solid in question A liquid which does not dissolve or react with the solid fills the free spaces in the bulb and a portion of the calibrated stem As the dilatometer is heated, the meniscus moves slowly as a result of the thermal expansion of the solid and liquid in the bulb, but, when a transition takes place, a large change of volume is recorded within a narrow range of temperatures in the neighbourhood of the transition-point An example of the use of the dilatometer in fixing transition-points is given in Expt 107



Fig 148
Dilatometer

The transition from one form of a solid to the other generally takes place only slowly, and, if crystals of the new phase are not already present, it may not start until the substance is heated or cooled considerably above or below the transition-point The dilatometric method, therefore, works best when about equal parts of the two solid forms are present By measuring the rate of expansion or contraction at temperatures a little below and above the transition-point, two temperatures can be found at one of which there is a slow expansion and at the other a similar slow contraction The mean of these two temperatures is taken as the transition-point

**Systems of two components** —When a system contains two components it may have as many as three degrees of freedom, for we can vary (i) temperature, (ii) pressure, and (iii) composition, usually expressed as the concentration of one or other of the two components A full diagrammatic representation of such a system would need a solid model, in which pressure, temperature and concentration would be plotted along three axes at right angles to one another For most purposes, however, we can use a series of plane diagrams, in which temperature and concentration are plotted against one another for a series of constant pressures, or pressure and concentration are plotted against one another for a series of fixed temperatures These plane diagrams are sections of the solid model, and the solid model can be built up quite readily from a series of such plane diagrams When only solid and liquid phases are present,

small changes of pressure have very little effect on the system, and a single temperature-concentration diagram can be used to express the results of all measurements, except those made under greatly increased pressures

**Salt hydrates** —A familiar example of a two-component system is that of a salt and water In the present section the behaviour of salt hydrates will be considered and that of salt solutions deferred, because they can be discussed under the reduced phase rule (p 540)

All hydrated salts have a water vapour-pressure, so that they lose water when placed in an evacuated globe, and yield the next lower hydrate or the anhydrous salt The loss of water continues until the water vapour-pressure in the gaseous phase is equal to the DISSOCIATION PRESSURE (p 540) of the hydrate, which corresponds exactly with the vapour-pressure of a liquid When equilibrium has been reached there are three phases, viz water vapour, solid hydrate and lower hydrate or anhydrous salt The phase rule predicts that this system must have one degree of freedom

$$F = C - P + 2, \quad C = 2, \quad P = 3, \qquad F = 1$$

Therefore, if we fix the temperature, the water vapour-pressure should have a fixed value, independent of the relative quantities of the two solid phases This is borne out by the experimental figures for a mixture of copper sulphate and water given in Table 64 The table also shows that the vapour-pressure remains constant only as long as there is no change in the nature of any of the phases Thus, if water is removed continuously from the first system given in the table, the liquid phase of saturated solution is eventually replaced by the solid trihydrate, $CuSO_4,3H_2O$ When this hydrate appears, the vapour-pressure drops abruptly from 290 mm to 234 mm , and remains constant at the latter figure until the removal of more water results in the production of a new system, viz

$$CuSO_4,3H_2O/CuSO_4,H_2O/\text{vapour}$$

Finally, further dehydration leads to the system,

$$CuSO_4,H_2O/CuSO_4/\text{vapour},$$

which has only a small vapour-pressure at 78°

TABLE 64 —VAPOUR-PRESSURES OF MIXTURES OF COPPER SULPHATE AND WATER AT 78° C

| System | Mols of water per mol of $CuSO_4$ | Vapour-pressure mm Hg | Phases |
|---|---|---|---|
| 1 | 6 05<br>5 13 | 289<br>291 | Saturated solution<br>$+CuSO_4,5H_2O$ + vapour |
| 2 | 4 13<br>3 71<br>3 41 | 234<br>238<br>232 | $CuSO_4,5H_2O$<br>$+CuSO_4,3H_2O$ + vapour |
| 3 | 2 61<br>2 10<br>1 75 | 142<br>145<br>148 | $CuSO_4,3H_2O$<br>$+CuSO_4,H_2O$ + vapour |

When the figures in Table 64 are plotted, a stepped curve is obtained, in which a sudden decrease in vapour-pressure is shown at the composition of each new hydrate Hence a study of the vapour-pressures of hydrated salts during dehydration makes it possible to detect intermediate hydrates and to determine their composition

**Deliquescence and efflorescence.**—The stability of a hydrate in air depends upon (i) the pressure of water-vapour in the air, and (ii) the vapour-pressures of the hydrate and of its saturated solution The partial pressure of water-vapour in the air may be taken as about 14 mm on an average day , but in frosty weather it is lower, and on " muggy " days when the weather is warm and wet, it is higher than this value The vapour-pressures of three common salts and of their saturated solutions are shown in Table 65

TABLE 65.—VAPOUR-PRESSURES OF HYDRATES AND OF SATURATED SOLUTIONS AT 20°

| | Hydrate | Saturated solution |
|---|---|---|
| $CaCl_2,6H_2O$ - - - | 2 5 mm | 7 5 mm |
| $CuSO_4,5H_2O$ - - - | 5 1 mm | 16 0 mm |
| $Na_2SO_4,10H_2O$ - - | 16 3 mm | 16 6 mm |

It will be seen from the table that a saturated solution of calcium chloride has a lower water vapour-pressure than that of the water-vapour in ordinary air This salt therefore absorbs moisture from the air until a dilute solution is formed with a water vapour-pressure approximately equal to that of the water-vapour in the atmosphere This process of liquefaction by absorption of moisture is described as DELIQUESCENCE On the other hand, Glauber's Salt, $Na_2SO_4,10H_2O$, is said to be EFFLORESCENT, because the crystals crumble in the air, owing to loss of moisture, giving rise to the anhydrous salt, since the vapour-pressure of the hydrate exceeds 14 mm The blue crystals of copper sulphate, $CuSO_4,5H_2O$, however, do not deliquesce, because the vapour-pressure of the saturated solution is *greater* than 14 mm , and they do not effloresce because the vapour-pressure of the pentahydrate is much *less* than 14 mm , so that the hydrate is perfectly stable in the air The trihydrate and monohydrate, which have much smaller vapour-pressures than the pentahydrate, will absorb water from the air to form the pentahydrate, but the product will remain dry and solid, because the pressure of water-vapour in the air is too small to convert the pentahydrate into a saturated solution

In general we can predict that only the more soluble salts will deliquesce, because a large concentration of solute is required to lower the vapour-pressure of water below that normally present in the air, but, when the air is saturated with water-vapour, salts which are only sparingly soluble may become deliquescent On the other hand, in the dry conditions of a severe winter when nearly all the water-vapour has been frozen out of the air, even calcium chloride does not deliquesce, and the hydrated crystals may actually become efflorescent

**Dissociation pressures.**—Many systems are known in which the gaseous phase is formed by substances other than water An important example of this type is the system $CaCO_3$, CaO, and $CO_2$ This system is made up of two components, since the composition of any phase can be expressed in terms of CaO and $CO_2$ The Phase Rule predicts that when the system is in equilibrium, the pressure of carbon dioxide must have a fixed value at each given temperature Thus

$$C = 2, \qquad P = 3(CaO,\ CaCO_3,\ CO_2),$$
$$\therefore\ F = C - P + 2 = 2 - 3 + 2 = 1$$

If less than this amount of carbon dioxide is present, some of the calcium carbonate will dissociate, if it is exceeded some of the carbon dioxide will combine with the lime to form chalk It is important to note that the DISSOCIATION PRESSURE is independent of the *amount* of the solids, and is therefore the same for chalk with a trace of lime as for lime with a trace of chalk

TABLE 66.—DISSOCIATION PRESSURE OF CALCIUM CARBONATE

| Reaction | Temperature | Dissociation pressure |
|---|---|---|
| $CaCO_3 \rightleftharpoons CaO + CO_2$ | 525° | 18 mm Hg |
| | 750° | 100 ,, |
| | 840° | 342 ,, |
| | 910° | 755 ,, |
| | 926° | 1022 ,, |

**Condensed systems.**—Since liquids and solids have only a small compressibility, the effect of pressure on the equilibrium of systems containing only liquids and solids is very small Thus, as long as the pressure is higher than the vapour-pressure of the system, so that no gaseous phase exists, small variations of pressure will not alter appreciably the form of the curves which represent the relationships between the other two variables, namely the temperature and the composition Such a system is termed a CONDENSED SYSTEM For condensed systems we may write a " reduced " phase rule,

$$F' = C - P + 1$$

This will give the remaining degrees of freedom which the system can possess, in addition to the pressure, which, as we have seen, is always capable of independent variation as long as it is higher than the vapour-pressure It is convenient to use this rule in the discussion of the following liquid-solid systems

1 **Components do not form a compound and are not miscible in the solid state.**—(*a*) *Potassium iodide and water* —If a very dilute solution of potassium iodide is cooled, the temperature falls until ice begins to separate just below 0° The removal of water as ice raises the concentration of the solution, so that the freezing-point falls progressively Fig 149 shows that the freezing-point curve $AC$ is cut at $C$ by another curve

*BC*, which represents the solubility of potassium iodide in water The solution is therefore saturated with iodide at this point, and further cooling causes the deposition of solid iodide as well as ice The temperature now remains constant until solidification is complete, because the composition of the liquid phase remains the same This is in harmony with the reduced phase rule, which predicts that an equilibrium-mixture of ice, salt and solution has no degrees of freedom

$$F = C - P + 1, \quad C = 2, \quad P = 3,$$
$$\therefore \quad F = 2 - 3 + 1 = 0$$

The point $C$ is called the EUTECTIC POINT It has two coordinates, namely the EUTECTIC TEMPERATURE, which is the lowest freezing-point

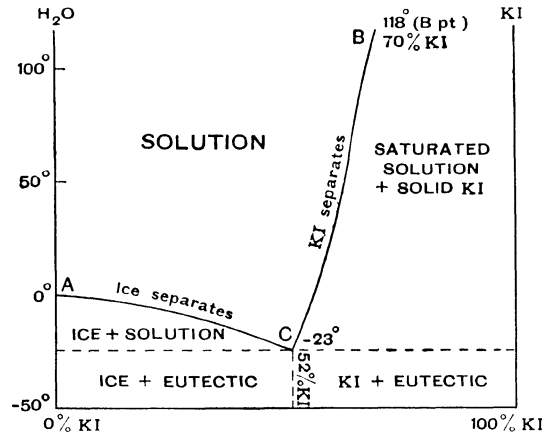



FIG 149 FREEZING-POINT AND SOLUBILITY DIAGRAM FOR POTASSIUM IODIDE AND WATER

of the system, and the EUTECTIC COMPOSITION, which gives the composition of the saturated solution of minimum freezing-point of the solid which separates from it

Freezing-point graphs of the above type are common in binary systems When the components were a salt and water, the eutectic solid was formerly described as a " cryohydrate," because it was thought that the solid was a chemical compound of salt and water, since, like a pure compound, it had a constant melting-point This view is incorrect because these solids are not homogeneous when viewed under the microscope, and their composition cannot usually be represented by a simple chemical formula

(*b*) *Zinc and cadmium* —Binary mixtures of metals sometimes give freezing-point composition graphs similar to the iodide-water example given above Thus the freezing-point of zinc is progressively lowered by the addition of cadmium, as shown by the line *AC* (Fig 150) and similarly that of cadmium by zinc, as shown by the line *BC* The two curves

intersect at the point $C$, which is therefore the eutectic point, since the freezing-point cannot be lowered further by the addition of either metal If liquid of this composition is cooled, zinc and cadmium will crystallise out side by side, and the temperature will remain constant until solidification is complete A liquid of any other composition will deposit nearly pure zinc* or cadmium, according to whether its composition is to the left or right of $C$ The temperature will fall progressively until the eutectic point is reached, and then will remain constant whilst zinc and cadmium crystallise out together Thus if liquid of composition $X$ (Fig 150) is cooled, the temperature falls until $Y$ is reached, when nearly pure zinc starts to crystallise out The removal of zinc from the liquid increases the concentration of cadmium, so that the temperature falls until the eutectic

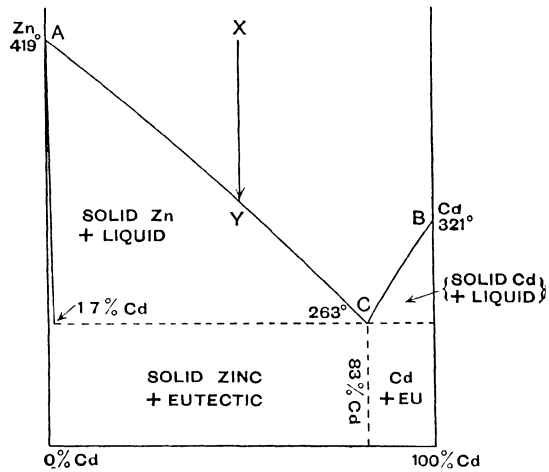



FIG 150 FREEZING-POINT DIAGRAM FOR ZINC AND CADMIUM

point is reached , it then remains constant until solidification is complete If the resulting solid is now slowly heated, melting will start when the temperature reaches that of the eutectic point $C$ The temperature will remain stationary until all the cadmium has passed into the liquid phase, and will then rise as indicated by $CY$ At $Y$ the liquid has the same composition as the mixture and hence melting will be complete

The freezing-point diagram given in Fig 150 can be determined by plotting cooling curves of the pure molten metals and of known mixtures of them. The procedure is similar to that in Expt 110, except that in this case the temperatures are too high for a mercury thermometer, and so must be measured by means of a thermocouple

2. **Components form compounds, but are not miscible in the solid state.** —(*a*) *Hydrates* —The freezing-point curves of binary mixtures provide valuable information with regard to the formation of compounds Thus Fig 151 shows the presence of six eutectics separated by five maxima

* Cadmium forms a solid solution with zinc up to a maximum of 1 7% Cd

in mixtures of water and sulphur trioxide The five maxima occur at compositions represented by the formulae

$$SO_3,5H_2O, \quad SO_3,3H_2O, \quad SO_3,2H_2O, \quad SO_3,H_2O, \quad 2SO_3,H_2O$$

We may therefore conclude that they represent the freezing-points of these compounds On this assumption, the progressive addition of sulphur trioxide to pure water first results in the formation of the compound, $H_2SO_4,4H_2O$, which depresses the freezing-point of water until at $-75°$ the eutectic point is reached The addition of more sulphur trioxide then raises the freezing-point, because the composition of the

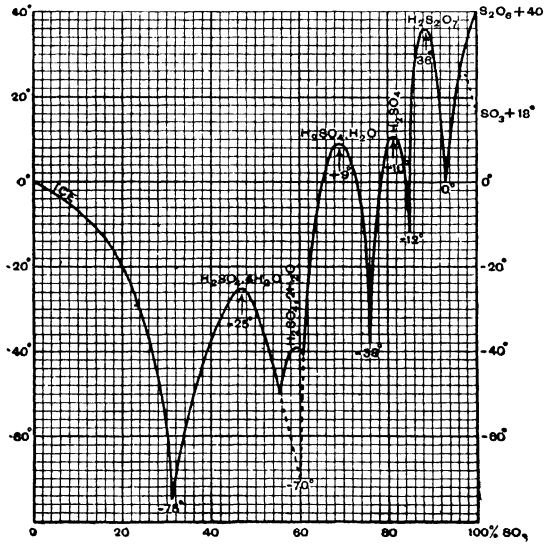



FIG 151 FREEZING-POINT DIAGRAM FOR SULPHUR TRIOXIDE AND WATER

mixture is approaching that of the hydrate, $H_2SO_4,4H_2O$ The addition of yet more sulphur trioxide results in the formation of a series of eutectics and maxima, the latter representing the freezing-points of the hydrates, $H_2SO_4,2H_2O$, $H_2SO_4,H_2O$, $H_2SO_4$ and $H_2S_2O_7$

It will be observed that all the maxima in Fig 151 are rounded This is due to the fact that none of the hydrates is completely stable, so that on melting they dissociate partially into their components, which act like impurities and depress the melting-point The sharpness of the maximum, therefore, gives a rough indication of the stability of the compound

In some cases a hydrate decomposes before its melting-point is reached, so that the usual maximum cannot be observed A change in the degree of hydration is then indicated by a break in the freezing-point or solubility curve Thus, when anhydrous sodium carbonate is added gradually to water, the freezing-point first falls to a eutectic at $-2°$ (Fig 136, p 504)

It then rises *towards* a maximum which, *if it existed*, would represent the freezing-point of the hydrate, $Na_2CO_3,10H_2O$ This maximum, however, is never reached, because the *decahydrate* decomposes at 32° into the *heptahydrate*, $Na_2CO_3,7H_2O$, and this in its turn decomposes at 35° into the *monohydrate*, $Na_2CO_3,H_2O$, without reaching its own melting-point The curve for $Na_2CO_3,H_2O$ slopes towards the left, showing that the solubility of this hydrate decreases with increasing temperature It stops short abruptly at the boiling-point of a saturated solution of the monohydrate, and could only be extended to the right-hand side of the diagram by working at pressures high enough to prevent the escape of steam at temperatures up to the melting-point of pure $Na_2CO_3$ The

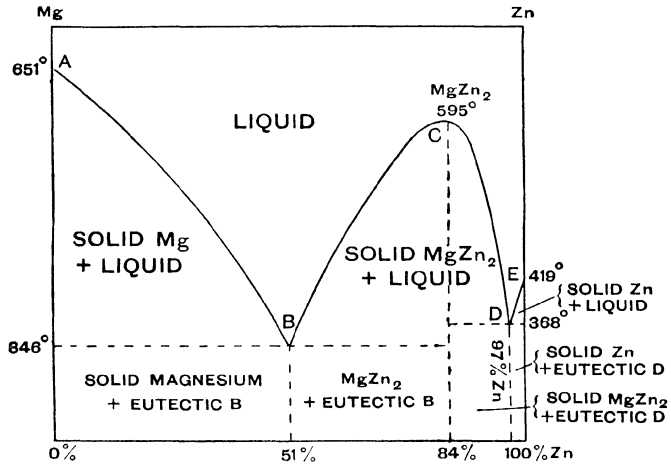



FIG 152 FREEZING-POINT DIAGRAM FOR MAGNESIUM AND ZINC

dotted lines represent metastable systems, which can only be realised in the absence of crystals of the stable phase (cf sulphur, p 536)

The equilibrium-diagram for sodium sulphate and water is also given in Fig 136 The decahydrate changes abruptly into the monohydrate at 32 383° The intermediate heptahydrate, $Na_2SO_4,7H_2O$, is metastable at all temperatures and is only formed in the absence of nuclei of the decahydrate

The reduced phase rule ($C-P+1=F$) tells us that binary systems can never have more than three phases in equilibrium , this is indicated by the above diagrams, where a liquid phase is never in equilibrium with more than two solid phases

(*b*) *Alloys* —Binary mixtures of some metals give equilibrium-diagrams of a similar type to that of sulphuric acid, thereby indicating the existence of compounds Thus the diagram for mixtures of magnesium and zinc (Fig. 152) shows that these metals form a compound, $MgZn_2$ Pure magnesium and the compound, $MgZn_2$, separate out at the eutectic *B*, whilst the compound and pure zinc crystallise out at the eutectic *D*

3 **Components form solid solutions but no compounds.**—So far we have only considered those binary mixtures which do not form solid solutions When this occurs, the diagrams are often extremely complicated, particularly if the components also form compounds Fig 153 represents the equilibrium-diagram for the isomorphous metals, platinum and gold, which are miscible in all proportions, both in the liquid and in the solid state, but do not form a compound, so that the system is relatively simple

There are two curves, the LIQUIDUS and the SOLIDUS The liquidus shows the temperature at which a liquid of given composition begins to deposit crystals, whilst the solidus gives the composition of the solid which is deposited at this temperature Thus, if a melt of composition $a$ is cooled, crystallisation will start at $b$, but the solid will have the composition represented by the point at which a horizontal line from the liquidus at $b$ intersects the solidus at $c$ Since the solid is richer in platinum than the liquid from which it crystallises, the residual liquid becomes richer in gold as crystallisation proceeds, and the freezing-point of the liquid falls along the liquidus curve towards the freezing-point of pure gold The gold-content of the solid phase also increases, as shown by the thin horizontal lines connecting the solidus and liquidus curves At $d$ the composition of the solid is the same as that of the original liquid mixture Solidification would then be complete if infinite time could be allowed for the crystals of the solid to become uniform in composition In practice, however, the composition of the crystals ranges from $c$ in the centre to nearly pure gold on the outside

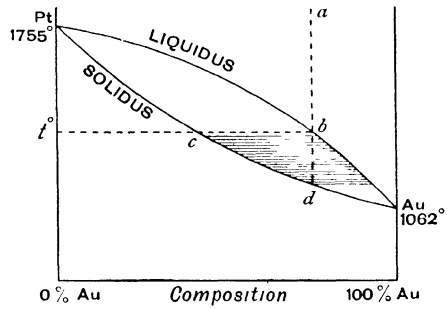



FIG 153 FREEZING-POINT DIAGRAM FOR PLATINUM AND GOLD

Since gold and platinum are completely miscible in the solid state, only one solid phase is possible The maximum number of phases (apart from the vapour) is therefore two, viz solid and liquid, and the system then has only one degree of freedom

$$F = C - P + 1, \quad C = 2, \quad P = 2, \quad \therefore \quad F = 1$$

Thus, at a given temperature, $t°$, the compositions of both phases are fixed, viz $c$ and $b$ Conversely if the composition of the solid phase is fixed, both the temperature and the composition of the liquid phase are also fixed.

EXPT 107 **Determination of the transition-point of sulphur by the dilatometer method.**

Some 30% sulphuric acid is boiled to expel dissolved air, and allowed to cool in a stoppered flask, which it fills completely About 10 grams of powdered roll sulphur are placed in a test tube and freed from imprisoned air by mixing with some of the boiled-out acid, in order to avoid the subse-

quent liberation of bubbles, which would invalidate the readings of volume The test tube is next filled to the top with the acid and a rubber stopper with one hole is inserted It is then heated to 80° in a bath of calcium chloride solution (50 grams of chloride to 100 grams of water), which has a high boiling-point During this preliminary heating the acid is allowed to overflow into the bath A piece of capillary tubing, 2 mm in diameter and 50 cms long, with a right-angled bend near one end, is then pushed into the stopper as shown in Fig 154 and attached to a centimetre scale The delay in inserting the capillary tube ensures that the level of the sulphuric acid will be near the beginning of the scale when measurements are made at 90° The bath is then heated and the reading on the scale is taken for every degree from 90° to about 100° The temperature must be raised very gradually because the transition from rhombic to prismatic sulphur is usually very slow to start The scale readings are plotted against the temperature and the transition-point is indicated by a sharp break in the curve More accurate results are obtained if measurements are also made as the test tube is cooled The transition temperature is then deduced from the mean value of the temperatures at which breaks occur on the heating and cooling curves

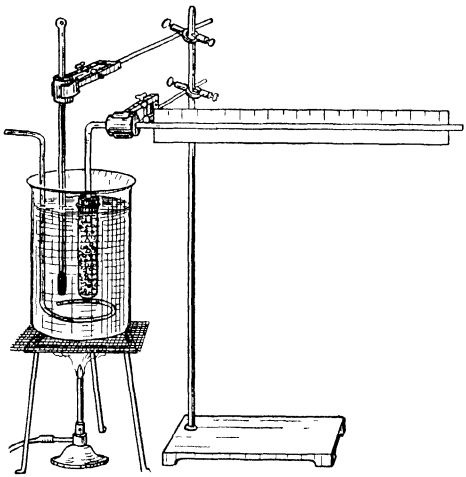


FIG 154 DILATOMETER FOR DETERMINING THE TRANSITION-POINT OF SULPHUR

EXPT 108 **Solubility curve for Glauber's salt.**

Place 100 c c of distilled water and about 60 grams of Glauber's salt in a small wide-mouthed bottle fitted with a rubber stopper Close the bottle, and place it in a water-bath maintained at 20°, shaking vigorously every five minutes for half an hour A small teat-pipette (*e g* a fountain-pen filler) should be kept in a dry test tube in the bath, in order to bring it to the same temperature as the solution After half an hour, allow the crystals to settle, and with the teat-pipette transfer 1½ to 2 c c of the clear saturated solution to a weighed dish Weigh rapidly, then place the dish in the steam-oven, and dry to constant weight From the weights of solution and of anhydrous sodium sulphate calculate the solubility in grams of $Na_2SO_4$ per 100 grams of solution.

Measure the solubility of the salt also at 25°, 30°, 35° and 40° Plot the solubility against the temperature and note the break in the curve at the transition-point.

EXPT 109 **Determination of the transition temperature of Glauber's salt by a thermal method**

Fit a specimen tube with a cork carrying a thermometer and a stirrer of stout copper wire Mount the tube by means of a cork in the neck of a wide-mouthed bottle, in order to protect it from draughts (compare Fig 130, p 494) Place in the tube 10 grams of clear (uneffloresced) fragments of Glauber's salt, and about ½ gram of anhydrous sodium sulphate Heat the tube in a water bath to about 36°-40°, when the crystals will melt to a thin mush of anhydrous sodium sulphate and water Insert the thermometer and stirrer in this mixture, dry the outside of the tube and mount it in the neck of the bottle Stir steadily, and read the temperature every minute A fall will first be observed, and finally the temperature will remain steady at the transition-point for several minutes If the temperature falls below 31° without a halt, introduce a small crystal of Glauber's salt to start the crystallisation of the hydrate

EXPT 110 **Freezing-point diagram for a binary mixture**

(*a*) Using the apparatus described in Expt 95, follow the rate of cooling of naphthalene and of *p*-nitrotoluene over a range of temperatures covering the freezing-points of the substances Plot cooling-curves, with temperatures as ordinates and time as abscissae Notice the lengths of time during which the temperature remains constant, and whether there is any " overcooling " of the melt below this temperature before crystallisation begins Then weigh out mixtures of the two substances as follows

| | Nitrotoluene | Naphthalene |
|---|---|---|
| I - - - | 2 | 8 |
| II - - - | 4 | 6 |
| III - - - | 6 | 4 |
| IV - - - | 8 | 2 |

In each case place the mixture in the tube, melt in a water bath, insert the thermometer and stirrer, wipe the outside of the tube and mount it in the bottle Stir steadily and read the temperature every minute

Notice the temperature at which crystals begin to separate in mixture No I, and mark on the cooling-curve the point at which a change of slope occurs The cooling of mixtures II, III and IV should be continued until a further prolonged arrest of temperature occurs This arrest marks the eutectic temperature at which the two constituents of the mixture crystallise together from a liquid which is saturated simultaneously with both components

Plot the initial freezing-points and the eutectic temperatures against the composition of the mixture, and complete the thermal diagram What conclusions can be drawn from the data as regards the formation of compounds ?

# CHAPTER XL

## THERMOCHEMISTRY

MANY chemical changes are accompanied by evolution of heat, and at one time it was supposed that the heat given out when two substances interact could be used as a measure of their chemical affinity for one another This supposition is only roughly correct , but a study of the heat changes which accompany chemical change is nevertheless of great interest, on account of the important link which it provides between the sciences of physics and chemistry This branch of physical chemistry is usually called THERMOCHEMISTRY

The amount of heat which is given out (or absorbed) in a chemical change is expressed in calories The CALORIE is usually defined as *the amount of heat required to raise one gram of water through* 1° C Since, however, the specific heat of water varies appreciably with temperature, it is necessary to specify the temperature of the water as well as the range of the heating For accurate work the calorie is therefore defined as *the heat required to raise one gram of water from* 15° *to* 16° C

**Intrinsic energy of chemical compounds.**—It follows from the law of conservation of energy (see below), that, when a process is accompanied by the evolution of heat, an equivalent amount of some other form of energy must have been transformed into heat Thus, in the reaction

$$Cu + S_a \rightarrow CuS + 11{,}600 \text{ calories},$$

11,600 calories of heat are evolved In order to explain this effect, we may suppose that the uncombined copper and sulphur and the copper sulphide produced from them exist on two different energy levels, and that the liberation of heat in the action formulated above is due to the fact that the copper and sulphur are on a lower energy level when in combination than when in a free state Alternatively, we may attribute to *each* substance a definite **intrinsic energy,** and suppose that, since no energy is lost in the transformation, these intrinsic energies, when a proper allowance is made for the heat liberated or absorbed in the process, must balance on either side of the equation It then follows that

Intrinsic energy of copper + intrinsic energy of sulphur
= intrinsic energy of copper sulphide + 11,600 calories

At the present time we have no means of knowing how much energy is contained in the complex system which constitutes an atom , nor can we tell what share of energy is associated with each atom in a chemical compound , but, since all chemical changes depend on the *difference* of the intrinsic energies of reactants and resultants, it is convenient to regard the

intrinsic energy of the free elements in their normal state as *zero* It then follows that, since the intrinsic energies of the elements on the left-hand side of the preceding equation are zero, the sum of the energies on the right-hand side of the equation must also be zero The *intrinsic energy* of copper sulphide must therefore be equivalent to − 11,600 calories The equation may therefore be rewritten in terms of intrinsic energies as follows

$$\begin{array}{lll} Cu + S_\alpha & \rightarrow CuS + 11{,}600 \text{ calories} \\ 0 \quad 0 & \quad -11{,}600 \end{array}$$

**Heat of formation of chemical compounds.**—The heat evolved during the combination of 63 6 grams of copper with 32 grams of sulphur is 11,600 calories This is described as the HEAT OF FORMATION of copper sulphide, and is obviously equal to the intrinsic energy of the compound, but with the sign reversed In general, *the heat of formation of a compound is measured by the number of calories of heat that are set free when the elements in their normal state unite to produce one gram-molecule of the compound*

TABLE 67 —HEATS OF FORMATION

| Chemical reaction | Calories |
|---|---|
| $\frac{1}{2}H_2 + \frac{1}{2}F_2 \rightarrow HF$ | +38,500 |
| $\frac{1}{2}H_2 + \frac{1}{2}Cl_2 \rightarrow HCl$ | +22,000 |
| $\frac{1}{2}H_2 + \frac{1}{2}Br_2 \rightarrow HBr$ | + 8,440 |
| $\frac{1}{2}H_2 + \frac{1}{2}I_2 \rightarrow HI$ | − 6,040 |
| $C + O_2 \rightarrow CO_2$ | +97,000 |
| $C + 2S \rightarrow CS_2$ | −25,400 |
| $P + 1\frac{1}{2}Cl_2 \rightarrow PCl_3$ | +76,600 |

The heats of formation of a few common compounds are given in Table 67 In order that the heat of formation of a compound may be defined accurately, however, it is important to state the exact condition both of the elements and of the compound Thus, when prismatic sulphur, $S_\beta$, is converted into rhombic sulphur, $S_\alpha$, 80 calories are liberated, that is

$$S_\beta \rightarrow S_\alpha + 80 \text{ cal}$$

The intrinsic energy of $S_\beta$ is therefore + 80 cal if $S_\alpha$ is taken as zero , and the heat of formation of copper sulphide from copper and prismatic sulphur would be greater by 80 calories

$$\begin{array}{lll} Cu + S_\beta = & CuS & + 11{,}680 \text{ cal} \\ 0 \quad 80 & & -11{,}600 \end{array}$$

In the preceding table all the elements are taken in their ordinary condition at atmospheric temperature, *e g* gaseous chlorine, liquid bromine and solid iodine , the sulphur is in the rhombic form, the carbon is in the form of charcoal and the phosphorus is white phosphorus A similar statement applies also to the products

**Endothermic and exothermic compounds.**—It will be seen from Table 67 that heat may be either liberated or absorbed in the formation of a chemical compound from its elements Chemical compounds are therefore divided into two classes . those which are formed from their elements

with evolution of heat are known as EXOTHERMIC COMPOUNDS, whilst those which are formed from their elements with absorption of heat are known as ENDOTHERMIC COMPOUNDS Carbon dioxide is an example of an exothermic compound, and carbon disulphide of an endothermic compound

Endothermic compounds contain more energy than their constituent elements, and are very reactive, very easily decomposed, and are only formed from their elements at high temperatures On the other hand, exothermic compounds can usually be produced from their elements at low or moderate temperatures, and are much less reactive and less easily decomposed than endothermic compounds

**Hess's law of thermoneutrality** —This law states that

*The heat evolved in any chemical change is independent of the manner in which it is carried out, whether in one or in many steps, provided that the initial and final states are the same in each case*

Thus starting with water, ammonia and hydrogen chloride gas, we can obtain a dilute solution of ammonium chloride either (i) by mixing hydrogen chloride and ammonia gases, and dissolving the ammonium chloride in a large excess of water, or (ii) by dissolving the ammonia and hydrogen chloride separately in water and then mixing the solutions Hess's Law states that the total heat change must be the same in either case, and this is confirmed by the following results, which were obtained in the formation of one gram-molecule of aqueous ammonium chloride

$$\begin{aligned} HCl\ gas + NH_3\ gas &= NH_4Cl & +42{,}100\ cal \\ NH_4Cl + Aq &= NH_4Cl,\ aq & -\ 3{,}900\ cal \\ \text{Total heat change} &= & 38{,}200\ cal \end{aligned}$$

$$\begin{aligned} HCl\ gas + Aq &= HCl,\ aq & +17{,}500\ cal \\ NH_3\ gas + Aq &= NH_3\ aq & +\ 8{,}400\ cal \\ HCl,\ aq + NH_3,\ aq &= NH_4Cl,\ aq & +12{,}300\ cal \\ \text{Total heat change} &= & 38{,}200\ cal \end{aligned}$$

Since the process of solution is usually accompanied by an absorption or liberation of heat, which is not complete until the solution is dilute, the symbol aq , as used above, indicates that the substance is in a solution which is so dilute that no appreciable heat change is produced by further dilution

**Measurement of the heat of formation of compounds** —In a very large number of cases it is impossible to prepare a compound from its constituent elements in such a way that its heat of formation can be measured directly In such cases the heat of formation is determined indirectly, often through the application of Hess's Law Thus the heat of formation of carbon monoxide, $C + \frac{1}{2}O_2 \rightarrow CO + x$ cal ,

is best determined by measuring in a calorimeter the heat produced when known quantities of carbon and of carbon monoxide are burnt to carbon dioxide, thus

$$\begin{aligned} &(i) \quad C + O_2 \rightarrow CO_2 + 97{,}000\ cal\ , \\ &(ii) \quad CO + \tfrac{1}{2}O_2 \rightarrow CO_2 + 68{,}000\ cal. \end{aligned}$$

The difference in the quantities of heat liberated in (i) and (ii) obviously represents the heat of combustion of carbon to carbon monoxide, or the heat of formation of carbon monoxide from its elements, thus

$$C + \tfrac{1}{2}O_2 \rightarrow CO + (97{,}000 - 68{,}000) \text{ cal} = 29{,}000 \text{ cal}$$

Organic reactions usually proceed too slowly to allow of a direct measurement of the heat changes involved, the heat of formation of an organic compound is therefore usually deduced by means of Hess's Law from its HEAT OF COMBUSTION, *i e* the heat liberated when one gram-molecular weight of the compound is burned to carbon dioxide and water Thus, the heat of formation of benzene is deduced as follows

The heat of combustion of benzene at constant pressure is

$$\text{(i)}\quad C_6H_6 + 7\tfrac{1}{2}O_2 = 6CO_2 + 3H_2O + 782{,}000 \text{ calories},$$

whilst those of carbon and hydrogen are

$$\text{(ii)}\quad C + O_2 = CO_2 + 97{,}000 \text{ calories},$$

$$\text{(iii)}\quad H_2 + \tfrac{1}{2}O_2 = H_2O \text{ (liquid)} + 68{,}150 \text{ calories}$$

Equation (i) can now be rewritten in terms of intrinsic energies

$$\underset{(C_6H_6)}{x} + \underset{(7\frac{1}{2}O_2)}{0} = -6 \times 97{,}000 - 3 \times 68{,}150 + \underset{(6CO_2)}{782{,}000} \underset{(3H_2O)}{} \text{ cals.},$$

whence $x$, the intrinsic energy of benzene, $= -4{,}450$ calories Therefore benzene is formed from its elements with the liberation of 4,450 calories, *i e* at constant pressure its heat of formation is **4,450** cals

**The effect of changes of volume on heats of reaction** —Gaseous reactions, unlike those occurring in the solid or liquid states, are often accompanied by large changes of volume In such cases the heat of reaction at constant pressure will differ from that at constant volume, because the system will do work against the atmosphere when an expansion occurs, and conversely The heat of reaction is always given *at constant pressure*, unless otherwise stated, but the value at constant volume can be readily deduced as follows

Let $W$ = the work done by the system, and $\delta v$ the expansion in volume when the pressure, $p$, is kept constant, then

$$W = p\,\delta v$$

The value of $\delta v$ is negative when a contraction occurs, $W$ is therefore also negative, indicating that the atmosphere does work on the system If the pressure is measured in atmospheres and the changes of volume in terms of gram-molecular volumes (unit vol = 22 4 litres), we may write

$$W = p\,V = nRT,$$

where $n$ is the increase in the number of gaseous gram-molecules brought about by the chemical change. In the synthesis of benzene the number of gaseous gram-molecules decreases by 3

$$6C \text{ (solid)} + 3H_2 \text{ (gaseous)} = C_6H_6 \text{ (liquid)} + 4{,}450 \text{ cals.}$$

The work done by this system is therefore

$$W = nRT = -3RT = -6T \text{ calories } (R = 2 \text{ calories}).$$

If we assume that $T$ is 290° Abs (= 17° C) then

$$W = -6 \times 290 = -1{,}740 \text{ calories}$$

The negative value of $W$ indicates that the atmosphere has done this quantity of work on the reacting system, so that the heat of formation of benzene at constant volume will be

$$4{,}450 - 1{,}740 = 2{,}710 \text{ calories}$$

No allowance has been made in the above calculation for the difference in volume between 6 gram-atoms of carbon and one gram-molecule of benzene, since this is negligible when compared with $3V$

**Heat of neutralisation.**—A very important type of chemical change, which can be carried out in aqueous solution, is the neutralisation of an acid by a base The amount of heat liberated in the neutralisation of a number of common acids and bases is shown in Table 68

TABLE 68.—HEATS OF NEUTRALISATION

| Base | Acid | Calories |
|---|---|---|
| KOH, aq | + HCl, aq | + 13,695 |
| NaOH, aq | + HCl, aq | + 13,700 |
| KOH, aq | + $HNO_3$, aq | + 13,705 |
| NaOH, aq | + $HNO_3$, aq | + 13,685 |
| $\frac{1}{2}Ca(OH)_2$, aq | + $HNO_3$, aq | + 13,950 |
| $\frac{1}{2}Ba(OH)_2$, aq | + $HNO_3$, aq | + 13,900 |
| NaOH, aq | + HF, aq | + 16,400 |
| KOH, aq | + HCN, aq | + 2,800 |
| $NH_4OH$, aq | + HCl, aq | + 12,270 |
| $NH_4OH$, aq | + HCN, aq | + 1,300 |

The most striking characteristic of these numbers is the constancy of the values obtained for the heat of neutralisation of a " strong " acid by a " strong " base This important regularity will be referred to again later (Chap XLV) When " weak " acids or " weak " bases are concerned, as in the last four lines of the table, the heat of neutralisation varies greatly

EXPT 111 **Heat of neutralisation of sodium hydroxide by acids.**

(*a*) Hydrochloric acid, (*b*) nitric acid, (*c*) sulphuric acid, (*d*) acetic acid

The following method gives very fair results and can be carried out in a short time 200 c c of $N/2$ sodium hydroxide (free from carbonate) are placed in each of four 500 c c flasks of known weight, $w$ The temperature, $t_1$, of the sodium hydroxide is measured with a thermometer graduated in tenths of a degree 200 c c of $N/2$ hydrochloric acid of known temperature, $t_2$, are added from a measuring cylinder to the first flask and the new temperature, $t_3$, is measured after the contents have been well mixed by shaking The operation is then repeated with the other acids The heat generated is given by the equation

$$q = \left(t_3 - \frac{t_2 + t_1}{2}\right)(400 + ws),$$

where $s$ = the specific heat of glass = 0 19

The proportion of alkali and acid used in each case is one-tenth of an equivalent weight, so that the heat of neutralisation will be $10q$

If more accurate results are required, the neutralisation is carried out in a thermos flask fitted with a cork, metal stirrer and Beckmann thermometer 200 c c of $N/10$ sodium hydroxide are run into the flask from a burette, and a small thin-walled bulb containing 20 c c of normal acid is suspended in the alkali until the thermometer records a steady temperature The bulb is then smashed by the stirrer and the maximum temperature recorded The water equivalent, $w$, of the flask and stirrer can be measured by finding the fall in temperature when, say, 200 c c of warm water are poured into it In the calculation the assumption is made that the neutralised liquid has the same capacity for heat as 220 grams of water, the error introduced by this assumption is under 1%

# CHAPTER XLI

## CHEMICAL EQUILIBRIUM

**Chemical equilibrium.**—A large number of chemical changes are known in which the interacting substances are not used up completely to form the products of the action Thus, if equivalent amounts of hydrogen and iodine are heated together in a sealed tube at 356°, only 80% of the theoretical amount of hydrogen iodide is formed, no matter how long the heating is continued Conversely, if pure hydrogen iodide is heated in a sealed tube to the same temperature, it is partly decomposed , but 80% of it remains unchanged, and no further decomposition takes place if the temperature is maintained at 356° for an indefinite period At this temperature, hydrogen, iodine, and hydrogen iodide in the proportions set out above are said to be in CHEMICAL EQUILIBRIUM with each other The system satisfies the test of a true equilibrium, since a mixture of the same composition is obtained whether one starts with pure hydrogen iodide or with a mixture of hydrogen and iodine in molecular proportions

This experimental fact rules out the possibility that, when the equilibrium is reached, hydrogen and iodine cease to combine together and hydrogen iodide ceases to decompose It must be supposed that these actions still go on, but with equal and opposite velocities, so that in each second just as much hydrogen iodide decomposes as is formed from hydrogen and iodine Two opposite actions are therefore proceeding in the equilibrium-mixture, namely

$$H_2 + I_2 \rightarrow 2HI$$

and

$$H_2 + I_2 \leftarrow 2HI ,$$

or, as it is usually written,

$$H_2 + I_2 \rightleftharpoons 2HI$$

According to this view, the composition of the equilibrium-mixture remains constant, not because chemical reactions are no longer taking place between the molecules, but because the speeds of the forward and back reactions have become the same

**Velocity of reaction.**—Since chemical equilibrium depends on the balancing of two opposite reaction-velocities, it is essential to investigate the factors which determine the velocity of a chemical change The principal factors are three in number, namely

(i) Temperature ;
(ii) Catalysis ,
(iii) Concentration

(i) *Influence of temperature* —A rise of temperature usually increases the velocity of a reaction very greatly, as discussed in Chap XLIII Chemical equilibrium, which depends on the *ratio* of two opposing velocities, is influenced by temperature, but to a much smaller extent than the absolute velocities of reaction

(ii) *Influence of catalysts* —The presence of catalysts has a very large effect upon the speed of a chemical change, and may increase a reaction-velocity a millionfold It can be shown, however (p 586), that the effect of catalysts upon the forward and back reactions must be exactly the same, since the final condition of equilibrium cannot be altered by the addition of a mere trace of a foreign substance Whilst, therefore, the influence of catalysts is of great importance when we are concerned with the speed at which a chemical change occurs in one direction or other, or with the velocity with which a system attains equilibrium, we need not consider their action when we are discussing the final condition of equilibrium in a given system

(iii) *Influence of concentration* —The effect of concentration on the speed of a chemical change was discussed fully by Guldberg and Waage in 1867 Their LAW OF MASS ACTION states that

*The velocity of a chemical change is proportional to the product of the "active masses" of the interacting substances,*

where the "active masses" may be identified with the *partial pressures* of the components of a gaseous system, or (less precisely) with the *concentrations* of the components of a solution Since the concentrations have an opposite influence on the "forward" and "back" reactions, they are the principal factor in determining the conditions of equilibrium in a given system when the temperature is kept constant

**Equilibrium in homogeneous systems.**—In HOMOGENEOUS SYSTEMS, *i e* systems in which all the interacting molecules are present in one phase, the "active masses" are usually identified with the concentrations of the reacting substances, *e g* in gram-molecules per litre Thus, if we consider the reaction

$$A + B \rightleftharpoons C + D,$$

the law of mass action then tells us that the speed of the reaction represented by the upper arrow is

$$v_1 = k_1 \times \textit{concentration of } A \times \textit{concentration of } B,$$

where $k_1$ depends upon temperature and catalysts, but is a constant under a given set of conditions This relation is expressed more concisely by using square brackets to represent the concentration of a given component, *e g*

$$v_1 = k_1[A][B]$$

Similarly, the velocity of the reverse reaction between $C$ and $D$ is given by

$$v_2 = k_2[C][D],$$

where $k_2$ is another constant When the system is in equilibrium $v_1 = v_2$

$$\therefore\ k_1[A][B] = k_2[C][D],$$

$$\therefore\ \frac{[C][D]}{[A][B]} = \frac{k_1}{k_2} = K \qquad (1)$$

The constant $K$ is known as the EQUILIBRIUM-CONSTANT The law of mass action therefore leads to the conclusion that

*At the equilibrium-point the product of the concentrations of the substances on the right-hand side of the equation divided by the product of the concentrations of the substances on the left-hand side of the equation is a constant*

Thus, by applying the law of mass action to the equilibrium of hydrogen iodide with hydrogen and iodine, we find that

$$HI + HI \rightleftharpoons H_2 + I_2,$$

$$K = \frac{[H_2][I_2]}{[HI]^2} \qquad (11)$$

By writing the left-hand side as HI + HI instead of 2HI, we see that the concentration of HI must be squared in the expression for the equilibrium-constant In general, if $n$ molecules of a substance take part in a reaction, the corresponding term in the equilibrium equation is the concentration of this substance raised to the $n$th power

**Verification of the law of mass action.**—In applying the law of mass action to a chemical equilibrium, there is no need for the reacting substances or the products to be present in equivalent amounts Excess of any of them may be present and the relation should still be true We can therefore test the law of mass action experimentally by analysing a number of equilibrium-mixtures, containing varying amounts of $A$, $B$, $C$, and $D$, in order to determine whether the concentrations of these substances in the various mixtures give identical values of $K$ The determination of the composition of an equilibrium-mixture is often rendered very difficult by the mobile character of the materials to be analysed Thus, if one of the components is removed by any of the ordinary analytical operations, *e g* by titration or precipitation, the original condition of equilibrium will be destroyed, and a further quantity of the missing component will be formed, in the endeavour to restore the equilibrium of the system For example, it is well known that iodine combines with potassium iodide to form a tri-iodide, as expressed by the reversible equation

$$KI + I_2 \rightleftharpoons KI_3$$

The amount of free iodine cannot, however, be determined by titration with sodium thiosulphate, since, as soon as some free iodine is removed, the tri-iodide dissociates and gives more iodine In this case an end point is obtained only when *all* the iodine, both free and combined, has been used up This behaviour is characteristic of all equilibria in which the forward and back reactions proceed with considerable speed Special methods have, therefore, to be adopted in the investigation of systems of this type (see p. 566)

In other cases, a chemical change which proceeds to equilibrium rapidly at high temperatures is found to take place only slowly at ordinary temperatures It is therefore possible by rapid cooling to fix the condition of equilibrium which prevails at the higher temperature, just as the high temperature form of steel can be fixed by " quenching " a piece of the hot

metal in cold water Bodenstein investigated the equilibrium of hydrogen iodide with hydrogen and iodine by sealing up known amounts of the reacting substances in small glass bulbs, which were heated at a given temperature for a sufficient time to ensure that equilibrium was established, the bulbs were then cooled rapidly to air temperature, opened, and the contents analysed

Consider the equation $$\underset{2x}{2HI} \rightleftharpoons \underset{a-x}{H_2} + \underset{b-x}{I_2}$$

If we start with $a$ gram-molecules of hydrogen, and $b$ gram-molecules of iodine in a volume $V$, and $2x$ gram-molecules of hydriodic acid are formed, then at equilibrium,

$$[H_2]=\frac{a-x}{V}, \quad [I_2]=\frac{b-x}{V} \quad \text{and} \quad [HI]=\frac{2x}{V},$$

$$\therefore \quad K=\frac{[H_2][I_2]}{[HI]^2}=\frac{(a-x)(b-x)}{4x^2} \qquad \text{(iii)}$$

Note that in this case the term $V$ cancels out from the numerator and denominator, and does not appear in the function which determines the value of $K$ This particular equilibrium is therefore not affected by changes in the volume occupied by the reacting gases, and is therefore *independent of the pressure* Bodenstein verified this conclusion by filling bulbs at pressures above and below atmospheric pressure, when he found that the same equilibrium was reached in each case

Equation (iii) was then tested by sealing up different quantities of hydrogen and iodine and estimating the amount of hydrogen iodide produced after heating until equilibrium was attained The results of these experiments are given in Table 69, where the quantities of each gas are given in cubic centimetres at N T P , and are therefore proportional to the number of gram-molecules present in a given quantity of the equilibrium-mixture The values of $K$ in the last column are approximately constant

TABLE 69 —DECOMPOSITION OF HYDROGEN IODIDE AT 356°

| Initial concentrations | | Equilibrium concentrations | | | Equilibrium constant |
|---|---|---|---|---|---|
| $H_2$ $(a)$ | $I_2$ $(b)$ | $H_2$ $(a-x)$ | $I_2$ $(b-x)$ | HI $(2x)$ | $K$ |
| 6 63 | 2 59 | 4 12 | 0 08 | 5 02 | 0 013 |
| 6 22 | 5 71 | 1 42 | 0 90 | 9 60 | 0 014 |
| 6 41 | 10 40 | 0 57 | 4 56 | 11 68 | 0 019 |
| 6 51 | 22 29 | 0 17 | 15 95 | 12 68 | 0 017 |

Table 69 illustrates also the effect of adding an excess of one component to an equilibrium-mixture In the first experiment hydrogen is present in excess and nearly all the iodine is converted into hydriodic acid Similarly, in the last experiment, where iodine is in excess, nearly all the hydrogen is used up.

**Influence of pressure and temperature on chemical equilibrium.**—The effect of changes of pressure and temperature can be predicted qualitatively by making use of LE CHATELIER'S THEOREM, which may be stated as follows

*If one of the conditions of a system in equilibrium be altered, the system will adjust itself in such a direction as partially to neutralise this change of condition*

(*a*) *Influence of temperature*.—Suppose that $U$ calories of heat are *evolved* in the balanced action,

$$A + B \rightleftharpoons C + D + U \text{ cal},$$

when the change proceeds completely from left to right, and conversely that $U$ calories are *absorbed* when the reverse action occurs In a system in equilibrium at $T°$ there will be certain equilibrium-proportions of $A$, $B$, $C$ and $D$ If the temperature is now raised to $T + 1°$, then, according to Le Chatelier's theorem, an adjustment of the system must occur which absorbs heat and tends to lower the temperature This can only be brought about by a change of some $C$ and $D$ into $A$ and $B$ That is, as the temperature is raised, the amount of $C$ and $D$ in the equilibrium-mixture diminishes, and that of $A$ and $B$ increases Generally, the theorem predicts that *as the temperature rises there will be an increase in the equilibrium-concentration of the substances which are formed by an endothermic change*

Le Chatelier's theorem gives only a qualitative indication of the direction in which an equilibrium is displaced by rise in temperature A quantitative relation between the heat of the reaction and the change in the equilibrium-constant has been obtained by van 't Hoff, and is expressed by the equation

$$\frac{d \log_e K}{dT} = -\frac{U}{RT^2}, \qquad \text{(iv)}$$

where $K$ is the equilibrium-constant, $U$ the heat evolved when the reaction goes completely from left to right, and $T$ the absolute temperature This equation holds strictly only for small concentrations and over very small intervals of temperature If, however, we assume that $U$ does not change appreciably between two temperatures, $T_1$ and $T_2$, which are not too widely separated, then this equation can be integrated to give the relation

$$\log_e \frac{K_1}{K_2} = \frac{U}{R}\left(\frac{T_2 - T_1}{T_1 T_2}\right),$$

and since $\log_e x = 2{\cdot}303 \log_{10} x$ and $R = 1\ 985$ cal., we have

$$\log_{10} \frac{K_1}{K_2} = \frac{U}{4\ 57}\left(\frac{T_2 - T_1}{T_1 T_2}\right) \quad \ldots\ldots \quad \text{(v)}$$

Equation (v) may be used to calculate $U$ from the values $K_1$ and $K_2$ found for the equilibrium-constant at temperatures $T_1$ and $T_2$

(*b*) *Influence of pressure*.—The influence of pressure on a chemical equilibrium can also be predicted by Le Chatelier's theorem Consider a reaction of the type

$$A + B \rightleftharpoons C$$

Since the number of molecules on the right-hand side of the equation is less than the number on the left-hand side, a change of $A + B$ into $C$ will produce a diminution in volume, or, if the system is kept at constant volume, it will cause a fall in pressure Hence it follows from Le Chatelier's theorem that the equilibrium-mixture will contain a larger amount of $C$ at higher pressures than at lower pressures

A chemical change of this type, which is of great industrial importance, is the synthesis of ammonia from nitrogen and hydrogen (p 180)

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

Table 70 shows some values of the equilibrium percentage of ammonia as found by Haber

TABLE 70 —FORMATION AND DISSOCIATION OF AMMONIA

| Temperature | Equilibrium percentage of $NH_3$ at | | |
|---|---|---|---|
| | 1 atm | 100 atm | 200 atm |
| 550° C | 0 0769 | 6·7 | 11 9 |
| 650 | 0 0321 | 3 02 | 5 71 |
| 750 | 0 0159 | 1 54 | 2 99 |
| 850 | 0 0089 | 0 874 | 1 68 |
| 950 | 0 0055 | 0 542 | 1 07 |

It will be seen that much larger amounts of ammonia are formed at higher pressures Moreover, the rapid fall in the equilibrium-concentration of ammonia as the temperature rises shows that a large amount of heat is evolved in its formation The successful application of this reaction to the fixation of atmospheric nitrogen depends upon the use of high pressures, and of a catalyst which will bring a mixture of gases to the equilibrium-point in a reasonable time and at as low a temperature as possible (p 180)

The effect of pressure on an equilibrium in a gaseous system can also be predicted quantitatively In the balanced action

$$\begin{array}{ccccc} N_2 & + & 3H_2 & \rightleftharpoons & 2NH_3, \\ 1-x & & 3(1-x) & & 2x \end{array}$$

if we start with one gram-molecule of nitrogen and three of hydrogen, and $2x$ gram-molecules of ammonia are formed, then the amounts of nitrogen, hydrogen, and ammonia in the equilibrium-mixture will be $(1-x)$, $3(1-x)$, and $2x$ respectively If the total pressure at equilibrium is $P$, then the partial pressure of a particular molecule is proportional to the ratio between the number of molecules of that kind and the total number of molecules This total number is obviously

$$1 - x + 3 - 3x + 2x = 4 - 2x.$$

Hence
$$p_{N_2} = P\frac{1-x}{4-2x},$$
$$p_{H_2} = P\frac{3(1-x)}{4-2x},$$
$$p_{NH_3} = P\frac{2x}{4-2x}.$$

Since partial pressures are a measure of the concentration, the mass action equation may be written

$$K = \frac{p^2_{NH_3}}{p_{N_2}p^3_{H_2}} = \frac{P^2\frac{4x^2}{(4-2x)^2}}{P\frac{1-x}{4-2x}\;P^3\frac{27(1-x)^3}{(4-2x)^3}},$$
$$K = \frac{4x^2(4-2x)^2}{P^2 27(1-x)^4}$$

If $x$ is small compared with unity, this equation can be simplified to

$$\frac{64x^2}{27} = KP^2 \quad \text{or} \quad x = K'P,$$

so that $x$ is proportional to $P$ It will be seen from Table 70 that the equilibrium-concentration of ammonia at 200 atmospheres is roughly double that at 100 atmospheres

**Dissociation of nitrogen peroxide.**—The law of mass action has also been applied to the dissociation of nitrogen peroxide

$$\underset{1-x}{N_2O_4} \rightleftharpoons \underset{2x}{2NO_2}$$

This can be followed by measurements of the relative density of the vapour, which varies from 23 for pure $NO_2$ to 46 for pure $N_2O_4$, when the density of hydrogen is taken as unity

If we start with one gram-molecule of $N_2O_4$, and if a fraction $x$ is dissociated when equilibrium has been reached, then the number of gram-molecules present will be

$$1-x+2x = 1+x$$

If, therefore, the pressure is kept constant at 1 atmosphere, the volume will increase in the ratio 1 $1+x$ Conversely, the vapour density will be lowered in the same ratio, so that

$$d = \frac{46}{1+x},$$

whence
$$x = \frac{46-d}{d}.$$

Table 71 gives the densities of nitrogen peroxide as found by Deville and Troost It will be seen that at 26·7°, 20 1% of the compound has dissociated, and that as the temperature rises the dissociation increases rapidly until at 140° it is complete

TABLE 71 —DISSOCIATION OF $N_2O_4$ (Deville and Troost)

| $t$ | $d(H_2=1)$ | $x$ | $K$ | $U$ |
|---|---|---|---|---|
| 26 7° | 38 3 | 0 201 | 0 168 | |
| 60 2° | 30 65 | 0 501 | 1 34 | −9960 cal |
| 100 1° | 25 7 | 0 790 | 6 64 | |
| 140° | 23 0 | 1 00 | | |

This rapid increase shows that the dissociation is accompanied by a large absorption of heat, which can be calculated as follows. At the working pressure of one atmosphere

$$p_{N_2O_4}=\frac{1-x}{1+x} \quad \text{and} \quad p_{NO_2}=\frac{2x}{1+x};$$

$$\therefore \; K=\frac{p^2_{NO_2}}{p_{N_2O_4}}=\frac{4x^2}{(1+x)(1-x)}=\frac{4x^2}{1-x^2}$$

The values of $K$ in the fourth column have been calculated by this formula and from them, by equation (v) (p 558), the value of $U$ in the last column The first observation at 26 7° is not used, since it is so near the boiling-point of the liquid (22°) that the gas laws will not hold and the density is probably too high

At higher temperatures, the density decreases still further owing to the fact that nitrogen peroxide dissociates into nitric oxide and oxygen

$$2NO_2 \rightleftharpoons 2NO + O_2$$

This further dissociation is complete at about 620°

**Dissociation of phosphorus pentachloride.**—Another illustration of the application of the law of mass action is found in the dissociation of phosphorus pentachloride Observations of the vapour density of this substance show that it is largely split up into an equilibrium-mixture of phosphorus trichloride and chlorine according to the equation

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2.$$

The application of Le Chatelier's theorem shows that a diminution in pressure must bring about a greater degree of dissociation

The equation for this dissociation is

$$\begin{array}{ccccc} PCl_5 & \rightleftharpoons & PCl_3 & + & Cl_2 \\ 1-x & & x & & x \end{array}$$

If we start with one gram-molecule of $PCl_5$, and if a fraction $x$ is dissociated, then the number of gram-molecules in the equilibrium-mixture is $(1-x)+x+x=1+x$ The predicted density for $PCl_5$ is 104 2 ($d_{H_2}=1$) The relative density of the equilibrium-mixture is therefore given by

$$d=\frac{104\ 2}{1+x},$$

whence

$$x=\frac{104\ 2-d}{d}.$$

Cahours found that the vapour density was 73·5 at 182° and 55·6 at 274° · substituting these values of $d$ in the above equation, we obtain $x = 0\ 417$ at 182° and $0\ 874$ at 274° The increase in the value of $x$ with temperature shows that the dissociation is endothermic, *i e* it takes place with absorption of heat

The law of mass action requires that a dissociation of this type shall be repressed by the presence of an excess of one of the products of dissociation This was verified by Wurtz, who used an apparatus of the Victor Meyer type and determined the vapour density of $PCl_5$ in an atmosphere of $PCl_3$

Conversely, since each molecule of phosphorus pentachloride produces two molecules when dissociated, Le Chatelier's theorem tells us that the degree of dissociation must *increase* as the pressure on the gas is diminished The same effect may be produced by dilution with an inert gas, *e g* nitrogen, since it is the concentration or partial pressure of the reacting substances which determines the composition of the equilibrium-mixture

**Homogeneous equilibrium in liquids.**—The examples of chemical equilibrium discussed above have been confined to gaseous systems, but similar equilibria can also occur in liquids An example of this type is given by the interaction between ethyl alcohol and acetic acid to form ethyl acetate (p 729) and water (Expt 115, p 570)

$$\underset{a-x}{C_2H_5\ OH} + \underset{b-x}{CH_3\ CO\cdot OH} \rightleftharpoons \underset{x}{CH_3\ CO\ OC_2H_5} + \underset{c+x}{H_2O}$$

If we start with $a$ molecules of alcohol, $b$ of acid, and $c$ of water in a volume $V$, then if $x$ molecules of ester are formed at equilibrium

$$[C_2H_5\cdot OH] = \frac{a-x}{V}, \quad [CH_3\cdot CO\ OH] = \frac{b-x}{V},$$

$$[CH_3\ CO\ O\ C_2H_5] = \frac{x}{V}, \qquad [H_2O] = \frac{c+x}{V},$$

and $$K = \frac{[CH_3\cdot CO\cdot O\cdot C_2H_5][H_2O]}{[CH_3\cdot CO\cdot OH][C_2H_5\ OH]} = \frac{x(c+x)}{(a-x)(b-x)}$$

Starting with equimolecular proportions of pure acid and alcohol (*i e* $a=1$, $b=1$, $c=0$), it has been found that $x = 0\ 667$, from which

$$K = \frac{0\ 667^2}{0\ 333^2} = 4\ 00.$$

Table 72 gives some of the data obtained by Berthelot and St Gilles for the amount of ester formed when $a$ gram-molecules of alcohol were allowed to react with 1 gram-molecule of acid In this case $b=1$, $c=0$, so that

$$K = 4{\cdot}00 = \frac{x^2}{(a-x)(1-x)}.$$

Multiplying out $$3x^2 - 4(a+1)x + 4a = 0,$$

from which $$x = \tfrac{2}{3}(1 + a - \sqrt{1 - a + a^2}). \quad \ldots\ldots\ldots\ldots\ldots \text{(vi)}$$

TABLE 72.—FORMATION OF ETHYL ACETATE FROM ALCOHOL AND ACETIC ACID (Berthelot and St Gilles)

| Mols of acid | Mols of alcohol | Mols of ester | |
|---|---|---|---|
| $b$ | $a$ | $x$(obs.) | $x$(calc.) |
| 1 00 | 0 08 | 0 078 | 0 078 |
| 1 00 | 0 28 | 0 226 | 0 232 |
| 1 00 | 0 33 | 0 293 | 0 311 |
| 1 00 | 0 50 | 0 414 | 0 423 |
| 1 00 | 0 67 | 0 519 | 0 528 |
| 1 00 | 1 00 | 0 665 | 0 667 |
| 1 00 | 1 50 | 0 819 | 0 785 |
| 1 00 | 2 00 | 0 858 | 0 845 |

In Table 72, the last column gives the value of $x$ calculated by equation (vi). It will be seen that the agreement between the observed and calculated values is good.

This reaction occurs without appreciable evolution or absorption of heat. By Le Chatelier's theorem it follows that the composition of the equilibrium-mixture will not be altered by rise in temperature and this has been verified by experiment.

**Equilibrium in heterogeneous systems.**—The reactions so far considered all take place in homogeneous gaseous or liquid systems. An example of a heterogeneous reaction is found in the dissociation of calcium carbonate,

$$CaCO_3 \rightleftharpoons CaO + CO_2,$$

which involves two solids and a gas. At first sight it is difficult to give a definite meaning to the "active mass" of the solid phases. We may, however, suppose that equilibrium is attained in the gaseous phase when

$$\frac{p_{CaO} \times p_{CO_2}}{p_{CaCO_3}} = K,$$

where $p_{CaO}$ and $p_{CaCO_3}$ represent the very small vapour-pressures of solid lime and calcium carbonate. But at constant temperature these vapour-pressures are independent of the amount of lime or calcium carbonate present, so that

$$p_{CO_2} = K\frac{p_{CaCO_3}}{p_{CaO}} = \text{constant}$$

The system is therefore only in equilibrium at a fixed temperature when a definite pressure of carbon dioxide is present. This is exactly the result that was obtained previously by the application of the Phase Rule (p. 540).

This example illustrates a general rule which is used in applying the law of mass action to heterogeneous equilibria, namely *the "active mass" of a solid is constant and independent of the amount present*.

**Activity of dissolved substances.**—We have seen that the simple law of mass action can be verified by measurements of the conditions of equilibrium in reversible gas-reactions, such as

$$H_2 + I_2 \rightleftharpoons 2HI \quad \text{or} \quad PCl_3 + Cl_2 \rightleftharpoons PCl_5.$$

But the law cannot usually be applied in the same simple way to reactions which occur in solution, since if molecular concentrations are used to represent the active masses of the components, it is found that the value of $K$ may vary substantially instead of being rigidly constant The equilibrium between acetic acid and alcohol is a remarkable exception, since on theoretical grounds the law should only hold for dilute solutions and not for concentrated solutions such as these

In order to secure a precise agreement with the law of mass action, it has become customary to make use of the ACTIVITIES of the various components, *i e* of quantities which are directly proportional to the true "active mass" of each component instead of their total concentrations For example, if one component of an equilibrium-mixture forms a hydrate, and if it is only the unhydrated material that enters directly into the interaction, we ought obviously to use the concentration of the free molecules in our equations and not the aggregate concentration of free and combined molecules This conception of "activity" is commonly expressed by means of equations such as,

$$a = cf,$$

where $a$ is the ACTIVITY,

$c$ is the total concentration,

and $f$ is the ACTIVITY COEFFICIENT,

*i e* the fraction of the total number of molecules which is directly available for the reaction in question We thus obtain a fixed value for the equilibrium-constant in an action, such as

$$A + B \rightleftharpoons C + D,$$

by writing $$K' a_1 a_2 = a_3 a_4,$$

instead of $$K c_1 c_2 = c_3 c_4,$$

where $c_1 c_2 c_3 c_4$ are the concentrations, and $a_1 a_2 a_3 a_4$ are the activities of the four components in any given solvent

The various methods for determining activities are discussed in books on advanced physical chemistry, but are beyond the scope of this volume

**Partition coefficients** —When iodine is added to a mixture of benzene and water, some of it is dissolved in each solvent After shaking, the system is found to reach an equilibrium in which iodine is divided in a definite ratio between the two solvents It will be found that, when the amount of iodine is varied, the ratio,

$$\frac{C_2}{C_1} = \frac{\textit{concentration of iodine in benzene}}{\textit{concentration of iodine in water}},$$

remains constant at constant temperature.

This behaviour, which is typical of many similar systems, is closely parallel to that of a gas dissolving in water under different pressures, where according to Henry's Law,

$$\textit{concentration of gas in solution} = K \times \textit{pressure}.$$

But since the pressure is a measure of the concentration of the gas,

$$\frac{\textit{concentration of gas in solution}}{\textit{concentration in gaseous phase}} = K,$$

which is exactly similar in form to

$$\frac{\textit{concentration in first liquid}}{\textit{concentration in second liquid}} = K$$

The latter constant is termed the PARTITION COEFFICIENT Expt 113 gives details for the study of the system carbon bisulphide-water-bromine, whilst Table 73 shows the constancy of the partition coefficient of mercuric bromide between water and benzene

TABLE 73 —PARTITION OF MERCURIC BROMIDE BETWEEN WATER AND BENZENE

| Concentration in water | Concentration in benzene | Partition coefficient |
|---|---|---|
| $C_1$ | $C_2$ | $C_1/C_2$ |
| 0 00320 | 0 00353 | 0 90 |
| 0 00634 | 0 00715 | 0 89 |
| 0 01147 | 0 01303 | 0 88 |
| 0 0170 | 0 0194 | 0 88 |

The preceding equations are examples of a wide generalisation, known as the NERNST DISTRIBUTION LAW, which states that

*When a heterogeneous system has reached equilibrium there is a definite ratio between the concentrations of the same molecular species in the various phases, provided that the temperature is kept constant*

The ratio is only constant when concentrations of the same molecular species are considered Thus Table 74 shows that the ratio $C_1/C_2$ of the equilibrium concentrations of acetic acid in carbon tetrachloride and water is not constant, but increases rapidly as the concentration increases It is known, however, from the elevation of the boiling-point of the solutions, that acetic acid has a normal molecular weight in water, but twice the normal molecular weight in carbon tetrachloride In the latter solvent there will therefore be an equilibrium,

$$\underset{(1-\alpha)c}{(CH_3\cdot CO\cdot OH)_2} \rightleftharpoons \underset{2\alpha c}{2CH_3\,CO\,OH}$$

If a small fraction $\alpha$ of the double molecules is dissociated into single molecules, then by the law of mass action,

$$\frac{4\alpha^2c^2}{(1-\alpha)c} = K \quad \text{or} \quad \alpha^2 = \frac{K(1-\alpha)}{4c}$$

If $\alpha$ is small, $1-\alpha$ may be taken as 1 so that $\alpha$ varies as $1/\sqrt{c}$. Hence

the concentration of single molecules of acetic acid in the carbon tetrachloride is

$$\alpha c = \text{const} \times c \times \frac{1}{\sqrt{c}}$$
$$= \text{constant} \times \sqrt{c}$$

Thus, if the partition law holds for the *single* molecules in both liquids, we should expect $\sqrt{c_1}/c_2$ to be constant The last column of Table 74 shows that this is nearly true

TABLE 74 —PARTITION OF ACETIC ACID BETWEEN CARBON TETRACHLORIDE AND WATER AT 25°

| Concentration in $CCl_4$ | Concentration in water | Partition coefficient | |
|---|---|---|---|
| $C_1$ | $C_2$ | $C_1/C_2$ | $\sqrt{C_1}/C_2$ |
| 0 0096 | 0 684 | 0 0140 | 0 143 |
| 0 0187 | 1 021 | 0 0183 | 0 132 |
| 0 0460 | 1 691 | 0 0266 | 0 127 |

Experiments based on the distribution law have proved of considerable value in elucidating problems such as the nature of molecules in solution and the degrees of hydrolysis of salts (p 630) Thus the nature of the per-iodide complex, formed by adding iodine to a solution of potassium iodide, was determined as follows

The partition coefficient of iodine between carbon disulphide and water was measured, using the thiosulphate method for estimating iodine An aqueous solution containing a known quantity of potassium iodide and iodine was then shaken up with carbon disulphide, which only extracts iodine The total concentration of iodine in each layer was measured, that in the aqueous layer representing *free iodine + iodine as complex*, since the iodide complex dissociates simultaneously with the removal of the free iodine The actual concentration of the latter was obtained by dividing the concentration of the iodine in the carbon disulphide layer by the partition coefficient

If the complex were $KI_3$ the equilibrium equation would be,

$$KI + I_2 \rightleftharpoons KI_3,$$

or more correctly, $$K^+ + I^- + I_2 \rightleftharpoons K^+ + I_3^-$$

This would give the following mass-action equation:

$$\frac{[I^-][I_2]}{[I_3^-]} = K.$$

Table 75 gives some of Dawson's measurements for different iodide-iodine concentrations, together with the values of K calculated for the above mass-action equation The constancy of K not only supports the assumption that the iodide is present mainly in the form of the complex.

ion $I_3^-$, but also provides an illustration of the validity of the law of mass action.

TABLE 75 —DISSOCIATION OF $KI_3$ AT 13 5° (Dawson)
*Concentrations in millimols per litre*

| Initial KI | Total iodine | Iodine in $CS_2$ | $[I_2]$ | $[KI_3]$ | [KI] | $K=\frac{[KI][I_2]}{[KI_3]}$ |
|---|---|---|---|---|---|---|
| 125 0 | 4 959 | 26 19 | 0 04190 | 4 917 | 120 1 | 0 00102 |
| ,, | 8 992 | 49 98 | 0 07998 | 8 912 | 116 1 | 0 00104 |
| ,, | 17 44 | 100 85 | 0 1613 | 17 28 | 107 7 | 0 00101 |
| ,, | 28 32 | 189 6 | 0 3033 | 28 02 | 97 0 | 0 00105 |

The actual calculation of $K$ is made clear by considering the first measurements in Table 75

The aqueous solution contained 4 959 millimols of iodine, both free and combined The disulphide layer contained 26 19 millimols of iodine per litre Dividing this by the partition coefficient, viz 625, the *free* iodine in the aqueous layer must have had a concentration of 0 0419 millimols per litre Subtracting this from the *total* iodine we have, concentration of combined iodine, $[KI_3]=[I_3^-]=4\ 917$ millimols per litre. The free KI is then obtained by subtracting the concentration $[KI_3]$ from the original concentration, so that

$$[KI]=[I^-]=125\ 0-4\ 9=120\ 1 \text{ millimols per litre}$$

Expressing all the concentrations in gram-molecules per litre, we find

$$K=\frac{[I^-][I_2]}{[I_3^-]}=\frac{0\ 1201\times 0\ 0000419}{0\ 004917}=0\ 00102$$

EXPT 112 **To illustrate qualitatively the effect of concentration on the position of an equilibrium.**

(*a*) *Hydrolysis of bismuth chloride* —Water is added to a solution of bismuth chloride in dilute hydrochloric acid until a white cloud of bismuth oxychloride is produced $BiCl_3+H_2O \rightleftharpoons BiOCl+2HCl$ On the addition of a little concentrated hydrochloric acid the mixture clears, showing that the hydrolysis has been reversed, as indicated by the lower arrow in the equation The equilibrium can be driven to the right again by the addition of more water

(*b*) *Interaction of ferric and thiocyanate ions* —The red colour produced by the addition of a thiocyanate to an aqueous solution of a ferric salt is probably due to the formation of the complex anion, $Fe(CNS)_6^{---}$,

$$Fe^{+++}+6CNS^- \rightleftharpoons Fe(CNS)_6^{---}$$

The reaction is reversible, hence the addition of more ferric or thiocyanate ions enhances the red colour of the mixture by driving the equilibrium towards the right The fading of colour which is caused by the addition of a large concentration of a salt, such as ammonium chloride, is due to a reduction in the relative " activity ", *i.e.* effective concentration, of the ferric and thiocyanate ions.

Prepare solutions of (i) ammonium thiocyanate, 1 gram per 100 c c , (ii) ferric chloride, 1 gram $FeCl_3,6H_2O$ + 5 c c HCl per 100 c c , (iii) saturated ammonium chloride, 50 c c Add 7 5 c c of (i) and (ii) to a litre of water and place 250 c c of the pale red mixture in each of four beakers To the first beaker add 50 c c of (i), to the second 50 c c of (ii), to the third 50 c c of (iii), and to the fourth 50 c c of water, so that it may be used for comparison It will be found that the colour deepens in the first two beakers, but fades considerably in the third beaker

EXPT 113 **Partition coefficient of bromine between carbon disulphide and water.**

An approximately $N/5$ solution of bromine water is prepared by vigorously shaking 5 c c of bromine with 800 c c of water in a stoppered litre flask When solution is complete, water is added to the mark The exact strength of this solution is then determined by pipetting portions of 20 c c into a flask containing 10 c c of 20% potassium iodide solution, and titrating the liberated iodine with $N/5$ thiosulphate

$$Br_2 + 2KI = 2KBr + I_2,$$
$$I_2 + 2Na_2S_2O_3 = 2NaI + Na_2S_4O_6$$

Since the fumes of bromine are very objectionable, it is necessary to fill the pipette by attaching it to an evacuated Winchester bottle which is fitted with a delivery tube and tap as shown in Fig 155

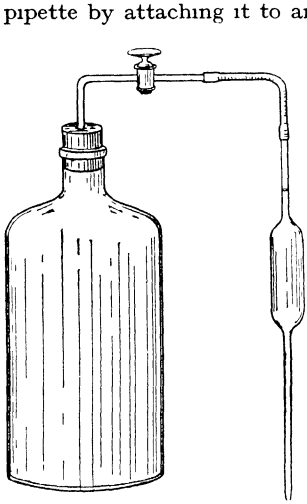


FIG 155 PIPETTE AND ASPIRATOR FOR USE WITH BROMINE

Portions of 100 c c of the bromine solution are then pipetted into six bottles containing respectively 25 c c , 50 c c , 75 c c , 100 c c , 150 c c , and 200 c c of carbon disulphide The bottles must be fitted with glass stoppers (ordinary 500 c c reagent bottles do excellently) and maintained at a constant temperature by immersion either in a thermostat or in a trough of cold water Equilibrium between the aqueous and disulphide layers is ensured by shaking the bottles every few minutes during a period of 20 minutes

The concentration of bromine in the aqueous layer of the first bottle (*i e* the one containing 25 c c $CS_2$) is determined by withdrawing 20 c c in a pipette, and titrating with $N/100$ thiosulphate after the addition of a few c c of potassium iodide solution From the other bottles, portions of 50 c c of the aqueous layer should be withdrawn for titration with the $N/100$ thiosulphate The concentration of bromine in the aqueous layers is so small that, with the exception of the first titration, it is possible to fill the pipette by suction with the mouth The concentration of bromine

in the carbon disulphide layers is calculated from the initial and final strengths of the aqueous layers The error involved by this indirect determination is negligible, if the volumes of carbon disulphide have been measured out accurately from a burette The concentrations of bromine in the aqueous and disulphide layers should be expressed in terms of $N/100$ thiosulphate per c c of solution and the partition coefficient, $K$, calculated thus

$$K = \frac{\text{c c of } N/100 \text{ thiosulphate per c c of carbon disulphide solution}}{\text{c c of } N/100 \text{ thiosulphate per c c of aqueous solution}}$$

The value of $K$ should be in the neighbourhood of 80 at 20° C

EXPT 114A **To determine the molecular formula of benzoic acid in toluene**

Benzoic acid is a weak acid and exists in aqueous solution principally as the simple molecule, $C_6H_5$ CO OH By comparing the ratio of the concentrations of this acid in contiguous layers of toluene and water, it is possible to draw conclusions as to the state of its molecules in toluene (compare acetic acid, p 565)

Pure benzoic acid, 12 0 grams, is weighed out and dissolved in toluene, the volume being made up to 500 c c in a calibrated flask Portions of this solution, viz 25 c c , 50 c c , 75 c c , 100 c c , 150 c c , and 200 c c , are placed in six stoppered bottles in a thermostat or trough of water The total volume of the solution in each bottle is brought up to 200 c c by the addition of toluene To each bottle is then added 100 c c of distilled water, which has been boiled to expel carbon dioxide, which interferes with the subsequent titration The bottles are shaken frequently during a quarter of an hour, and then portions of 50 c c of the lower aqueous layer are removed with a pipette The entry of toluene into the pipette is prevented by blowing gently through it as it is being lowered into the bottle The concentration of the benzoic acid is estimated by titration with $N/40$ barium hydroxide solution (p 123), the end-point being indicated by using phenolphthalein as indicator This titration can be carried out more quickly and accurately if a rough preliminary titration has been made with say 20 c c of the aqueous layer The concentration of the acid should be expressed in terms of c c $N/40 Ba(OH)_2$ per one c c of solution That for the toluene layer is calculated by dividing 200 (=volume of toluene) by the quantity of acid initially present less the quantity in the water, the quantities being stated in c c $N/40$ $Ba(OH)_2$ If the formula of the molecule of the acid in toluene is represented as $(C_6H_5 CO OH)_n$, then the value of $n$ is that whole number which gives a constant value to $K$ in the equation

$$K = \frac{(\text{concentration of benzoic acid in water})^n}{(\text{concentration of benzoic acid in toluene})}$$

Two assumptions, which are only roughly true, have been used in deducing this equation (p 565), viz that the benzoic acid molecule exists almost solely as (i) $C_6H_5$ CO OH in water and (ii) $(C_6H_5 CO OH)_n$ in toluene The ionisation of the acids in the weakest aqueous solution used above is about 14% , but this error is roughly compensated by an even greater dissociation of the associated molecules in toluene

EXPT 114B **To determine the formula of the cuprammonium ion.**

When an excess of ammonia is added to a solution of cupric sulphate a deep blue solution containing a complex cuprammonium ion is formed

$$Cu^{++} + xNH_3 \rightleftharpoons Cu(NH_3)_x^{++}$$

In the following experiment a large excess of ammonia is used, so that the dissociation of the complex ion may be ignored

By means of a pipette place 25 c c of *N* ammonia in a separating funnel, followed by 25 c c of *M*/10 cupric sulphate Shake the mixture thoroughly, then add to it 75 c c of chloroform from a measuring cylinder and shake for about ten minutes Allow the mixture to settle, then run off 50 c c of the lower chloroform layer into a measuring cylinder and transfer half of this to a stoppered bottle containing about 25 c c of water and a few drops of methyl orange Titrate this liquid with *N*/40 hydrochloric acid, being careful to shake at intervals Having obtained a rough end-point with 25 c c of the chloroform, add the other 25 c c from the cylinder and thus obtain a fairly exact end-point

Repeat the above experiment with a fresh supply of ammonia, etc , but do not discard the chloroform, because it can be washed with plenty of water, dried with calcium chloride and distilled for use again

To calculate the value of $x$ assume that the partition coefficient of ammonia between water and chloroform is 26 1 As a hint, calculate g -mols free ammonia in chloroform, hence g -mols free ammonia in aqueous layer, subtract the sum of these from the original quantity of ammonia to get the number of g -mols ammonia combined with 0 0025 g -ions of copper

EXPT 115 **Equilibrium in the interaction of alcohol and acetic acid.**

Weigh into three drawn-out test tubes

(*a*) About 3 grams glacial acid
,, 1 gram absolute alcohol
(*b*) About 2 grams glacial acetic acid
,, 2 grams absolute alcohol
(*c*) About 1 gram glacial acetic acid
,, 3 grams absolute alcohol

Seal off the tubes and heat in a bath of water at about 60° for five to six hours Allow to cool, open the tubes, rinse out with cold water and titrate rapidly with normal NaOH (free from carbonate), using phenolphthalein as indicator. Also titrate a weighed amount of the glacial acetic acid used From your results calculate the number of molecules of ester formed in each case Set out the results in tabular form as follows

| *Tube* | *Mols acid.* | *Mols alcohol.* | *Molecules ester* | |
|---|---|---|---|---|
| | | | (*a*) Found | (*b*) Calc |

The numbers in the last column can be calculated by the equation on p 562

# CHAPTER XLII

## VELOCITY OF CHEMICAL CHANGE

In Chapter XLI the law of mass action was applied to chemical systems which are in equilibrium, and a formula was deduced for the equilibrium-constant by postulating that at equilibrium the forward and back reactions take place with equal velocities In the present chapter the law of mass action is used to predict the velocity of reactions which proceed to completion in one direction *i e* the reverse reaction is regarded as negligible under the conditions considered

**Reactions of the first order.**—In the simplest type of reaction the changes of concentration which occur are limited to a single component, and are confined to molecules which appear only once in the equation Changes of this type are known as *reactions of the first order*, or UNIMOLECULAR REACTIONS An example of this group of changes is given by the decomposition of oxalic acid in the presence of a large excess of hot concentrated sulphuric acid

$$(COOH)_2 \rightarrow CO + CO_2 + H_2O.$$

Although the sulphuric acid plays a vital part in this decomposition (since it combines with the water which is liberated by the decomposition of the acid), its concentration remains substantially constant throughout the reaction, provided that it was initially present in large excess Under these conditions, therefore, only the concentration of the oxalic acid alters, so that the chemical change may be regarded as a unimolecular reaction

The course of the decomposition can be followed by heating a mixture of concentrated sulphuric acid and oxalic acid to 100° on a water bath Portions of the mixture are withdrawn from time to time with a pipette, and run into excess of water, when the decomposition ceases immediately The oxalic acid is then estimated by titration with permanganate The results given in Table 76 were obtained by the method described in Expt 116 (p 580)

According to the law of mass action, the rate of change should be proportional to the amount of oxalic acid present Since, however, this amount decreases progressively as the action proceeds, the actual rate of change diminishes continually, and the rate of reaction can only be defined in terms of the concentration of the material which still remains unchanged.

The validity of the law of mass action can be tested roughly by determining the amount of oxalic acid which is changed during two similar

intervals in the course of the action, and comparing these rates of change with the amounts of unchanged material still present at the middle of the two intervals Thus, in Table 76, the loss of oxalic acid during the first five hours is equivalent to 5 4 c c of permanganate solution, or an average rate of 1 08 c c per hour The concentration of oxalic acid on the same scale was 23 1 at the beginning of this interval, and at the end of 5 hours 17 7, so that the average concentration during this time was 20 4 Similar pairs of observations, but differing by two and a half hours, are contained in the table It will be seen that the average loss per hour decreases, but that it is always proportional to the concentration of the oxalic acid This is shown by the constancy of the numbers in the last column, which were obtained by dividing the average loss by the average concentration of the unchanged acid

TABLE 76 —DECOMPOSITION OF OXALIC ACID

| Time (hours) | Titration with permanganate (c c of N/10 solution) | Average loss per hour | Average concentration | Rate of decomposition = Average loss —Average concentration |
|---|---|---|---|---|
| 0 | 23 1 | 1 08 | 20 4 | 0 054 |
| 5 0 | 17 7 | | | |
| 7 50 | 15 5 | 0 74 | 14 6 | 0 051 |
| 10 0 | 13 65 | | | |
| 12 5 | 12 0 | 0 60 | 11 2 | 0 054 |
| 15 0 | 10 5 | | | |
| 17 5 | 9 2 | 0 44 | 8 65 | 0 051 |
| 20 0 | 8 1 | | | |

A neater and more accurate treatment of the problem can be given by using the methods of the differential and integral calculus Let the initial concentration of oxalic acid be $a$ molecules per litre After a time $t$ let $x$ molecules be decomposed. From the law of mass action it follows that at the time $t$,

$$\textit{rate of reaction} = k(a - x), \text{ where } k \text{ is a constant}$$

The rate of decomposition at the time $t$ may be written $dx/dt$, where $dx$ is a very small change in $x$ during a very small interval of time $dt$ We can therefore write the equation as follows .

$$\frac{dx}{dt} = k(a - x). \tag{1}$$

Integration of this equation gives

$$x = a(1 - e^{-kt}), \tag{11}$$

where $e = 2\ 718$ is the base of the natural system of logarithms If the value of $k$ is known, this equation may be used to calculate $x$, and the values thus found may be compared with those obtained experimentally ,

but it is more convenient to change the equation into a form by means of which $k$ can be calculated Thus

$$x = a - ae^{-kt}, \quad \text{or} \quad a - x = ae^{-kt},$$

or

$$\frac{a}{a-x} = e^{kt}$$

Taking logarithms,

$$\log_e \frac{a}{a-x} = kt,$$

or

$$k = \frac{1}{t} \log_e \frac{a}{a-x} \qquad \text{(iii)}$$

$$= \frac{2\ 303}{t} \log_{10} \frac{a}{a-x} \qquad \text{(iv)}$$

(since $\log_e a = 2\ 303 \log_{10} a$) Equation (iv) is the characteristic equation of a unimolecular reaction or reaction of the first order Table 77 gives the values of $k$ which are obtained when this equation is applied to the data given above for the decomposition of oxalic acid The constancy of $k$ shows that this decomposition can be regarded as a unimolecular change

TABLE 77.—DECOMPOSITION OF OXALIC ACID

| Time, hours ($t$) | Titration ($a - x$) | $k^* = \frac{2\ 303}{t} \log_{10} \frac{a}{a-x}$ |
|---|---|---|
| 0 0 | 23 1 | |
| 5 00 | 17 7 | 0 0532 |
| 7 50 | 15 5 | 0 0531 |
| 10 0 | 13 65 | 0 0526 |
| 12 5 | 12 0 | 0 0522 |
| 15 0 | 10 5 | 0 0525 |
| 17 5 | 9 20 | 0 0525 |
| 20 | 8 10 | 0 0523 |

**Significance of the velocity coefficient.**—The constant $k$ is termed the VELOCITY COEFFICIENT of the unimolecular reaction It represents the fraction of the original substance which would change in unit time if the concentration were maintained at unity Thus, putting $dt = 1$, and $a - x = 1$, the equation $dx/dt = k(a - x)$ becomes $k = dx$ Thus $k = 0\ 00088$ for the reaction discussed above means that 0 00088 of the oxalic acid present is decomposed every minute The value of $k$ obviously depends on the units of time chosen, and in order to express this fact one should write $k = 0\ 00088$ per minute, or 0 0526 per hour

For a reaction of the first order $k$ does *not* change if the units in which $a$ and $a - x$ are measured are altered Thus, suppose we change to units

* The time is usually measured in minutes, in which case the first value of $k$ would be 0 00087

$n$ times smaller than those used originally, then $a$ becomes $na$, and $a-x$ becomes $n(a-x)$, so that

$$k=\frac{1}{t}\log_e\frac{na}{n(a-x)}=\frac{1}{t}\log_e\frac{a}{a-x},\text{ as before,}$$

since the $n$'s cancel out This is only true for unimolecular reactions , for reactions of a higher order the numerical value of $k$ depends upon the units in which the concentrations of the reacting substances are measured It is because the units used do not matter in a reaction of the first order that the titration figures were employed in calculating Table 76, instead of reducing them to concentrations expressed as gram-molecules per litre

**The inversion of cane-sugar.**—The rate of hydrolysis of cane-sugar to glucose and fructose was measured by Wilhelmy in 1850, and has been studied subsequently by many other investigators From the equation,

$$\underset{\text{Cane-sugar}}{C_{12}H_{22}O_{11}}+H_2O\rightarrow\underset{\text{Glucose}}{C_6H_{12}O_6}+\underset{\text{Fructose}}{C_6H_{12}O_6},$$

it would be expected that the reaction would be of the *second* order, since the concentrations of cane-sugar and of water both change as the reaction proceeds Except, however, in very concentrated solutions, the concentration of water remains nearly constant, since only a very small fraction of the total amount of water present is used up in the hydrolysis The velocity of the change will therefore be given by

$$\frac{dx}{dt}=k[C_{12}H_{22}O_{11}][H_2O]$$
$$=k'[C_{12}H_{22}O_{11}],$$

where $k'=k[H_2O]$, and is constant

This reaction can be followed readily by polarimetric measurements, since cane-sugar is dextro-rotatory whilst the mixture of glucose and fructose is laevorotatory It is indeed for this reason that the hydrolysis is usually described as the INVERSION OF CANE-SUGAR The rate of inversion in pure water is too slow to be measured In order to secure suitable readings at convenient intervals of time, it is therefore necessary to speed up the action by the addition of a catalyst (p 585), namely 0·9$N$ hydrochloric acid, in the experiment quoted above Since, however, the concentration of the acid, like that of the large excess of water, does not change appreciably during the inversion of the sugar, the action maintains its unimolecular character

**Other unimolecular actions.**—The two unimolecular actions which have been considered up to the present are all concerned with organic substances It is noteworthy that most of the reactions met with in inorganic chemistry (*e g* the reactions between ions which are so important in qualitative analysis) take place with a velocity which is too high to be measured There are, however, some inorganic reactions which proceed sufficiently slowly for measurements of velocity to be made Thus the decomposition of pure hydrogen peroxide is extremely slow, but can be accelerated to any desired extent by the addition of a catalyst

$$H_2O_2=H_2O+\tfrac{1}{2}O_2.$$

The rate of decomposition can then be followed very easily, either by titrating the residue of hydrogen peroxide with potassium permanganate, or by measuring from time to time the volume of oxygen which has been evolved This action is found to obey the unimolecular law, whatever the nature of the substance which is added in order to accelerate the decomposition (see Expt 120)

The hydrolysis of esters in the presence of acids (Expt 121) and the decomposition of gaseous nitric anhydride, $N_2O_5$, are other well-known reactions which proceed according to the unimolecular law

**Reactions of the second order.**—When the concentrations of two of the molecules taking part in a reaction are altering, the change is known as a *reaction of the second order*, or a BIMOLECULAR REACTION A familiar example is the saponification of an ester by an alkali Thus ethyl acetate is saponified by caustic soda according to the equation

$$\underset{(a-x)}{CH_3\ CO\ OC_2H_5} + \underset{(a-x)}{NaOH} = \underset{x}{CH_3\ CO\ ONa} + \underset{x}{C_2H_5OH}$$

If we start with $a$ gram-molecules each of ethyl acetate and caustic soda, the rate of change at time $t$, when the amount of ester saponified is $x$, will be given by

$$\frac{dx}{dt} = k[\text{ester}][NaOH] = k(a-x)^2 \qquad (v)$$

When integrated this equation becomes

$$k = \frac{1}{at}\frac{x}{a-x} \qquad (vi)$$

The action formulated above proceeds only very slowly in cold dilute solutions, and can be stopped altogether by neutralising the free alkali with a mineral acid The hydrolysis of the ester in presence of a dilute mineral acid is also a very slow process The amount of caustic soda which is left over, when a part of the ester has been saponified, can therefore be estimated by running a known volume of the solution into a slight excess of acid, and titrating the excess of acid with standard alkali Expt 117 gives details for studying the rate of this change , and some typical results are set out in Table 78 It will be seen that equation (vi) gives a fairly constant value for the velocity coefficient, whereas the coefficients in the last column, which are for the unimolecular equation, decrease rapidly

TABLE 78.—SAPONIFICATION OF ETHYL ACETATE

($a = 16\ 00$)

| $t$ (min) | $x$ | $k_2 = \frac{1}{at}\frac{x}{a-x}$ | $k_1 = \frac{1}{t}\log_e\frac{a}{a-x}$ |
|---|---|---|---|
| 5 | 5 76 | 0 0070 | 0 089 |
| 15 | 9 87 | 0 0067 | 0 077 |
| 25 | 11 68 | 0 0069 | 0 060 |
| 35 | 12 59 | 0 0066 | 0 050 |
| 55 | 13 69 | 0 0067 | 0 039 |

If unequal amounts of ester and alkali are taken, the formula becomes a little more complicated Let the initial concentrations be $a$ mols of ester and $b$ mols of alkali, and let $x$ mols of these be used up at a time $t$ Then the law of mass action gives, for the rate of change at this instant,

$$\frac{dx}{dt} = k(a-x)(b-x) \quad \ldots \quad \ldots\ldots\ldots \quad \ldots \qquad \text{(vii)}$$

On integration this becomes

$$k = \frac{1}{t(a-b)} \log_e \frac{b(a-x)}{a(b-x)} \qquad .. \qquad \text{(viii)}$$

**Other bimolecular reactions** —Sodium thiosulphate reacts with bromacetic ester according to the equation

$$CH_2Br \cdot COOC_2H_5 + Na_2S_2O_3 = CH_2(NaS_2O_3)COOC_2H_5 + NaBr$$

This bimolecular reaction can easily be followed by estimating the unchanged thiosulphate with iodine

The thermal decomposition of nitrogen peroxide into nitric oxide and oxygen is also bimolecular and can be followed by measuring the pressure of the system :

$$2NO_2 \rightarrow 2NO + O_2$$

At temperatures above 600° the reverse change is negligible

**Reactions of the third order.**—The reduction of ferric chloride by stannous chloride involves the interaction of three molecules and may therefore be taken as an example of a TERMOLECULAR REACTION or *reaction of the third order*

$$2FeCl_3 + SnCl_2 \rightarrow 2FeCl_2 + SnCl_4$$

The law of mass action predicts that the rate of the action will be given by

$$\frac{dx}{dt} = k[FeCl_3]^2[SnCl_2]$$

Thus, if we start with $a$ mols of each, the rate of the reaction at time $t$, when $x$ mols have reacted, will be given by the equation

$$\frac{dx}{dt} = k(a-x)^3 \qquad . \ldots\ldots\ldots\ldots \qquad \text{(ix)}$$

On integration this equation becomes

$$k = \frac{1}{2t}\left(\frac{1}{(a-x)^2} - \frac{1}{a^2}\right) \qquad \ldots\ldots\ldots\ldots \qquad \text{(x)}$$

Table 79 gives some data obtained by Noyes, who followed the progress of the reduction by withdrawing samples of the solution at definite intervals of time, adding mercuric chloride to destroy the unchanged stannous chloride ($SnCl_2 + 2HgCl_2 = SnCl_4 + Hg_2Cl_2$), and then estimating the ferrous chloride in the usual way with standard dichromate It will be seen that these data give a very steady value for the termolecular velocity coefficient.

TABLE 79.—REDUCTION OF FERRIC CHLORIDE BY STANNOUS CHLORIDE.
$[SnCl_2] = [FeCl_3] = 0.0625N = a$

| $t$ | $x$ | $k = \frac{1}{2t}\left(\frac{1}{(a-x)^2} - \frac{1}{a^2}\right)$ |
|---|---|---|
| 1 | 0.01434 | 88 |
| 3 | 0.02664 | 87 |
| 7 | 0.03612 | 84 |
| 11 | 0.04102 | 87 |
| 40 | 0.05058 | 85 |

**Reactions of higher orders.**—Reactions of a higher order than three are very rare in spite of the fact that many reactions are known in which more than three molecules are required to complete the chemical equation This is probably due to the fact that chemical changes often take place in successive stages, the slowest of which determines the actual speed

**Determination of the order of a reaction.**—(i) The first and most obvious method of finding the order of a chemical change is to determine whether the course of the change can be expressed by a unimolecular, bimolecular or termolecular equation For this purpose it is necessary to measure the amount of substance changed after various periods of time By substituting the values thus obtained in the expressions for the velocity coefficient of a unimolecular, bimolecular, or higher reaction, it will readily be seen which of these expressions gives the most satisfactory constant

An example of this method is given in Table 78, where the column headed $k_1$ gives the coefficient calculated by a unimolecular formula from the data in the second column, whilst the column headed $k_2$ gives the coefficients calculated by means of a bimolecular formula It will be seen that $k_1$ decreases rapidly as the action progresses, but that the values of $k_2$ remain steady throughout, thus showing that the saponification of ethyl acetate is a bimolecular and not a unimolecular reaction

(ii) Another method is to measure the time required for a given fraction of the change to be completed Two experiments must be carried out at concentrations $c_1$ and $c_2$ Let the times at which the reaction is half-completed be $t_1$ and $t_2$, then

$$\frac{t_2}{t_1} = \left(\frac{c_1}{c_2}\right)^{n-1}. \qquad \text{(xi)}$$

where $n$ is the order of the reaction Thus, when $n = 1$, $t_1 = t_2$, *i.e. in a unimolecular reaction the time for half-change is the same at all concentrations.* Similarly, in a bimolecular action, if the concentration is doubled, the time required for the change to be half-completed is halved, and so on.

An example of the application of this method is given by the work of Hinshelwood on the reduction of nitric oxide by hydrogen, as represented by the equation .

$$2NO + 2H_2 \rightarrow N_2 + 2H_2O.$$

This equation shows the ultimate products of the action correctly but indicates that the reaction should be quadrimolecular The course of the reaction was followed by noting by means of a manometer the pressure of the gaseous mixture at definite intervals, whilst its volume and temperature were kept constant Different initial pressures of the reactants were taken and the time for one half of the reaction to take place was measured Since the pressure of a gas is a measure of its concentration, the values $p_1$ and $p_2$ in the two experiments were substituted for $c_1$ and $c_2$ in equation (xi) The values obtained for $n$ in different experiments approached 3, showing that the reaction is apparently termolecular and not quadrimolecular as might be supposed from the above equation In order to explain this result, it has been suggested that the change includes a slow action in which nitric oxide and hydrogen interact to form nitrogen and hydrogen peroxide according to a termolecular equation,

$$2NO + H_2 \rightarrow N_2 + H_2O_2,$$

followed by a rapid reduction of the hydrogen peroxide to water by the action of a second molecule of hydrogen as shown in the equation

$$H_2O_2 + H_2 \rightarrow 2H_2O$$

(iii) A third method of determining the order of a complex reaction is known as OSTWALD'S ISOLATION METHOD It depends on making a series of experiments in which all but one of the reacting substances is taken in large excess, so that the rate of the reaction with respect to one substance only is studied This method has been applied to the reaction between potassium iodide and potassium ferricyanide, which can be represented by the equation,

$$3KI + 2K_3FeC_6N_6 = 2K_4FeC_6N_6 + KI_3,$$

or

$$3I' + 2[Fe(CN)_6]''' = 2[Fe(CN)_6]'''' + I_3'$$

When excess of potassium iodide was taken (so that its concentration was almost constant), the rate of liberation of iodine followed a bimolecular law, *i e* two molecules of ferricyanide took part in the change When excess of ferricyanide was used, the reaction was found to be termolecular, indicating that three molecules of potassium iodide took part The action is therefore quinquemolecular, since the rate is given by the equation,

$$\frac{dx}{dt} = k[K_3Fe(CN)_6]^2[KI]^3$$

**Complexity of chemical change.**—In the preceding pages we have considered a number of ideal types of chemical change in which a definite number of molecules of the initial materials are converted completely, and without loss, into a definite number of molecules of the various products These ideal changes are, however, by no means universal, since the simple action, represented by a formal chemical equation, is often complicated by secondary changes of various kinds , and even when the course of the action can be expressed by a simple unimolecular or bimolecular equation, it does not follow that the changes which are actually occurring

are anything like as simple as the equations used to represent them Some of the principal sources of complexity are set out below

(*a*) *Simultaneous actions* —In many cases the course of a chemical change is complicated by the fact that two or more reactions may be proceeding simultaneously and independently Thus, when propyl chloride is acted on by caustic potash, the alkali may either remove hydrogen chloride, or replace the chlorine by hydroxyl according to the schemes set out below

$$CH_3\ CH_2\ CH_2Cl + KOH \begin{cases} \rightarrow CH_3\ CH\ CH_2 + KCl + H_2O \\ \rightarrow CH_3\ CH_2\ CH_2OH + KCl \end{cases}$$

In practice, both propylene (p 671) and propyl alcohol (p 677) are formed Moreover, the yield of these two products can be varied by changing the conditions Thus, alcoholic potash gives mainly propylene, whilst aqueous potash gives mainly propyl alcohol

(*b*) *Consecutive actions* —In certain cases the course of the reaction is complicated by the fact that a number of changes take place consecutively Thus the hydrolysis of ethyl malonate (p 751) and of the esters of other dibasic acids proceeds in two stages

$$CH_2\begin{cases} CO\ OC_2H_5 \\ CO\ OC_2H_5 \end{cases} + H_2O \rightarrow CH_2\begin{cases} CO_2H \\ COOC_2H_5 \end{cases} + C_2H_5{\cdot}OH, \qquad \text{I}$$

$$CH_2\begin{cases} CO_2H \\ CO\ OC_2H_5 \end{cases} + H_2O \rightarrow CH_2\begin{cases} CO_2H \\ CO_2H \end{cases} + C_2H_5\ OH \qquad \text{II}$$

Stage II is usually much slower than stage I, and the existence of two stages can therefore be detected by measurements of the rate at which the hydrolysis proceeds When one stage is very much slower than the others, the whole course of the change may be controlled by it, like traffic held up by a " bottle-neck " The reaction may then appear to be of a lower order than that of the simplest chemical equation which can be used to represent it

(*c*) *Reversible actions* —Many chemical changes proceed to an equilibrium instead of going completely from left to right Thus, although saponification of an ester by an alkali proceeds to completion, the hydrolysis of the ester in the presence of an acid is a reversible action and should therefore be represented by an equation with double arrows, thus

$$CH_3 \cdot CO \cdot OCH_3 + H_2O \rightleftharpoons CH_3\ CO\ OH + CH_3 \cdot OH$$

When the amount of water present is large, the back action may be neglected , if, however, smaller amounts of water are used, the influence of the accumulating products must be allowed for by adding to the equation a new term to represent the speed of the back action In practice it is found that, if the forward and back actions taken separately conform to a unimolecular law with velocity coefficients $k_1$ and $k_2$, the combined action *in either direction* can be represented by a unimolecular equation with a velocity coefficient $k_1 - k_2$

(*d*) *Catalysed actions* —A large number of chemical actions, which give a constant velocity coefficient in a unimolecular equation, are seen on closer examination to be really bimolecular actions, in which the concentration of one reactant remains constant or nearly constant Thus the hydrolysis of methyl acetate in the presence of acids should be written.

$$CH_3\ CO\cdot OCH_3 + H_2O + \overset{+}{H} \rightleftharpoons CH_3\ CO\ OH + CH_3\cdot OH + \overset{+}{H}$$

In aqueous solution, the concentration of water does not change appreciably, nor does the concentration of the hydrogen ion, so that a unimolecular law is followed

(*e*) *Surface actions* —An action which is catalysed by a solid surface may obey the unimolecular law merely because the chemical change is controlled by physical conditions such as diffusion or absorption Thus the decomposition of phosphine by heat is represented by the equation,

$$4PH_3 = P_4 + 6H_2,$$

and should therefore obey a quadrimolecular law, but in practice the change is found to follow a unimolecular law It can be shown, however, that the reaction occurs almost entirely on the surface of the vessel, since the rate of change is largely increased when the vessel is filled with glass-wool in order to increase its surface In such a case the number of molecules of gas reaching the surface in unit time will be proportional to the pressure, and the rate at which the gas reacts will therefore follow a unimolecular law whatever be the order of the reaction at the glass surface, provided that, as in this case, the reaction is more rapid than the rate of diffusion

The decomposition of hydrogen peroxide in the presence of solid catalysts is another example of this type, in that the decomposition takes place at the surface of the catalyst Since the surface action is very rapid, the rate of the reaction depends upon the rate of diffusion on to the catalyst, and is therefore directly proportional to the concentration of the hydrogen peroxide

EXPT 116 **The decomposition of oxalic acid**

Prepare sulphuric acid of about 88% strength by mixing 250 c c of the pure acid (s g 1 843) with 35 c c of water Heat 250 c c of this acid in a round-bottomed flask on a water bath, and when the temperature has reached a steady value of about 99 5° add about 4 grams of powdered crystallised oxalic acid Shake the flask at intervals until the oxalic acid has dissolved, then withdraw 10 c c of the mixture with a pipette (arranged in series with a U-tube for safety), and run into 50 c c of water in a conical flask. Since decomposition of the oxalic acid stops immediately on dilution with water, the time is recorded from the moment at which the pipette has discharged about half its contents Estimate the strength of the oxalic acid by heating the diluted portion to 65°, and titrating with $N/10$ permanganate At the end of an hour, and subsequently at intervals of half an hour, withdraw further portions of 10 c c of the acid mixture and estimate as above. It is a good plan to duplicate each titration by

withdrawing two portions of 10 c c at each interval If the two titrations diverge by more than 0 2 c c they should be checked by a third titration If the end-point is overshot, estimate the excess of permanganate by adding excess of potassium iodide and titrate back with $N/10$ thiosulphate

Calculate the velocity coefficient, $k$, by substituting the value of the initial permanganate titration for $a$, and subsequent titrations for $a - x$, in the unimolecular equation

$$2\ 3 \log \frac{a}{a-x} \frac{1}{t} = k$$

The time $t$ should be expressed in minutes

EXPT 117 **Saponification of ethyl acetate**

(*a*) *Preparation of caustic soda free from carbonate* —Dissolve 22 grams of stick caustic soda, from a freshly-opened bottle, in about 900 c c of water Add to this 5 grams of freshly-slaked lime, suspended in 100 c c of water, and allow to stand in a stoppered bottle The clear solution is syphoned off from the precipitate into stock bottles This roughly $N/2$ solution can be stored in a bottle fitted with a burette and guard-tubes of soda lime as in Fig 156 The tubes, *AA*, contain soda lime , by opening the clip, *B*, and sucking through the tube, *C*, the burette can be filled without exposing the solution to the air In order to prevent sticking it is essential that the tap of the burette should be well greased with vaseline

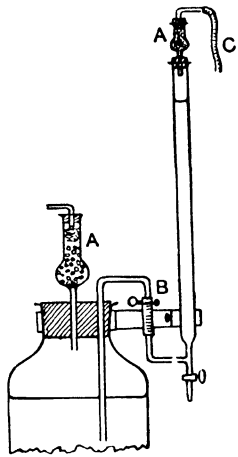


FIG 156 BURETTE FOR USE WITH SODIUM HYDROXIDE

Determine the strength of the caustic soda by titration with a standard acid From the burette run into a 250 c c standard flask the exact volume of caustic soda solution that will make 250 c c of $N/10$ NaOH, and make up to the mark with distilled water which has been recently boiled to remove carbon dioxide

(*b*) *Measurement of velocity of saponification of ethyl acetate* —Dissolve 4 4 grams of redistilled ethyl acetate in boiled-out water, and make up to 500 c c to obtain a tenth-normal solution Place 200 c c of this solution and 200 c c of the $N/10$ NaOH in two clean dry corked flasks in a thermostat at 25° Whilst the flasks are attaining this temperature, place 25 c c of $N/10$ HCl in each of five small flasks After 20 minutes pour the alkali into the ester, and then pour the mixture back into the flask which originally contained the alkali Withdraw 25 c c and run into the hydrochloric acid in one of the small flasks

Note the time when the pipette is half empty, and estimate the excess of acid by titration with $N/20$ baryta solution, using phenolphthalein as indicator Withdraw further portions after 15, 30, 45 and 60 minutes, and estimate in the same way the amount of caustic soda remaining

(*c*) *Calculation of a velocity coefficient*—Since equivalent quantities of ester and alkali were used, the velocity coefficient can be calculated by the formula

$$k = \frac{1}{at}\frac{x}{a-x}$$

Express $a$ and $x$ in gram-equivalents per litre

EXPT 118 **Order of the reaction between potassium persulphate and potassium iodide**

Potassium persulphate liberates iodine from potassium iodide according to the equation $K_2S_2O_8 + 2KI = 2K_2SO_4 + I_2$

In dilute solutions the reaction is sufficiently slow to be followed by estimating the liberated iodine from time to time with thiosulphate

Make up 100 c c of normal acetic acid, and 500 c c each of about $N/10$ potassium persulphate (6 7 grams) and $N/10$ potassium iodide (8 3 grams) Bring the solutions to a constant temperature in a thermostat at 20°, together with a flask containing 90 c c of distilled water Now pour from measuring cylinders 10 c c of the acetic acid, 200 c c of iodide, and 100 c c of the persulphate, into the flask containing the water Note the time at which the persulphate was added, and shake the flask to obtain a uniform mixture Follow the course of the reaction by withdrawing portions of 50 c c at intervals of 20, 40, 60, 90, 120, 150 and 180 minutes, and estimate the iodine with $N/200$ thiosulphate For the later titrations portions of 25 c c instead of 50 c c portions can be withdrawn Record the time from the end of the titration, which must be carried out as rapidly as possible

Repeat the above experiment by adding the same volumes of iodide, etc , as before, to a flask containing 490 c c of distilled water The concentrations of the reactants are thus one half of their value in the first experiment Estimate the iodine as before Draw a graph for each experiment by plotting the volume of thiosulphate required against the time Read from the graph the times required for the *same fraction* of the reaction to take place (*e g* $t_1$ for the first experiment at 30 c c thiosulphate, and $t_2$ for the second experiment at 15 c c thiosulphate) and substitute these values in equation (xi), page 577,

$$\frac{t_2}{t_1} = \left(\frac{c_1}{c_2}\right)^{n-1} = 2^{n-1},$$

where $n$ is the order of the reaction The result should be checked by taking several readings from the graph

# CHAPTER XLIII

## THE MECHANISM OF CHEMICAL CHANGE

**Influence of temperature on the rate of chemical change** —The speed of most chemical changes increases rapidly with a rise of temperature, *e g* a rise of 10° C often doubles the rate of change The ratio $k_{t+10}/k_t$, which is described as the TEMPERATURE COEFFICIENT OF THE ACTION, is set out for a number of chemical changes in Table 80

TABLE 80 —TEMPERATURE COEFFICIENTS OF REACTION VELOCITY

| Reaction | Temperature coefficient |
|---|---|
| $C_6H_6 + 3Cl_2 \xrightarrow{ICl_3} C_6H_6Cl_6$ | $k_{25°}/k_{15°} = 1\ 05$ |
| $EtAc + KOH \longrightarrow EtOH + KAc$ | $k_{35°}/k_{25°} = 1\ 82$ |
| $EtAc + H_2O \xrightarrow{HCl} EtOH + HAc$ | ,, $= 2\ 5$ |
| $C_{12}H_{22}O_{11} + H_2O \xrightarrow{HCl} 2C_6H_{12}O_6$ | ,, $= 4\ 13$ |
| $2N_2O_5 \longrightarrow 4NO_2 + O_2$ | ,, $= 3\ 98$ |
| $H_2 + I_2 \longrightarrow 2HI$ | $k_{705°}/k_{695°} = 1\ 53$ |

The temperature coefficient is usually between 2 and 3 , but the chlorination of benzene in the presence of iodine trichloride has an unusually low coefficient, and low values are also usually found for photochemical actions, *i e* actions which are brought about by exposure to light The inversion of cane-sugar, on the other hand, gives an abnormally high value It will be shown below that the influence of temperature on the rate of chemical change is an important factor in studying the mechanism by which the action proceeds, and that a number of interesting theories, including the theory of molecular activation, have been based upon observations of this property

**Kinetic theory of gaseous reactions.**—It has already been stated that by far the larger proportion of the reactions hitherto studied are of the first, second or third orders The rarity of reactions of higher orders is readily understood from the kinetic theory, since interaction can only occur when the right kinds of molecules collide It is evident that the chances of a simultaneous collision between four or five or more molecules is very small, and that reactions involving smaller numbers of molecules will be much more common

The simplest theory of chemical change is that which postulates that it is only necessary to bring together the right number and the right kind of molecules, when they will interact immediately to form the products of the reaction This theory is perhaps correct when applied to ionic reactions (Chapter XLV), which are in fact almost instantaneous, but the simple "collision theory" breaks down completely when attempts are made to deduce quantitative results, either as regards the *velocity* or as regards the *temperature coefficient* of chemical changes of other types

(i) In a simple bimolecular action between gases, where the number of collisions per second can be calculated from the kinetic theory, the number of pairs of molecules which undergo chemical change is found to be much smaller than the number which collide , it is, therefore, obvious that only a small fraction of the collisions are fruitful in the sense that they give rise to the products of the reaction, since if all the collisions were fruitful the action would be complete in a fraction of a second

(ii) Again, if we assume that the rate of a bimolecular action depends only on the number of collisions in unit time between the reacting molecules, it can be calculated from the kinetic theory that the temperature coefficient for 10° should be 1 04 Since in most cases much higher values are found, it is necessary to look for some other factors which may be concerned in bringing about chemical reactions

(iii) Finally, in the case of unimolecular actions, it is difficult to explain why the change should not be instantaneous if the action is really unimolecular and all the molecules are in a condition to undergo the change which is under consideration

**Arrhenius's theory of molecular activation** —The explanation of these observations which is most widely accepted is due to Arrhenius He suggested that the large temperature coefficients of chemical change can be explained by supposing that, in a system undergoing chemical change, there are a few ACTIVATED MOLECULES, which are in a condition to undergo chemical change, and that all the others are inert until they become activated in their turn This would explain why all the molecules in a unimolecular reaction do not change simultaneously The rapid increase of velocity with rising temperature can then be accounted for by supposing that the proportion of activated molecules increases rapidly with the temperature

This conclusion is very reasonable if we suppose that the activated molecules differ from the others in that they contain a larger amount of energy, since, according to the theory of probabilities, the number of molecules which have a kinetic energy exceeding a given value increases very rapidly as the temperature rises

At the present time discussion centres around the question as to how the activated molecules gain their extra energy In certain cases it is probable that, since chance collisions can give to a few molecules a velocity which is greater than the average, this extra kinetic energy can in some way be transformed into potential energy and make the molecule reactive In other cases it is almost certain that the products of the action, which will possess extra energy owing to the heat liberated by the chemical

change, can by collision activate molecules which have not yet reacted

**Catalysis.**—In 1835, Berzelius directed attention to a number of actions which were accelerated by the presence of an added substance which appeared to play no part in the change This phenomenon he described as CATALYSIS (Greek unloosen), and attributed it to a special " catalytic force " Although the conception of a catalytic force has now been abandoned, the term catalysis is used to describe all cases where *the rate of the reaction is altered by the addition of a substance which remains chemically unchanged* As a rule the added substance is described as a CATALYST when it accelerates the change, and as a NEGATIVE CATALYST when it retards the action

**Characteristics of catalytic actions.**—The most important characteristics of catalytic actions are as follows .

(1) *The catalyst remains unchanged at the end of the action* —This refers only to the chemical composition of the catalyst, since its physical form may be modified profoundly Thus, when coarsely broken manganese dioxide is used to catalyse the decomposition of potassium chlorate, the pieces are found to be disintegrated to a very fine powder at the end of the action In the same way, platinum, when used as a catalyst to promote the combination of hydrogen and oxygen, becomes coated with a finely-divided black powder, and this finely-divided platinum is a much more powerful catalyst than the polished metal

(2) *A small quantity of catalyst often has an appreciable effect* —In many cases a very small amount of catalyst produces an appreciable effect Thus Bredig found that 1 8 c c of oxygen were liberated per minute when only 0 00017 gm of colloidal platinum was added to a litre of hydrogen peroxide solution, and that the catalyst was as active after 10 litres of gas had been evolved as it was originally Titoff found that copper sulphate at a concentration of only $10^{-12}$ gram-molecules per litre caused an appreciable increase in the rate of oxidation of sodium bisulphite by air

For homogeneous systems (p 586), in which the catalyst and reactants are in the same phase, it is often found that the rate of the reaction is proportional to the concentration of the catalyst, but this rule does not hold when the action has a chain mechanism (p 278) In the case of heterogeneous systems, such as the combination of gases at the surface of a solid catalyst, the rate is proportional to the surface area of the catalyst, and this depends upon the fineness of subdivision of the catalyst (see hydrogen-oxygen action above)

In some cases a large amount of catalyst is required because one of the products reacts with the catalyst Thus in Friedel-Crafts reaction (p 779) a relatively large quantity of aluminium chloride is required to catalyse the combination of an aromatic compound with a halogen derivative,

$$\underset{\text{Benzene}}{C_6H_6} + \underset{\substack{\text{Methyl}\\\text{chloride}}}{CH_3Cl} \xrightarrow{AlCl_3} \underset{\text{Toluene}}{C_6H_5{\cdot}CH_3} + HCl,$$

because the catalyst combines with the product and is thus removed

(3) *A catalyst alters the speed of the action, but does not alter the final state of equilibrium* The interaction of alcohol and acetic acid to form ethyl acetate and water,

$$C_2H_5OH + CH_3CO OH \rightleftharpoons CH_3CO OC_2H_5 + H_2O,$$

is accelerated by acids, as also is the converse process of hydrolysis of ethyl acetate by water The final position of equilibrium is, however, unchanged, provided that the amount of acid used is small , *the forward and the backward changes must therefore be accelerated to the same extent*

It can be shown by thermodynamical reasoning that this proposition must be true whenever the catalyst is present only in small quantity, since the addition of a minute amount of a foreign substance cannot alter to any appreciable extent the energy of a system in equilibrium However, the presence of a large amount of catalyst may alter the nature of the solvent or of one of the products and thereby cause an apparent alteration in the equilibrium-constant Thus, although the equilibrium-constant for the reversible hydrolysis of ethyl acetate, in presence of small amounts of hydrochloric acid, has a uniform value of 4 4, which is independent of the concentration of the acid, the value of the constant is raised considerably in presence of large amounts of hydrochloric acid, and is actually doubled when the strength of the acid is raised to about 20%

(4) Ostwald's suggestion that *a catalyst cannot start a reaction but only increase or decrease its speed* is possibly incorrect, since there are many cases in which a catalyst appears to be merely *a reagent which is reproduced as a product of the reaction*, and is therefore essential to its progress

Ostwald compared a catalyst to a lubricant which enables a machine to move faster, or to a whip which urges on a reluctant horse Thus, he supposed that the interaction of hydrogen and oxygen gas proceeds at ordinary temperatures, and in the absence of any catalyst, although the rate is far too slow to measure The introduction of platinum black is then supposed merely to increase the speed of this pre-existing change

Definite evidence in favour of this view is difficult to find, since common experience shows that it is almost impossible to eliminate all catalytically active substances in a given reaction It has, however, been found possible by drastic purification to arrest the progress of some chemical changes so completely that no reaction appears to take place In such cases, however, it is always possible that a reaction is taking place, but that it is too slow to be detected even over a period of months or years

Experiments by Baker and others have indicated that a number of reactions, such as the combination of ammonia with hydrogen chloride, and the union of nitric oxide with oxygen, do not take place in the absence of moisture Some of these results have been questioned by later experimenters, so that it is not yet possible to give a definite answer as to whether the reactions are really initiated by moisture, even though traces of it may have a very pronounced catalytic effect.

**Homogeneous catalysis.**—It is convenient to divide catalytic actions into two groups, namely HOMOGENEOUS CATALYSIS, in which all the substances concerned are in one phase, and HETEROGENEOUS CATALYSIS, in

which two or more phases are present Examples of homogeneous catalysis are found in the action of water-vapour in promoting the burning of gaseous mixtures of hydrogen or carbon monoxide with oxygen, in the oxidation of sulphur dioxide to sulphur trioxide by oxides of nitrogen (p 256), and in the influence of acids in promoting the hydrolysis of cane-sugar (p 574) and esters in aqueous solutions

**Heterogeneous catalysis.**—Cases of heterogeneous catalysis, in which the catalyst forms a separate phase from the bulk of the reaction-mixture, are very numerous, and are often of great technical importance Finely-divided platinum is a very effective catalyst for changes such as the oxidation of sulphur dioxide to the trioxide (p 259) or the oxidation of ammonia to nitric oxide (p 196) Finely-divided nickel promotes the addition of hydrogen to unsaturated compounds, and is used (p 718) for the hardening of vegetable oils by combination with hydrogen, the solid products being used for margarine Charcoal assists the combination of carbon monoxide with chlorine to produce **phosgene,** $COCl_2$, a poisonous gas which is used in the manufacture of dyes In the Deacon process, which is now obsolete, copper chloride was used to promote the oxidation of hydrogen chloride by air (p 276) Finally, mention may be made of manganese dioxide, which catalyses the decomposition of potassium chlorate into oxygen and potassium chloride (p 230)

**Catalysis by enzymes.**—Another important group of catalysts of this class are the ENZYMES These are complex organic compounds which are produced by living plants and animals, but are readily destroyed by heat They form colloidal solutions in water and are very effective catalysts for a number of reactions Thus, the enzyme *invertase*, which occurs in yeast, converts sucrose into glucose and fructose by a process of hydrolysis, then other enzymes which are present in yeast bring about alcoholic fermentation (p 679)

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{\text{Invertase}} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

$$C_6H_{12}O_6 \longrightarrow 2C_2H_5OH + 2CO_2$$

**Autocatalysis** —Some reactions are known in which the products of the action act as catalysts Thus, the hydrolysis of ethyl acetate by water is accelerated by the acetic acid produced by the hydrolysis, and the value of the unimolecular velocity coefficient $k$ (which is very small at first) therefore increases rapidly as the action proceeds This phenomenon is known as AUTOCATALYSIS

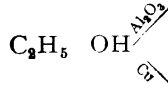
A case of autocatalysis which is of technical importance is the decomposition of the organic nitrates, such as nitro-cellulose, which are used as explosives This action takes place very slowly, but it is accelerated by oxides of nitrogen, which are formed in the decomposition If, therefore, decomposition once sets in, it may proceed more and more rapidly until a spontaneous explosion takes place In order to prevent this decomposition, *stabilisers* are added, usually derivatives of urea, which react with any trace of oxides of nitrogen produced by incipient decomposition, and thus make the explosive safe and stable

**Mechanism of catalytic changes.**—Since practically all chemical changes can be catalysed by some substances, it does not appear probable that the manner in which a catalyst acts will always be the same. Two theories of catalysis are set out below

(*a*) *The "intermediate compound" theory* postulates that the catalyst combines with one of the reagents to form a more reactive intermediate compound Explanations of this kind have been suggested for many cases of catalytic action (pp 257 and 788) The existence of an addition compound, however, is not of itself evidence that the reaction proceeds through this compound, since cases are known in which the compound in question is less reactive than the substance from which it is formed Thus, the oxidation of ferrous sulphate by air is catalysed by nitric oxide , but the formation of the dark brown compound, $FeSO_4$, NO, which gives the colour in the " brown ring " test for nitrates, cannot be used to account for the catalytic action, since it is found that the nitric oxide in this compound is less efficient than free nitric oxide in promoting the oxidation In this case catalysis is probably due to the formation of nitrogen peroxide, $NO_2$, which is a very powerful oxidising agent It is indeed obvious that, although the formation of an intermediate compound may be essential to catalytic activity, the progress of the action would be prevented if the compound were too stable In general, therefore, it is unlikely that the essential intermediate compound will be capable of isolation under the same conditions as those which prevail when it is acting as a catalyst

(*b*) *The adsorption theory* was put forward as a physical explanation of the catalytic power of certain surfaces, such as that of finely-divided nickel and platinum, the activity of which was difficult to explain by the " intermediate compound " theory These surfaces are remarkable for their power of adsorbing substances, notably gases, the degree of adsorption and catalytic activity increasing with their fineness of sub-division The increase in the velocity of the reaction was therefore attributed to the close contiguity of the reactants in the adsorbed films The surface would only retain its catalytic activity, however, if the products of the reaction were less easily adsorbed than the reactants , some surfaces, which have great absorbent power, have therefore little or no catalytic activity

This simple physical theory of catalysis has been proved to be incomplete by the discovery that the course of a reaction may be altered profoundly by changing the solid catalyst Thus (i) when ethyl alcohol vapour is passed over aluminium oxide at 300°, the principal products are ethylene and water, whilst (ii) when finely divided copper is used as the catalyst, at the same temperature, the chief products are acetaldehyde and hydrogen .




$$C_2H_5OH \xrightarrow{Al_2O_3} C_2H_4 + H_2O, \quad \ldots \quad (i)$$

$$C_2H_5OH \xrightarrow{Cu} CH_3CHO + H_2 \quad \ldots \quad (ii)$$

This observation suggests that the adsorbed molecules of alcohol are oriented differently on alumina and on copper, and that they decompose

in different ways because of this difference in the manner in which they are attached to the solid surface In other words, adsorption by the active surface of a catalyst is probably not a mere physical process of condensation, but a chemical operation of " chemisorption " in which valency-forces are called into play In general, therefore, catalysis both in homogeneous and in heterogeneous systems may be attributed to the formation of unstable intermediate complexes, which require a smaller energy of activation than the original reactants for the chemical change to take place

**Inhibitors and catalyst poisons.**—It is characteristic of a catalyst that it is reproduced as a product of the reactions in which it takes part, and can therefore be used over and over again without being consumed For this very reason, however, catalysed actions are extremely sensitive to the presence of any substance which will interact with the catalyst in such a way as to prevent it from playing its usual part, since, for every molecule of the catalyst which is thus " put out of action," many hundreds of other molecules may be prevented from undergoing chemical change Substances which retard chemical change by destroying the efficiency of an essential catalyst are generally described as ANTI-CATALYSTS or CATALYST POISONS In particular, any substance which is adsorbed more strongly than the reactants at the surface of a solid catalyst may be expected to act as a poison Thus, when hydrogen peroxide is decomposed under the influence of colloidal platinum or of the enzyme haemase (Expt 119), it is found that the platinum and the enzyme are both rendered inactive by the presence of certain " poisons " although the effects produced are often widely different in the two cases Table 81 shows the concentrations of these " poisons " which are required in order to reduce the velocity of the decomposition of hydrogen peroxide to half its original value

TABLE 81.—CONCENTRATION OF CATALYST POISON, IN GRAM-MOLS PER LITRE, REQUIRED TO REDUCE THE RATE OF DECOMPOSITION OF HYDROGEN PEROXIDE TO ONE HALF

| Poison | Catalyst | |
|---|---|---|
| | Colloidal platinum | Haemase |
| $H_2S$ - - - | $3 \times 10^{-6}$ | $1 \times 10^{-6}$ |
| HCN - - - | $5 \times 10^{-8}$ | $1 \times 10^{-6}$ |
| $HgCl_2$ - - | $5 \times 10^{-7}$ | $5 \times 10^{-7}$ |
| Aniline - - | $2 \times 10^{-4}$ | $2.5 \times 10^{-3}$ |
| CO - - - | very poisonous | no poisoning |
| HCl - - - | $3 \times 10^{-4}$ | $1 \times 10^{-5}$ |
| $HNO_3$ - - | no poisoning | $4 \times 10^{-6}$ |

Since very small amounts of " poison " have such a marked effect on the velocity of a catalysed process, many industrial operations depend for their success on the complete elimination of all traces of " poisons " from the raw materials which are used Thus, the technical preparation of

sulphuric acid by the " contact " process only becomes possible when the gases (formed by burning sulphur or pyrites in a suitable proportion of air) are freed from every trace of arsenic before being brought into contact with the platinum catalyst

Retardation of a reaction by traces of a foreign substance may also occur in reactions which are not known to be dependent on the presence of a catalyst Cases such as these are usually described as examples of NEGATIVE CATALYSIS, since it looks at first sight as if these foreign substances produce a retardation in just the same direct way as a positive catalyst produces an acceleration of the reaction It is now believed that many reactions which are very sensitive to minute traces of negative catalysts or inhibitors are CHAIN REACTIONS (p 278), *i e* reactions in which an active molecule or free radical or atom hands on its energy to other molecules, so that the initial activation of one molecule brings about chemical change in a long series of other molecules until some accident occurs whereby the chain is broken and activation must be started again from some new centre The inhibitor acts either by removing an active atom or molecule, which is responsible for the propagation of the chain, or else by poisoning the surface of the containing vessel, thereby preventing it from initiating the reaction. Thus in daylight the combination of hydrogen and chlorine (p. 278) probably proceeds according to the following chain mechanism

$$Cl_2^* \text{ (activated by light)} \rightarrow Cl + Cl$$
$$Cl + H_2 \rightarrow HCl + H$$
$$H + Cl_2 \rightarrow HCl + Cl$$

By this mechanism a single atom of chlorine can bring about the combination of 100,000 molecules of hydrogen and chlorine The interaction is, however, powerfully inhibited by traces of nitrogen trichloride In order to explain this inhibition, it is supposed that the chains are broken through the removal of chlorine atoms by collision with molecules of nitrogen trichloride

$$NCl_3 + Cl \rightarrow N + 2Cl_2, \quad N + N = N_2$$

Thus if only 1% of the atoms of chlorine interact with $NCl_3$ instead of with $H_2$, the yield of hydrogen chloride would be reduced in the ratio of 1000 to 1, and no further explanation is needed in order to explain the sensitiveness of the reaction to the influence of inhibitors

EXPT 119 **Influence of temperature on the rate of oxidation of hydrogen iodide by hydrogen peroxide**

The velocity of this reaction can easily be compared at various temperatures by noting the time taken for similar mixtures to liberate the same quantity of iodine First prepare solutions of (i) *acidified potassium iodide* (20 grams of KI + 50 c c of 20% $H_2SO_4$ in two litres of water), (ii) *hydrogen peroxide* approximately $N/5$ (5 c c of 30% $H_2O_2$ per 500 c c , (iii) $N/10$ *sodium thiosulphate*, and (iv) *starch paste* Then place in a beaker 200 c c of the iodide solution, 10 c c. of the thiosulphate, a few drops of starch, and

finally 10 c c of the peroxide Iodine is liberated by the peroxide, but is immediately removed by the thiosulphate until the latter is all used up, the mixture then goes blue owing to the formation of the blue starch-iodine complex The time taken, after the addition of the peroxide, for the production of the blue colour is measured, and the mean temperature is taken as the average of the initial and final temperatures of the mixture

The experiment is repeated with similar quantities of the reagents, but at temperatures up to 50° The temperature is best controlled by heating the iodide solution, before the addition of the other ingredients, and then measuring the temperature after they have been added The temperature can be kept constant to within half a degree by heating the mixture occasionally with a Bunsen burner If greater accuracy is required the mixture can be kept at a constant temperature in a thermostat

In each experiment the production of the blue colour represents the point at which the same quantity of iodine has been liberated The relative velocities at different temperatures are therefore inversely proportional to the time, $t$, taken for the blue colour to develop The connection between the temperature and the velocity of the reaction is shown by plotting the logarithm of the reciprocal of the time, $t$, against the temperature, $T$ The value of $t$ should be in the neighbourhood of 10 minutes at 20°, and 2 5 minutes at 40°

EXPT 120 **Catalysis of the decomposition of hydrogen peroxide by haemase.**

Procure a quantity of fresh ox-blood, allow it to stand till a clot forms, and then pipette off 1 c c of the clear serum (which contains the catalyst haemase) and dilute to 1 litre with distilled water Prepare one litre of approximately $N/5$ neutral hydrogen peroxide solution by diluting 50 c c of 20 vol $H_2O_2$ to 200 c c , and adding sodium hydroxide until just neutral to litmus The solution is then made up to one litre and standardised with $N/10$ $KMnO_4$

(*a*) Place 200 c c of the dilute neutral hydrogen peroxide and 20 c c of the serum solution in separate flasks in a thermostat at 25° When the solutions have reached the temperature of the thermostat, add the serum to the peroxide, mix thoroughly and note the time At intervals of 10, 20, 30, 60 and 90 minutes, withdraw 10 c c of the peroxide mixture (20 c c in later titrations), run into sulphuric acid, which stops the decomposition and estimate the peroxide by titration with $N/10$ $KMnO_4$ The volumes of permanganate per 10 c c $H_2O_2$ may be substituted for $a - n$ in the unimolecular equation (IV) (p 573) In deducing the corresponding value of $a$, allowance is made for the fact that 200 c c of the original peroxide were diluted with 20 c c of serum

(*b*) The experiment may be repeated, using only half the amount of catalyst, when approximately half the former value will be found for the velocity coefficient

(*c*) It may also be repeated, using colloidal platinum (Expt 134, p 648) as a catalyst

EXPT 121 **Rate of hydrolysis of methyl acetate in the presence of acids at 15° and 20°.**

(*a*) Prepare a solution of hydrochloric acid which is within 1 per cent of semi-normal strength Place 100 c c of this acid in a corked flask, and immerse in a thermostat at 25° After half an hour, add 5 c c of methyl acetate and shake Note the time of addition of methyl acetate, then withdraw 5 c c immediately with a dry pipette, and run into 20 c c of cold distilled water in a small flask Titrate this solution rapidly with $N/10$ NaOH or $Ba(OH)_2$ solution, using phenolphthalein as indicator Withdraw further samples of 5 c c after intervals of 10, 20, 30, 40, 60, 80 and 100 minutes, and titrate as before Leave the flask tightly corked in the thermostat for 2 days, and titrate again to get the reading corresponding to complete hydrolysis

If the apparatus shown in Fig 156 is not available, the alkali should be re-standardised at the time of the final titration and a correction applied if its strength has altered Calculate the velocity coefficient from the formula

$$k = \frac{2\ 303}{t} \log_{10} \frac{c_\infty - c_0}{c_\infty - c_t},$$

where $c_0$ = titration at the start, $c_t$ = the titration after $t$ minutes, and $c_\infty$ = the final reading when hydrolysis is complete

(*b*) Repeat the experiment at 15° Use a large vessel of water as a thermostat and keep the temperature at 15° by adding warm or cold water from time to time Calculate the ratio $k_{25}/k_{15}$

# CHAPTER XLIV

## ELECTROLYSIS AND ELECTROLYTIC DISSOCIATION

**Conductors and non-conductors.**—Substances differ enormously in the resistance which they offer to the passage of electricity. Thus, if the same voltage is applied to a bar of silver and to a bar of sulphur of the same dimensions, the current through the silver is many million million million times as great as that which flows through the sulphur. The relation between the electrical pressure, the resistance, and the current in a conductor is given by OHM'S LAW, which states that *the current flowing through a conductor is proportional to the applied voltage and inversely proportional to the resistance* This law may be written

$$I = \frac{E}{R},$$

where $I$ is the current, $E$ is the electrical pressure, and $R$ is the resistance

The *current* is usually measured in amperes, the AMPERE being defined as *the current which deposits* 1 118 *milligrams of silver per second from a solution of silver nitrate* in a voltameter of specified form (p 596), the quantity of electricity which then passes in one second is called a COULOMB The *electrical resistance* is measured in ohms, the OHM being defined as *the resistance at* 0° *of a column of mercury* 106 3 *cm in length and weighing* 14 4521 *grams* * The *pressure* is measured in volts The VOLT is defined merely as *the pressure which is required to send a current of one ampere through a resistance of one ohm*

**Specific resistance and specific conductivity.**—The resistance of a conductor depends upon its shape as well as upon the material of which it is made. Hence, in order to compare the resistance of different substances, it is necessary to consider a standard form of conductor The SPECIFIC RESISTANCE of a substance is defined as the resistance in ohms of a cube of 1 cm side, when a difference of potential of 1 volt is applied to two opposite faces The reciprocal of the specific resistance is named the SPECIFIC CONDUCTIVITY and is usually denoted by the symbol $\kappa$ Thus $\kappa = 1/R$ Units of conductivity are sometimes termed "reciprocal ohms," or more shortly "mhos" (mho = ohm written backwards), in the same way a reciprocal megohm has been called a "gemmho"

Table 82 gives the specific resistances and conductivities of a number of substances and solutions It will be seen from the table that metals, fused salts, and certain aqueous solutions (usually solutions of salts, acids and bases) possess an appreciable conductivity and are classed as electrical conductors On the other hand, substances such as glass and sulphur

* The cross-section of such a column is approximately a square millimetre.

have only a very small conductivity and are usually termed non-conductors

TABLE 82.—SPECIFIC RESISTANCES AND CONDUCTIVITIES AT 18°

| Substance | $R$ = Specific resistance Ohms | $\kappa$ = Specific conductivity Mhos | Class |
|---|---|---|---|
| Silver | 0 00000166 | 602,000 | Metallic conductor |
| Copper | 0 00000178 | 562,000 | ,, ,, |
| Zinc | 0 0000061 | 164,000 | ,, ,, |
| Bismuth | 0 000119 | 8,400 | ,, ,, |
| Gas carbon | 0 005 | 200 | ,, ,, |
| Fused NaCl | 0 30 | 3 33 | Electrolyte |
| $N$ $H_2SO_4$ | 2 56 | 0 391 | ,, |
| $N$ KOH | 5 00 | 0 200 | ,, |
| $N$ KCl | 10 59 | 0 0944 | ,, |
| Pure water | $25 \times 10^6$ | $0\ 04 \times 10^{-6}$ | Non-conductor |
| Soft glass | $5 \times 10^{11}$ | $2 \times 10^{-12}$ | ,, |
| Sulphur | $4 \times 10^{15}$ | $2\ 5 \times 10^{-16}$ | ,, |

**Metallic conduction and electrolytic conduction**.—Two classes of conductors can be recognised in the substances set out in the preceding table When a current is passed through a copper wire, the wire is heated by the passage of the current, but is otherwise unchanged, and, when the current is cut off, it regains its original properties as soon as it has cooled down to its original temperature When, however, an electric current is passed through dilute sulphuric acid, the passage of electricity through the solution is accompanied by a chemical decomposition, since hydrogen is given off at one electrode and oxygen at the other, and this decomposition continues as long as the current flows

Substances which conduct electricity without suffering any permanent change are termed METALLIC CONDUCTORS All metals belong to this class and also a few substances which are not definitely metallic, *e g* gas carbon, selenium, and arsenic, which all have a small "metallic" conductivity

Most other pure substances are non-conductors both in the solid and in the liquid state, but alkalis and salts, which are very poor conductors when solid, are excellent conductors when fused, and are at the same time decomposed by the passage of the current. Substances which conduct electricity and simultaneously undergo a chemical change were described by Faraday as ELECTROLYTES (*i e* decomposed by electricity) To this class belong fused salts and a large number of solutions, *e g* aqueous and alcoholic solutions of salts, acids and bases Pure water is such a feeble electrolyte that it is often classed as a non-conductor

**Faraday's laws of electrolysis.**—From a long study of the phenomena of electrolysis, Faraday arrived at the following conclusions

(1) *The products of electrolysis appear only at the electrodes,* i e *the points at which the current enters and leaves the solution* In general, the electrolyte is resolved into two parts, one of which appears at each elec-

trode The "positive" electrode, at which the current enters the solution (according to the old convention, which treats the current as a flow of *positive* electricity), is called the ANODE, the "negative" electrode, at which the current leaves the solution, is called the CATHODE The radicals into which the electrolyte is resolved can be divided into two classes The metals and hydrogen appear at the cathode, or negative electrode, and (since opposite kinds of electricity attract one another) are said to be ELECTROPOSITIVE groups The non-metals and acid radicals appear at the anode, or positive electrode, and are said to be ELECTRONEGATIVE groups

(ii) *The amount of chemical decomposition is proportional to the quantity of electricity which passes through the electrolyte* This law, which is generally known as FARADAY'S FIRST LAW OF ELECTROLYSIS, implies that the amount of decomposition is independent of the temperature of the solution, of the current-density, and of the form or material of the electrodes and vessel When the conditions are such that the electrolysis is not complicated by secondary reactions, this law holds with great accuracy Thus the weight of silver deposited from a solution of silver nitrate, under specified conditions, is so strictly proportional to the current that it has been adopted as the basis of the international definition of the ampere

(iii) *When different compounds are decomposed by the same quantity of electricity, the weights of the products obtained are proportional to their chemical equivalents* This law is generally known as FARADAY'S SECOND LAW OF ELECTROLYSIS When 1 coulomb of electricity (a current of 1 ampere for 1 second) is passed through solutions of silver nitrate, of copper sulphate, and of dilute sulphuric acid, the amounts of silver, copper and hydrogen liberated are silver 1 118 milligrams, copper 0 32935 milligram, hydrogen 0 010446 milligram These numbers, which represent the amount of the product liberated by unit quantity of electricity, are known as the ELECTROCHEMICAL EQUIVALENTS of these elements Faraday's law states that *the electrochemical equivalents are proportional to the chemical equivalents* It can be tested by dividing the chemical equivalent by the electrochemical equivalent

| | | | |
|---|---|---|---|
| Silver - - - | 107 88 | —0 001118 | =96,495 |
| Copper - - - | 31 78 | —0 00032935 | =96,494 |
| Hydrogen - - | 1 0078 | —0 000010446 | =96,496 |

One gram-equivalent of any of these substances is therefore liberated by **96,500 coulombs** of electricity This important unit of electrical quantity is termed the FARADAY, and indicated by the symbol $F$ Hence the number of gram-equivalents of electrolyte decomposed in any electrolytic cell by a total flow of $It$ coulombs is given by $It/F$, where $I$ = the current in amperes, $t$ = time in seconds, and $F$ = 96,500 coulombs

**Decomposition of electrolytes** —In order to account for the facts that (i) the products of electrolysis are liberated only at the electrodes and (ii) a definite amount of electricity is associated with each equivalent of salt decomposed, Faraday supposed that the current was carried by particles charged with positive or negative electricity These were called

IONS (Greek ἴω, I go), because they moved to the electrodes under the influence of the current.

The metals and hydrogen were assumed to form positive ions because they were liberated at the CATHODE (the negative pole), whilst non-metals and acid radicals were assumed to give negative ions because they were liberated at the ANODE (the positive pole)

To account for Faraday's second law of electrolysis it is necessary to assume that the electric charges on an ion are directly proportional to its valency Thus if the sodium ion is represented with a single charge, $Na^+$, the cupric ion must have two charges, $Cu^{++}$, since twice as much electricity is required to deposit one gram-atom of copper as is required to deposit one gram-atom of sodium Similarly, if the chloride ion has a single negative charge, $Cl^-$, the sulphate radical must have two negative charges, $SO_4^{--}$

For convenience of printing, a dot is often used to represent a positive charge and a dash to denote a negative charge Thus the positive ions or CATIONS, as they are called, given by sodium, silver, copper and aluminium may be represented by the symbols, Na , Ag , Cu , Al , whilst the negative ions, so called ANIONS, given by the chloride, nitrate and sulphate radicals may be written as Cl′, $NO_3'$, $SO_4''$

During the electrolysis the ions are assumed to travel unchanged through the solution and to give up their electric charges at the electrodes The primary products thus set free may react (i) with one another, (ii) with the electrode or (iii) with the electrolyte to give *secondary products* Thus the decomposition of water into its elements, by the electrolysis of dilute sulphuric acid with platinum electrodes, was formerly explained as follows The sulphuric acid yields hydrogen ions, H , and sulphate ions, $SO_4''$ , the hydrogen ions are discharged at the cathode to give gaseous hydrogen, whilst the sulphate ions are discharged at the anode to give sulphate radicals, $SO_4$, which attack the water to give oxygen and reform sulphuric acid, as indicated in the scheme

*At cathode*, $\quad H \rightarrow H\ ,\ 2H = H_2$

*At anode*, $\quad SO_4'' \rightarrow SO_4\ ,\ 2H_2O + SO_4 = 2H_2SO_4 + O_2$

In recent years the accepted views on many electrolytic reactions have been modified by the recognition that the primary products of electrolysis depend upon the " discharge potentials " of the ions at the electrodes The ion which requires the smallest E M F for its discharge as a neutral atom or radical (by receiving or giving electrons) will always be deposited at the electrode in preference to the other ions The E M F required for the discharge of a given ion depends upon the composition of the electrode and on the concentration of the ion, though in the case of the metals it is generally true to say that the relative E M F 's are in accord with the position of the metal in the electrochemical series, *i e* the higher the metal is in the series the higher the E M F required for the discharge of its ion

A dilute solution of sulphuric acid in water contains hydrogen ions, sulphate ions and hydroxyl ions, OH′, the latter being present in minute concentration from the electrolytic dissociation of the water

$$H_2O \rightleftharpoons H^+ + OH'$$

On electrolysis with platinum electrodes, the hydrogen ions are discharged at the cathode, whilst hydroxyl ions, $OH'$, are discharged at the anode because they require a lower E M F for discharge than the sulphate ions. The removal of these ions causes more water molecules to dissociate to re-establish the above equilibrium, the electrolysis may therefore be represented by the scheme

$$\begin{aligned} &At\ cathode, \quad H + e = H, \quad 2H = H_2 \\ &At\ anode \quad OH' - e = OH, \quad 4OH = 2H_2O + O_2, \end{aligned}$$

where $e$ represents an electron, *i e* the cathode gives electrons to the cations and the anode receives electrons from the anions

The same considerations must be applied to other electrolyses For example, a solution of brine contains sodium ions, $Na$, and chloride ions, $Cl'$, from the salt, and hydrogen ions and hydroxyl ions from the water On electrolysis with graphite electrodes, hydrogen ions, *not* sodium ions, are discharged at the cathode, whilst chloride ions are discharged at the anode

$$\begin{aligned} &At\ cathode, \quad H + e = H, \quad 2H = H_2 \\ &At\ anode, \quad Cl' - e = Cl, \quad 2Cl = Cl_2 \end{aligned}$$

The progressive removal of hydrogen ions causes more water molecules to dissociate,

$$H_2O \rightarrow H + OH',$$

so that eventually the concentration of hydroxyl ions is equivalent to that of the sodium ions, *i e* the salt has been converted into sodium hydroxide When a mercury cathode is used, as in the Castner-Kellner alkali cell (p 97), the E M F required to discharge sodium ions is less than that required for hydrogen ions, hence sodium is liberated and dissolves in the mercury to form an amalgam The latter is decomposed by water in another cell in which it is made the anode to an iron cathode

$$\begin{aligned} &At\ cathode, \quad H + e = H, \quad 2H = H_2 \\ &At\ anode, \quad Na - e = Na \end{aligned}$$

The above hydrogen ions are provided by the dissociation of the water,

$$H_2O \rightarrow H + OH',$$

so that after the decomposition the solution contains sodium ions and hydroxyl ions in equivalent concentration, *i e* sodium hydroxide is present

When a solution of copper sulphate is electrolysed with copper electrodes, cupric ions, $Cu$, are discharged at the cathode, whilst at the anode copper atoms give up electrons and pass into solution as cupric ions Sulphate ions are not discharged because a higher E M F is required to remove a pair of electrons from them than in the case of the copper atoms on the anode

$$\begin{aligned} &At\ cathode, \quad Cu + 2e = Cu \\ &At\ anode, \quad Cu - 2e = Cu \end{aligned}$$

**Arrhenius's theory of electrolytic dissociation.**—Faraday supposed that ions were produced by the action of the electric current on the electrolyte, and that when no electric current was passing an aqueous solution of a

salt or acid did not contain any ions Clausius pointed out, however, that, since electrolytes obey Ohm's law accurately, all the electrical energy of the current must be used up in driving ions through the solution, and that none of it could be expended in splitting up neutral molecules into ions The latter must, therefore, already be free in the solution Clausius supposed that a small fraction of the salt was ionised by molecular collisions and that a condition of equilibrium resulted as shown by the equation,

$$NaCl \rightleftharpoons Na + Cl',$$

the smallness of the dissociation being indicated by the broken line of the upper barb

In 1887, however, Arrhenius suggested that, instead of only a trace of the electrolyte being ionised, most salts were already very largely dissociated in solution, and tended to dissociate completely at great dilutions

$$NaCl \rightleftharpoons Na^{\cdot} + Cl'$$

This revolutionary doctrine was introduced in order to account for the observation of Kohlrausch, that *the efficiency of a salt in carrying the electric current increases with dilution*, when allowance is made for the quantity of salt available for electrolysis

This effect can be shown very easily by converting the specific conductivity into an EQUIVALENT CONDUCTIVITY in order to correct for the dilution of the solution For this purpose the specific conductivity is multiplied by the number of cubic centimetres which contain 1 gram-equivalent of the solute Thus if $\kappa$ is the specific conductivity, and $\Lambda$ the equivalent conductivity,

$$\Lambda = \kappa V = \kappa/c,$$

where $V$ is the volume in c c containing 1 gram-equivalent, and $c$ is the concentration in gram-equivalents per c c The MOLECULAR CONDUCTIVITY is defined in a similar way, but the volume used is that containing *one gram-molecule* of the substance instead of *one gram-equivalent*

An alternative way of picturing the equivalent conductivity of a salt is to think of a pair of electrodes 1 cm apart, forming the walls of a large parallel-sided trough One gram-equivalent of salt is dissolved in any desired quantity of water, say $V$ c c , and poured into the trough The specific conductivity $\kappa$ is then defined by the conduction through a single centimetre cube of the solution, whilst the equivalent conductivity $\Lambda$ is given by the conduction over the whole area covered by the solution, *i e* by $\kappa V$ Kohlrausch's discovery can be expressed by saying that the conductivity of the salt increases progressively when the volume of liquid in the trough is increased by the addition of pure water

An illustration of this phenomenon is given in Table 83, which shows the specific and equivalent conductivities of potassium chloride in aqueous solutions. It will be seen that, as the dilution increases, the equivalent conductivity $\Lambda$ rises at first rapidly and then more slowly, and approaches a constant value in very dilute solutions This limiting value is called the EQUIVALENT CONDUCTIVITY AT INFINITE DILUTION, and is written $\Lambda_\infty$ *

* When the strength of the solution is expressed as a *concentration* instead of a dilution, the symbols $\Lambda_c$ and $\Lambda_0$ are used instead of $\Lambda_v$ and $\Lambda_\infty$ We then write $\alpha = \Lambda_c/\Lambda_0$ instead of $\alpha = \Lambda_v/\Lambda_\infty$

TABLE 83.—SPECIFIC AND EQUIVALENT CONDUCTIVITIES OF POTASSIUM CHLORIDE SOLUTIONS AT 18°

| Concentration, $c$ Equivalent/litre | Dilution $V$ c.c. | Specific conductivity $\kappa$ | Equivalent conductivity $\Lambda = \kappa V$ | $\alpha = \frac{\Lambda_v}{\Lambda_\infty}$ |
|---|---|---|---|---|
| 1 | 1,000 | 0.09824 | 98.2 | 0.757 |
| 0.5 | 2,000 | 0.05100 | 102.0 | 0.784 |
| 0.1 | 10,000 | 0.01120 | 112.0 | 0.861 |
| 0.02 | 50,000 | 0.002395 | 119.8 | 0.921 |
| 0.01 | 100,000 | 0.001220 | 122.0 | 0.938 |
| 0.0001 | 10,000,000 | 0.00001291 | 129.1 | 0.993 |
| 0 | $\infty$ | — | 130.1 | 1.000 |

Arrhenius assumed that in electrolytic conduction the current was carried only by the ions. The limiting conductivity corresponded therefore to a complete dissociation of the molecules of the salt into ions, and the fraction of the salt which was dissociated at a given dilution $V$ was given by $\alpha = \Lambda_v/\Lambda_\infty$ * The ratio $\alpha$ was termed the DEGREE OF DISSOCIATION of the salt, and it will be seen from the last column of Table 83 that, according to Arrhenius's theory, in a normal solution of potassium chloride, more than three-quarters of the salt is dissociated into ions.

**Osmotic pressure of electrolytes.**—Arrhenius found strong support for his theory of electrolytic dissociation, by showing that it could be used to interpret the *i*-factor which van 't Hoff had introduced into the gas-equation in order to express the anomalous osmotic pressure of electrolytes, $PV = iRT$ (p. 512). According to his theory, a molecule of a binary electrolyte in very dilute solution is already dissociated into two ions. If these ions exerted the same osmotic pressure as an equal number of molecules, *i.e.* if the gas-laws could be applied to *ions* as well as to *molecules*, the dissociation of molecules into ions would be accompanied by an increase of osmotic pressure, and this increase could be used to determine the number of ions in solution. Thus we should find a value $i = 2$ for a binary electrolyte in dilute solution, as Whetham found when he compared the osmotic pressures of cane-sugar and of potassium chloride by the freezing-point method, and showed that the depression of the freezing-point of a dilute aqueous solution of potassium chloride was exactly twice as great as that of an equimolecular solution of cane-sugar. Ternary electrolytes, such as potassium sulphate and barium chloride,

$$K_2SO_4 \rightleftharpoons 2K + SO_4'' \qquad BaCl_2 \rightleftharpoons Ba + 2Cl',$$

give *i*-factors which are greater than 2, but the limiting value of *three* has never been approached experimentally.

In order to apply his theory to solutions which were not infinitely dilute, Arrhenius made the further assumption, which is now recognised as incorrect, that the "mobility" of the ions (p. 607), or their efficiency in transporting the current, is constant in all dilute solutions in a given solvent and at a given temperature. The degree of dissociation, $\alpha$,

* See footnote on opposite page

of an electrolyte, *i.e.* the proportion of molecules converted into ions at a given dilution, could then be calculated from the ratio $\alpha = \Lambda_v/\Lambda_\infty$ (p 599) and compared with the values calculated from van 't Hoff's *i*-factor by means of the obvious relation,

$$i = 1 + (n - 1)\alpha,$$

where $n$ is the number of ions produced by the complete ionisation of one molecule of the electrolyte. Conversely, the *i*-factor could be deduced (i) from measurements of conductivity with the help of the preceding equation, and compared with (ii) the *i*-factor deduced directly or indirectly from measurements of osmotic pressure It was claimed that the results obtained by the two methods were concordant, *e g*

| | (i) | (ii) | | (i) | (ii) |
|---|---|---|---|---|---|
| KCl - | - 1 82 | 1 82 | $K_2SO_4$ | - 2 38 | 2 16 |
| $NaNO_3$ | - 1 86 | 1 82 | $BaCl_2$ - | - 2 54 | 2 63 |

The concordance is, however, now admitted to be purely fortuitous, since the difference between the *i*-factor and the integral numbers 2 and 3, in the case of STRONG ELECTROLYTES such as those cited above, is now attributed to other causes than incomplete ionisation (see below)

**The theory of complete ionisation.**—Arrhenius's theory of electrolytic dissociation postulates that in dilute solutions the free ions of a salt are enormously in excess of the neutral molecules It therefore implies that a pair of atoms of potassium and chlorine, carrying opposite electric charges and therefore attracted to one another by electrical as well as by chemical forces, are actually in a more stable condition than when united to form a neutral molecule Since the heat of formation of potassium chloride from potassium metal and chlorine gas is more than 100,000 calories,

$$K(\text{metal}) + \tfrac{1}{2}Cl_2(\text{gas}) = KCl + 106{,}000 \text{ cal},$$

it was almost incredible that the salt should decompose spontaneously into free atoms on mere dissolution in water, and even less credible that it should decompose into free atoms carrying opposite electric charges

A partial explanation of the electrolytic dissociation of the salt could be found by reviving the original idea of Arrhenius, that the electrolytically active salt is hydrated, *i e* that the ions have a greater affinity for water than has the neutral salt, since the addition of water must then promote the ionisation of the salt This explanation is in harmony with the fact that electrical conductivity is only developed in a limited group of IONISING SOLVENTS, including (in addition to water) liquid sulphur dioxide, liquid hydrogen cyanide, and liquid ammonia Moreover, these solvents possess a large amount of residual affinity, and form a large number of addition compounds The amount of energy liberated in the formation of these addition compounds is not large, however, and would scarcely be expected to suffice for the complete decomposition of a stable salt into its component atoms

Modern physics has now established that many solid salts are ionised even in the solid state, and that the ions are so stable that they are incapable of discharging their opposite electric charges to form a neutral mole-

cule of the salt Thus, a crystal of potassium chloride is regarded as a mere aggregate of potassium and chloride ions (Fig 129, p 493), and the only "molecules" that can be formed (*e g* in strong solutions or in the vapour of the salt) are pairs of ions, forming electrically neutral "doublets" Since, however, the ions in these doublets are held together only by the electrostatic attraction of their opposite charges, and are not united by any real chemical "bond," they are perfectly free to interchange partners, and thus to undergo very rapid "double decomposition"

The theory of complete ionisation indicates that the formation of potassium chloride from its elements should be represented by the equation

$$K(\text{metal}) + \tfrac{1}{2}Cl_2(\text{gas}) = K^+Cl^- + 106{,}000$$

The greatest stumbling-block against the acceptance of the existence of free ions in solution, namely the enormous amount of energy required to bring about ionisation, is thus removed, since the ions in question already exist in the solid salt, and only require to be pushed apart by the molecules of the ionising solvent

The theory of complete ionisation postulates that the variations of molecular conductivity and of osmotic activity in dilute solutions of strong electrolytes are not due to variations in the *number* of ions, as Arrhenius supposed, but to variations in their *activity*, resulting from the phenomenon of ELECTROSTRICTION, *t e* the mutual attraction of oppositely charged ions, giving rise to a modified distribution of these ions in the solution The existence of ionic doublets in strong solutions is admitted, since there must be some tendency for oppositely charged ions to cling together in pairs, but their concentration is supposed to be very much smaller than that of the neutral molecules postulated by Arrhenius's theory of electrolytic dissociation

In aqueous solutions the number of ion-pairs is at a minimum, since the small size and large dipole moment of the water molecules enable them to condense around the ions of the salt (p 503), and thus effectively to separate them On the other hand potassium iodide, although completely ionised in the solid state and in dilute aqueous solutions, is found (after making full allowance for the effects of electrostriction) to be dissociated only to the extent of about 93% in a $N/1000$ solution in benzonitrile These results are in accordance with the NERNST-THOMSON RULE which associates ionising properties with media of high dielectric constant (*e g.* water = 80, benzonitrile = 26, as compared with about 2 for hydrocarbons), on the ground that the work required to separate two ions, against the electrostatic forces which they exert upon one another, is inversely proportional to the dielectric constant of the medium

**Complete and reversible ionisation.**—Although many electrolytes retain their ionic structure in the crystal, others form real molecules, in which the opposite electric charges of the ions are neutralised by one another, and the radicals of the ions are united by chemical bonds In these cases, we must suppose that molecules as well as ions can persist in solution, especially at high concentrations, the progressive ionisation of the salt in dilute solutions must then be attributed to an electrolytic dissociation

of neutral molecules, exactly as postulated in Arrhenius's theory Some examples of complete and reversible ionisation are set out below

| Complete ionisation | Reversible ionisation |
|---|---|
| $Na\,Cl' \rightleftharpoons Na + Cl'$ | $HCN \rightleftharpoons H + CN'$ |
| $K\,OH' \rightleftharpoons K + OH'$ | $HCl \rightleftharpoons H + Cl'$ |
| $Ba\,Cl_2'' \rightleftharpoons Ba + 2Cl'$ | $HgCl_2 \rightleftharpoons Hg + 2Cl'$ |

Compounds of the first type, which includes the *alkalis* and the majority of the *metallic salts*, usually behave as " strong electrolytes " (p 622) when fused, or when dissolved in a good ionising solvent The second type includes a large number of " weak electrolytes " , but compounds of this type may behave as strong electrolytes if the bond between the radicals is too weak to serve as an effective check on the ionisation of the molecule This second type includes the *acids*, which are all capable of forming real molecules These molecules persist in the liquid state, but are ionised by contact with water, probably according to a scheme such as

$$H_2O + HCl \rightleftharpoons H_3O + Cl',$$

where the cation is not a free proton, but an " oxonium ion," possessing all the properties that are commonly attributed to a hydrogen ion in aqueous solution Some *mercury* salts are also included in the list, since X-ray analysis has shown that compounds of this element may have a molecular instead of an ionic structure

Whilst therefore the theory of complete ionisation applies to nearly all metallic salts, including the metallic hydroxides, the theory of electrolytic dissociation is still valid in its original form in the case of weak acids and weak bases, as well as in the limited group of weak salts

**Measurement of electrical conductivity of electrolytes** —The determination of the conductivity of an electrolyte is complicated by the fact that, if a direct current is used with the usual " Wheatstone bridge " apparatus, the products of electrolysis collect at the electrodes and set up a back E M F which materially increases the apparent resistance of the electrolyte This difficulty is overcome by using an alternating current, as produced by an induction coil, and a telephone in place of a galvanometer to detect the flow of current The apparatus used is shown diagrammatically in Fig 158 The accumulator, *A*, works the small induction coil, *I C* , which supplies from its secondary coil an alternating current to the Wheatstone bridge The latter consists of a uniform wire stretched over a metre scale and attached at each end to stout brass strips, *B*, *B*. The circuit is completed by bridging the gaps between these

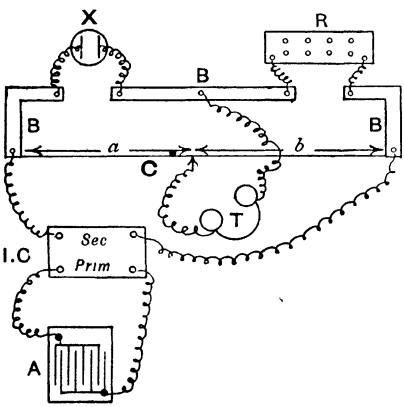



FIG 158 APPARATUS FOR MEASURING ELECTROLYTIC CONDUCTIVITY

strips, with (1) the *conductivity cell*, $X$, containing the solution to be tested, and (2) a *resistance-box*, $R$. A pair of head-telephones is connected to the centre strip, $B$, and to a contact, $C$, which can be moved to any desired position along the bridge wire The cell, $X$, must be maintained at a constant temperature by immersion in a thermostat, since the conductivity of an electrolyte varies with the temperature

When the apparatus is connected up in this manner, a sound will be heard in the telephones , but in one position of the movable contact, $C$, the sound will be reduced to a minimum When this adjustment has been made, then

$$\frac{\text{resistance of } X}{\text{resistance of } R} = \frac{a}{b},$$

$$i\,e \quad \text{resistance of } X = \frac{a}{b} R,$$

where $R$ is the known resistance corresponding with the plugs which have been removed from the resistance-box, whilst $a$ and $b$ are the lengths of wire between the movable contact and the ends of the bridge wire The most accurate results are obtained when $a$ is nearly equal to $b$ Plugs should therefore be removed from the resistance-box until the point of adjustment comes near the centre of the wire, *e g* between 40 cm and 60 cm on the scale

A simple *conductivity cell*, suitable for Expts 122 *et seq* , is shown in Fig 159 The electrodes are of platinum and are welded to stout platinum wires which are sealed through two glass tubes supported by an ebonite cap A little mercury is placed in each tube, so that contact can be made with the electrodes by means of copper wires dipping into the mercury The electrodes should extend nearly to the wall of the outer vessel, which is preferably made of resistance glass to avoid contamination by alkali The size and distance apart of the electrodes are varied in different cells so that measurements may be made with solutions of high or low conductivity Thus for poor conductors a cell is used with plates which are relatively large and close together, and conversely

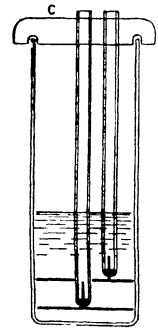



FIG 159
CONDUCTIVITY CELL

In order to calculate the specific conductivity of an electrolyte, $E$, from the observed resistance, $R_E$, of the cell which contains it, the CAPACITY of the latter must be known Since the electrodes of an ordinary cell are always slightly irregular, its capacity cannot be determined by direct measurement , instead, the cell is filled with a solution, *e g* $N/50$ KCl, of known specific conductivity as deduced from measurements made with a standard cell of accurately known dimensions, and the resistance, $R_{KCl}$, of the cell is found The factor, $X$, by which the observed conductivity, $1/R_{KCl}$, must be multiplied to give the true specific conductivity, $K_{KCl}$, of the solution is a measure of the "capacity" of the cell and is called the CELL CONSTANT Thus

$$K_{KCl} = X \frac{1}{R_{KCl}} \quad \text{or} \quad X = K_{KCl} \times R_{KCl} \qquad \text{(i)}$$

The specific conductivity, $K_E$, of an electrolyte, $E$, is then calculated, from the equation,

$$K_E = X \frac{1}{R_E}, \qquad ..(ii)$$

where $R_E$ is the resistance of the cell when it is filled with the electrolyte, $E$

No allowance has been made in equation (i) for the conductivity of the water, viz $1/R_{H_2O}$, since freshly distilled water, uncontaminated by carbon dioxide, has a conductivity which is less than one thousandth of that of the potassium chloride Its omission from equation (ii) also introduces no appreciable error when solutions are used which have a conductivity similar to that of $N/50$ KCl However, when poor conductors are used, the conductivity of the water must be measured and allowed for as indicated below

$$K_E = X \left\{ \frac{1}{R_E} - \frac{1}{R_{H_2O}} \right\} \qquad .. \qquad (iii)$$

**The independent migration of ions.**—From a long study of the conductivity of salt solutions, Kohlrausch discovered that the equivalent conductivity at infinite dilution, $\Lambda_\infty$, of any electrolyte could be written as the sum of two components, one due to the cations and the other due to the anions Kohlrausch's LAW OF INDEPENDENT MIGRATION OF IONS may be expressed by the equation,

$$\Lambda_\infty = \Lambda_K + \Lambda_A,$$

where $\Lambda_K$ is termed the MOBILITY of the cation and $\Lambda_A$ the MOBILITY of the anion According to this law there should be a constant difference between the values of $\Lambda_\infty$ for the sodium and potassium salts of the same acid radical Thus at 18°

$$\left.\begin{array}{ll} (1)\ \Lambda_{\infty KCl} & = \Lambda_K + \Lambda_{Cl'} = 130\ 1 \\ (2)\ \Lambda_{\infty NaCl} & = \Lambda_{Na} + \Lambda_{Cl'} = 109\ 0 \end{array}\right\} \Lambda_K - \Lambda_{Na} = \mathbf{21\ 1.}$$

$$\left.\begin{array}{ll} (3)\ \Lambda_{\infty KNO_3} & = \Lambda_K + \Lambda_{NO_3'} = 126\ 5 \\ (4)\ \Lambda_{\infty NaNO_3} & = \Lambda_{Na} + \Lambda_{NO_3'} = 105\ 3 \end{array}\right\} \Lambda_K - \Lambda_{Na} = \mathbf{21\ 2.}$$

$$\left.\begin{array}{ll} (5)\ \Lambda_{\infty KI} & = \Lambda_K + \Lambda_{I'} = 131\ 2 \\ (6)\ \Lambda_{\infty NaI} & = \Lambda_{Na} + \Lambda_{I'} = 110\ 0 \end{array}\right\} \Lambda_K - \Lambda_{Na} = \mathbf{21\ 2.}$$

The same rule applies to the anions , thus the chloride and nitrate of a metal exhibit a constant difference, which does not depend on the nature of the cation, *e.g*

$$\Lambda_{\infty KCl} - \Lambda_{\infty KNO_3} = \Lambda_{Cl'} - \Lambda_{NO_3'} = 130\ 1 - 126{\cdot}5 = \mathbf{3\ 6.}$$

$$\Lambda_{\infty NaCl} - \Lambda_{\infty NaNO_3} = \Lambda_{Cl'} - \Lambda_{NO_3'} = 109\ 0 - 105\ 3 = \mathbf{3\ 7.}$$

The above law is of considerable value in deducing the limiting conductivity $\Lambda_\infty$ of weak electrolytes, which cannot be measured directly owing to the very great dilution required for complete ionisation Thus the limiting conductivity of acetic acid is obtained by adding the limiting

conductivity of sodium acetate (a strong electrolyte) to that of hydrochloric acid, and subtracting that of sodium chloride

$$(1)\ \Lambda_{\infty NaAc} = \Lambda_{Na} + \Lambda_{Ac'} = 78\ 5$$
$$(2)\ \Lambda_{\infty HCl} = \Lambda_{H} + \Lambda_{Cl'} = 380\ 4$$
$$(3)\ \Lambda_{\infty NaCl} = \Lambda_{Na} + \Lambda_{Cl'} = 109\ 0$$
$$(1) + (2) - (3) = \Lambda_{H} + \Lambda_{Ac'} = \Lambda_{\infty HAc} = 350 \text{ at } 18^\circ$$

**Transport numbers.**—The reason for the above additive relationship may be made clearer by considering more closely the process of conduction by ions The ions in a solution which is not undergoing electrolysis will be moving at random in all directions, when the electrodes are connected to the battery, however, the anions will be attracted towards the anode and will begin to move towards it, and similarly the cations will begin to move towards the cathode Those which are nearest to the electrodes will arrive first and give up their charges, but others will be drawn from different parts of the solution as electrolysis proceeds The passage of the current through the solution is therefore due to the neutralisation at the electrodes of the electric charges of the ions, and depends, not only upon the number of ions and the charge which they carry, but also upon the speed at which they move through the solution under a given electric potential

It might seem at first sight that, since equal numbers of positive and negative ions are neutralised, the anions and cations must move with the same speed This is not usually the case, and it is readily seen that, if the ions have different speeds, the salt as a whole will drift in the direction of the faster-moving ion In Fig 160, let $ABCD$ be a section across a tube of solution undergoing electrolysis, under the action of a current flowing from left to right Let us suppose that cations move to the right with a velocity, $U$, which is twice as great as $V$, the velocity with which the anions move to the left As soon, however, as a few positively charged ions have crossed the plane $ABCD$, in excess of the number of negatively charged ions which have crossed in the opposite direction, the solution to the right of this plane will become positively charged and that to the left negatively charged There will therefore be strong electrostatic forces set up which will prevent the anions going to the left and will drag them to the right in the train of the faster-moving cations As a result, the salt as a whole will drift in the direction of the faster-moving ion

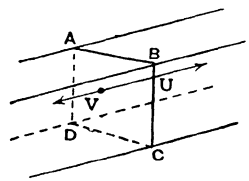



FIG 160 DIAGRAM TO ILLUSTRATE THE MOVEMENT OF IONS

It was shown by Hittorf that this drifting or transport of the electrolyte can be used to calculate the relative velocities of the anion and cation This can be seen diagrammatically in Fig 161 Line I of this diagram represents the solution of a salt, $BA$, which splits up into ions, $B'$ and $A'$. The thick lines represent the electrodes, and the dotted lines are imaginary planes which cut off the central portion of the liquid from the portions around the electrodes

(i) Let us suppose that $B$ and $A'$ have the same velocity We therefore move the $B$ ions one place to the right, and the $A'$ ions one place to the left The result is shown in **IIa** The unpaired ions will then be discharged at the electrodes, and the condition of affairs will be that represented in **IIb**, where the discharged ions are shown outside the electrodes

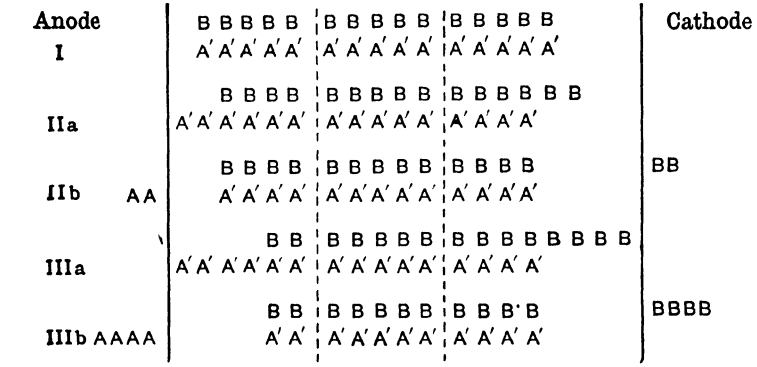



FIG 161 DIAGRAM TO ILLUSTRATE THE MIGRATION OF IONS

In this diagram, each compartment contained 5 molecules of the salt in stage **I**, the anode and cathode compartments in **IIb** have each lost one molecule of salt, and the losses in these two compartments are the same, because we have supposed that the anion and cation move with the same velocity

(ii) Now let us suppose that the cation $B$ moves three times as rapidly as the anion $A'$ Stepping $B$ three places to the right, and $A'$ one place to the left, we get the conditions in **IIIa**, and when unpaired ions are discharged **IIIb** results Here the anode compartment has lost three molecules of salt and the cathode compartment only one Thus it follows that

$$\frac{\textit{loss at anode}}{\textit{loss at cathode}} = \frac{\textit{speed of cation}}{\textit{speed of anion}}$$

Note that the loss at each electrode is proportional to the speed of the ion which is *leaving* it It is obvious from the diagram that this will only be true when the concentration in the central compartment is unchanged, and the experiment must be carried out so that all the losses occur in the anode and cathode compartments

Since the greater speed of an ion assists the passage of the current, we may suppose that a fraction $n$ of the total current is carried by the anion and a fraction $1 - n$ is carried by the cation It follows from the diagram that

$$n = \frac{\textit{fall in concentration round cathode}}{\textit{total fall in concentration round anode and cathode}}$$

The ratio $n$ was termed by Hittorf the TRANSPORT NUMBER of the anion.

Obviously $1-n$ is the transport number of the cation Let $U$ = velocity of the cation, and $V$ = velocity of the anion Then

$$\frac{n}{1-n} = \frac{\textit{loss at cathode}}{\textit{total loss}} \times \frac{\textit{total loss}}{\textit{loss at anode}} = \frac{V}{U}$$

If $U = V$, $\frac{n}{1-n} = 1$ and $n = 0\,5$.

Expt 125 (p 612) gives the details for the determination of the transport number of the nitrate ion, $NO_3'$, in a solution of silver nitrate

**Mobilities of ions.**—By the aid of transport numbers, it is possible to divide the equivalent conductivity of a salt into two parts, which are proportional to the speeds of the anion and of the cation Thus, for KCl, we can take the experimentally determined values $\Lambda_\infty = 130\,1$ and $n = 0\,503$ for the limiting conductivity of the salt and the transport number of its anion The fraction of this limiting conductivity due to the anion Cl′ is therefore $130\,1 \times 0\,503 = \mathbf{65\,5}$, and that due to the cation K is $130\,1 \times 0\,497 = \mathbf{64\,6}$ These values are termed the IONIC MOBILITIES

When one of a pair of mobilities is known the other may be calculated from Kohlrausch's law, $\Lambda_\infty = \Lambda_K + \Lambda_A$. Thus for NaCl $\Lambda_\infty = 109\,0$ and $\Lambda_{Cl'} = 65\,5$,

$$\Lambda_{Na} = 109\,0 - 65\,5 = \mathbf{43\,5}.$$

We can now get two independent values for the nitrate ion, since

$$\Lambda_{KNO_3} = 126\,5, \quad \Lambda_K = 64\,6, \quad \Lambda_{NO_3'} = \mathbf{61\,9}.$$
$$\Lambda_{NaNO_3} = 105\,3, \quad \Lambda_{Na} = 43\,5, \quad \Lambda_{NO_3'} = \mathbf{61\,8}.$$

TABLE 84.—IONIC MOBILITIES AT 18°

| Cations | | Anions | |
|---|---|---|---|
| H | 315 2 | $OH'$ | 174 |
| Na | 43 4 | $Cl'$ | 65 5 |
| K | 64 6 | $Br'$ | 67 7 |
| $NH_4$ | 64 7 | $I'$ | 66 6 |
| Ag | 54 0 | $NO_3'$ | 61 8 |
| $\frac{1}{2}Ca$ | 51 9 | $\frac{1}{2}SO_4''$ | 68 5 |
| $\frac{1}{2}Cu$ | 45 9 | $\frac{1}{2}CrO_4''$ | 72 0 |

Table 84 gives the IONIC MOBILITIES of a number of ions at 18° * By adding together the numbers for the ions concerned, the equivalent conductivity of any salt at infinite dilution can be predicted Thus the calculated value of $\Lambda_\infty$ for calcium chloride is $\frac{1}{2}CaCl_2 = 51\,9 + 65\,5 = 117\,4$, the observed value is 117 2

**Absolute velocity of ions.**—The absolute velocity of an ion in centimetres per second under a potential gradient of one volt per cm is calculated by dividing the mobility of the ion by 96,500 The reasoning on which this calculation is based is as follows

Consider a cube of side 1 cm, in which electrolysis is taking place between two opposite faces with a difference of potential of 1 volt The ions which will be discharged per second will be those which are $U$ cm

* These are commonly represented by the symbols $u$ and $v$, so that $\Lambda_\infty = u + v$.

from the cathode and those which are $V$ cm from the anode, where $U$ and $V$ are the velocities in centimetres per second of cation and anion under the unit potential gradient of 1 volt/cm If the solution has a concentration of $c$ equivalents per c c , then the number of gram-equivalents discharged $= c \times (U + V)$, since this is the number of ions within the given distances from the two electrodes Since each gram-equivalent of ions carries one faraday, or 96,500 coulombs, the total quantity of electricity which is discharged at the electrodes per second is $96{,}500c \times (U + V)$ This is equal, however, to the current passing through the unit cell under a pressure of 1 volt, and is numerically equal to the *specific conductivity* $\kappa$ of the solution as defined on p 593 above It therefore follows at once that

$$\kappa = 96{,}500c(U + V).$$

The *equivalent conductivity* of the solution is

$$\Lambda = \frac{\kappa}{c} = 96{,}500(U + V)$$

If the solution is very dilute $\Lambda = \Lambda_\infty = \Lambda_K + \Lambda_A$ ,

$$U = \frac{\Lambda_K}{96{,}500} \quad \text{and} \quad V = \frac{\Lambda_A}{96{,}500},$$

or

$$\Lambda_K = 96{,}500\,U, \quad \Lambda_A = 96{,}500\,V$$

For the hydrogen ion $\Lambda_H = 315\ 2$ at 18° ,

$$\therefore\ U = \frac{\Lambda_H}{96{,}500} = \frac{315\ 2}{96{,}500} = \mathbf{0\ 00327}\ \text{cm /sec at } 18°$$

Thus this ion, which has a much larger mobility than others, only moves at a very slow speed through water when driven by a potential gradient of 1 volt per centimetre This very slow movement is due to the resistance offered by the liquid, *i e* to its viscosity It is found in fact that, when the viscosity of a liquid is lowered by heating, the conductivity increases almost proportionately (p 609)

The movement of ions can be observed directly in certain cases An arrangement due to Lodge for measuring the velocity of the hydrogen ion is described in Expt 126 Similar arrangements, in which the movement of a coloured boundary (*e g* between solutions of $K_2Cr_2O_7$ and $K_2CO_3$) is measured, have been used by other workers in order to determine the absolute velocities of the ions In general, the velocities measured directly in this way agree approximately with the values calculated from the ionic mobilities

**Influence of temperature on conductivity.**—The *resistance* of a metallic conductor usually increases when the temperature is raised, and falls when the temperature is lowered In the case of certain pure metals, indeed, the resistance is roughly proportional to the absolute temperature, and then falls abruptly to zero, a few degrees before the absolute zero is reached, *e g* at the boiling-point of liquid helium On the other hand, the *conductivity* of aqueous electrolytes is found to increase rapidly as the temperature is raised. Since this increase (about 3% per degree at 0°)

corresponds roughly with the increase in the fluidity of the water, it is probably due to the increasing *mobility* of the ions and not to an increase in the *number* of free ions

TABLE 85 —VARIATION OF CONDUCTIVITY AND VISCOSITY WITH TEMPERATURE $N/100$ KCl

| Temperature $t$ | Specific conductivity $\kappa \times 10^4$ | Viscosity $\eta$. | $\eta\kappa \times 10^6$ |
|---|---|---|---|
| 0 | 7 76 | 0 01793 | 1 392 |
| 5 | 8 96 | 0 01522 | 1 364 |
| 10 | 10 19 | 0 01311 | 1 336 |
| 15 | 11 47 | 0 01142 | 1 310 |
| 20 | 12 78 | 0 01006 | 1 286 |
| 25 | 14 12 | 0 00893 | 1 260 |
| 30 | 15 52 | 0 00800 | 1 240 |

Table 85 gives some data for $N/100$ KCl solution , the conductivity increases and the viscosity decreases rapidly as the temperature rises If the influence of the lowered viscosity were the only factor to be considered, and the effect were a proportional one, then the product of viscosity and conductivity should be constant The last column of the table shows that this quantity $\kappa \times \eta$ is nearly constant, but decreases slowly as the temperature rises The diminution in the value of the product can be explained by supposing that the ratio $\alpha = \Lambda/\Lambda_\infty$ is less at higher temperatures

EXPT 122 **Conductivity of aqueous solutions of acetic acid.**

A conductivity cell of the type shown in Fig 159 is cleaned by washing it with warm chromic acid and distilled water The electrodes are then coated with platinum black to increase their effective surface area, so as to minimise the danger of polarisation during the subsequent measurements of conductivity This is done by filling the cell with a solution of 3 grams of chloroplatinic acid and 0 02 gram of lead acetate in 100 c c of water, and connecting the electrodes through a reversing switch to a 4-volt accumulator battery Electrolysis is allowed to proceed for 20 minutes, the current being reversed every minute

When the electrodes have thus been coated with an even layer of platinum black, the platinising liquid is poured back into the stock bottle and the electrodes are rinsed with water The cell should then be filled with dilute (5%) sulphuric acid, and the electrolysis continued for 30 minutes, reversing the current every minute (This treatment removes impurities occluded by the platinum black ) Finally the electrodes are well washed with distilled water and are left immersed in distilled water until required

Freshly distilled water with a conductivity of not more than $4 \times 10^{-6}$ mhos at 25° is required for the preparation of the solutions used below If water of this purity cannot be obtained from the laboratory still, it is advisable to redistil with a little potassium hydrogen sulphate, using a condenser of resistance glass to avoid contamination by alkali The middle

third of the distillate is collected in a bottle made of resistance glass Care should be taken to avoid contamination by atmospheric carbon dioxide The precise conductivity, $1/R_{H_2O}$, of the water should be determined by measuring the resistance, $R_{H_2O}$, which it gives to the cell at 25°

The cell constant $X$ is now determined by filling the cell with a solution of $N/50$ KCl and measuring the resistance, $R_{KCl}$, which it gives to the cell, when this is maintained at 25° in a thermostat The potassium chloride solution is prepared by dissolving 0 7456 gram of pure fused KCl in 500 c c of conductivity water and has a specific conductivity of 0 002778 at 25° The cell constant $X = 0\ 00278 \times R_{KCl}$ (see p 603)

An approximately normal solution of acetic acid is prepared by diluting 40 c c of glacial acetic acid to 500 c c with conductivity water The exact normality of this solution is determined by diluting 25 c c of it to 250 c c and titrating portions of 10 c c of the latter with $N/20$ barium hydroxide. Incidentally the calibration of the 10 c c pipette should be checked, as should also the calibrations of the flasks and pipette used below An exactly normal solution of acetic acid is now obtained by diluting the necessary volume of the above acetic acid to 500 c c

| Dilution $V$ | Resistance $R$ | Specific conductivity $\kappa$ | Equivalent conductivity $\Lambda$ | Degree of dissociation $\alpha = \frac{\Lambda}{\Lambda_\infty}$ * | Dissociation constant $K = \frac{\alpha^2}{(1-\alpha)V}$ |
|---|---|---|---|---|---|
| 500 c c | $R_1$ | $\kappa = X\left[\frac{1}{R_1} - \frac{1}{R_{H_2O}}\right]$ | $\Lambda = \kappa \times 1000$ | | |
| 1000 c c | $R_2$ | $\kappa = X\left[\frac{1}{R_2} - \frac{1}{R_{H_2O}}\right]$ | $\Lambda = \kappa \times 2000$ | | |
| 2000 c c | $R_3$ | $\kappa = X\left[\frac{1}{R_3} - \frac{1}{R_{H_2O}}\right]$ | $\Lambda = \kappa \times 4000$ | | |
| etc to $N/256$ | $R_9$ | $\kappa = X\left[\frac{1}{R_9} - \frac{1}{R_{H_2O}}\right]$ | $\Lambda = \kappa \times 256{,}000$ | | |

The cell resistance, $R_{HAc}$, for normal acetic acid is next determined For this purpose the cell is rinsed out with the acetic acid before being filled, and its resistance is not measured until the temperature of the acid has reached that of the thermostat, viz 25° In the meantime an $N/2$ solution of acetic acid is prepared by placing 50 c c of the normal acid in a 100 c c flask and making up the volume to the mark with conductivity water The resistance of this acid is determined with the same precautions of rinsing and temperature control Acids of $N/4$, $N/8$, $N/16$, $N/32$ strength, etc., are similarly prepared by diluting 50 c c of the $N/2$, $N/4$, $N/16$ acids, etc., to 100 c c with conductivity water, and their resistances are determined Acetic acid is a weak electrolyte, so that the conductivity of the water

* $\Lambda_\infty$ at 25° = 387·9.

should be allowed for in calculating the specific and equivalent conductivities of the above solutions The results should be set out as indicated above The calculation (in the seventh column) of the dissociation-constant of acetic acid from Ostwald's dilution law should be left until the next chapter has been read

EXPT 123 **Titration, using conductivity as an indicator**

Place 10 c c of $N/10$ HCl in the cell and measure its conductivity From a burette add 2 c c of $N/10$ NaOH and measure the conductivity again Repeat, adding the alkali 2 c c at a time until 16 c c have been added Plot the conductivities against the amount of NaOH added The points will fall on two straight lines, the intersection of which gives the end-point This is because the ions H and OH' have much larger mobilities than other ions, so that a minimum conductivity is reached at the neutral point This method is useful for titrating coloured solutions in which indicators cannot be used

EXPT 124 **Determination of the solubility of barium oxalate**

Pure barium oxalate is prepared by mixing approximately equivalent quantities of boiling dilute barium chloride and ammonium oxalate solutions, and washing the precipitate with plenty of boiling water These precautions not only prevent the formation of colloidal barium oxalate, but also minimise the danger of the precipitate absorbing salts from the solution Some of the oxalate is thoroughly agitated with distilled water in a conductivity cell and left for several hours in a thermostat at 25° The conductivity of this solution is then measured, and the specific conductivity calculated by applying the cell constant after correcting for the conductivity of the water (see above) The solubility of barium oxalate is then calculated by assuming that it is completely ionised in its saturated solution, as this is very dilute, and that its equivalent conductivity at infinite dilution is 137 38 at 25° C The latter can be deduced from the equivalent conductivities of other more soluble barium and oxalate salts, and does not require a previous knowledge of the solubility of barium oxalate The calculation is as follows

The specific conductivity, $\kappa$, of the saturated barium oxalate solution

$$= X\left(\frac{1}{R_{BaC_2O_4}} - \frac{1}{R_{H_2O}}\right)$$

Let $V$ = volume in c c containing one gram-equivalent of barium oxalate, viz $\frac{1}{2}BaC_2O_4 = 112\ 67$ grams

$$V\kappa = \text{equivalent conductivity} = 137\ 38,$$

$$V = \frac{137\ 38}{\kappa},$$

$\therefore$ Solubility in grams per litre at 25°

$$= \frac{112\ 67}{\frac{V}{1000}} = \frac{112\ 67 \times \kappa \times 1000}{137\ 38}$$

EXPT 125 **Transport number for silver in silver nitrate**

The *transport apparatus* is shown in Fig 162 The anode *A* consists of a stout silver wire soldered to a copper lead and sealed into the end of a glass tube with sealing wax The cathode, *C*, is a small plate of platinum foil The apparatus is filled, to a point a little above the bridge joining the two tubes, with a dilute solution of silver nitrate In order to allow any gases evolved to escape, slots should be cut in the corks which carry the electrodes

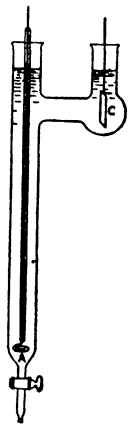



FIG 162 TRANSPORT APPARATUS

The transport apparatus is connected in series with a simple *silver voltameter*, Fig 163 This consists of a wide-necked bottle closed by a rubber stopper pierced with three holes Two of these hold glass tubes, into which the wires from the electrodes are sealed, the third is left open to allow gases to escape The electrodes consist of sheets of platinum foil, about 3 cm × 2 cm , mounted on platinum wires, and should be fixed parallel and about 3 cm apart

Prepare a solution containing one-tenth of a gram-equivalent of silver nitrate in 1000 *grams* of solution Fill the transport apparatus with this solution, and weigh 100 grams of the solution into the voltameter Connect the two pieces of apparatus in series and apply direct current from the lighting circuit (if available) for 1 to 2 hours If direct current from the mains is not available, use a battery of accumulators (giving a pressure of about 50 volts) for 3 to 6 hours

Meanwhile, weigh out two 50 gram lots of the solution of silver nitrate, and titrate with decinormal potassium thiocyanate (see p 432). When the electrolysis is complete, run off through the tap into a weighed flask a volume of the solution corresponding roughly with that which would fill the long anode-limb of the transport apparatus up to the bridge, weigh the flask and solution, and titrate with $N/10$ KCNS Also transfer the liquid from the voltameter to a suitable flask, rinse out the bottle and electrodes with distilled water, and titrate the whole with the $N/10$ KCNS solution The method of calculation is shown by the following example



FIG 163 VOLTAMETER

50 grams of the original solution required 48 7 c c of $N/10$ KCNS

100 grams of this solution was placed in the voltameter, after electrolysis this solution required only 28 6 c c KCNS The total quantity of electricity is therefore proportional to

$$2 \times 48\ 7 - 28\ 6 = 68\ 8 \text{ c c. } N/10 \text{ KCNS}$$

The anode solution weighed 39·5 gm and required 74 9 c c of $N/10$ KCNS Of this, however, 68 8 c c is due to the silver dissolved from the anode by $NO_3'$ ions The amount of the original silver nitrate left at the anode is

therefore proportional to 74 9 – 68 8 = 6 1 c c But silver originally present in this weight of solution is proportional to

$$\frac{39\,5}{50} \times 48\,7 = 38\,5 \text{ c c}$$

$$\therefore \text{ Loss of silver} = 38\,5 - 6\,1 = 32\,4 \text{ c c}$$

The transport number for silver $(1 - n)$ is given by

$$1 - n = \frac{\textit{loss at anode in equivalents}}{\textit{total quantity of electricity in equivalents}} = \frac{32\,4}{68\,8} = \mathbf{0\,471.}$$

The transport number for the nitrate ion is therefore **0 529.**

EXPT 126 **Demonstration of movement of hydrogen ion** (Lodge)

Shake 3 grams of powdered agar-agar with 100 c c of boiling water, and heat in a water bath until solution is complete Add phenolphthalein to the hot solution and then caustic soda drop by drop till a deep purple colour is produced Pour the hot solution into a tube bent twice at right



FIG 164 LODGE'S APPARATUS FOR DEMONSTRATING THE MOVEMENT OF IONS

angles (Fig 164), until the vertical limbs are half-filled, and allow the solution to set When cold, support the tube in a dish of cold water, place dilute sulphuric acid over the jelly in the left-hand limb, and a solution of common salt in the right-hand limb Close the tubes with corks carrying small spirals of platinum wire to serve as electrodes, and with a groove cut in each cork to permit gases to escape Connect to the lighting circuit, if direct current is available, taking care that the limb containing the acid is the anode As the hydrogen ions are attracted towards the cathode, the phenolphthalein is decolorised, and the boundary between the colourless and coloured jelly will be seen to move steadily from the anode to the cathode The speed depends upon the dimensions of the apparatus and the applied voltage With a tube about 8 mm diameter and 25 cm distance between the electrodes, a pressure of 200 volts gives a speed of several centimetres per hour It is necessary to immerse the tube in a bath of water, since otherwise the heat developed by the passage of the current may melt the jelly.

## CHAPTER XLV

### APPLICATIONS TO ELECTROLYTES OF THE LAW OF MASS ACTION

**The " strength " of acids.**—The earliest method of judging the strength of an acid was by its ability to liberate other acids from their salts Thus, sulphuric acid was regarded as a stronger acid than nitric or hydrochloric acid because the latter acids could be set free from their salts by the action of sulphuric acid We now know that this method is untrustworthy, because these reactions give rise to a chemical equilibrium, and the ultimate course of the action depends much more on the relative volatility of the acids than on their strengths Thus in the reversible actions represented by the equations,

$$KNO_3 + H_2SO_4 \rightleftharpoons KHSO_4 + HNO_3,$$
$$NaCl + H_2SO_4 \rightleftharpoons NaHSO_4 + HCl,$$

the change proceeds to completion in the sense of the upper arrow *when the mixture is heated* This displacement is almost inevitable in view of the fact that nitric acid and hydrogen chloride are much more volatile than sulphuric acid, and can therefore be driven off as fast as they are formed, without boiling off the less volatile sulphuric acid When, however, nitric acid is added to potassium sulphate *in the cold*, potassium nitrate crystallises out and the action proceeds in the reverse direction In the same way when hydrochloric acid is added to a solution of silver sulphate, the action proceeds from left to right in the equation

$$2HCl + Ag_2SO_4 \rightarrow 2AgCl + H_2SO_4,$$

*i e* hydrochloric acid displaces sulphuric acid from silver sulphate and gives rise to a quantitative yield of silver chloride

In reality, these actions are all reversible, and it is the sparing solubility of the potassium nitrate and the insolubility of silver chloride which cause the actions to proceed in the opposite direction from that of the actions which serve for the commercial preparation of nitric and hydrochloric acids, which in their turn are determined by the volatility of the acids It is therefore obvious that, if the relative strengths of acids are to be judged by their " avidity " for a base, a method must be adopted for measuring the distribution of the base between the competing acids which does not upset the equilibrium This has been accomplished by means of thermal measurements and measurements of volume, details of which are given in the next section

In terms of the theory of electrolytic dissociation, Arrhenius defined an

acid as a substance which gave hydrogen ions by reversible dissociation in solution

$$HCl \rightleftharpoons H + Cl', \quad H_2SO_4 \rightleftharpoons 2H + SO_4''$$

The concentration of hydrogen ions produced by the electrolytic dissociation of an acid was then used as a measure of its strength Acids which were largely ionised in solution, *e g* hydrochloric acid, were therefore described as STRONG ACIDS, whilst those which were only ionised to a small extent, *e g* acetic acid, were described as WEAK ACIDS This classification was in good agreement with earlier impressions, derived from their sour taste and action upon indicators, as well as from the vigour with which different acids acted upon metals or upon chalk It was also claimed that the strength of an acid as deduced from its degree of dissociation, $\alpha$ (p 599), was in harmony with values deduced from measurements of avidity (p 615) and of catalytic activity (p 617)

The preceding definitions still hold good with only slight modification, since *the strength of an acid is now defined by its readiness to give a hydrogen ion or proton to a base*, such as water,

$$HCl + H_2O \rightleftharpoons H_3O + Cl' \text{ instead of } HCl \rightleftharpoons H + Cl',$$

and measurements of conductivity, *when corrected for the effects of electrostriction*, are accepted as a valid method for deducing the concentration of oxonium ions, *i e* of hydrated hydrogen ions in a solution, and therefore as giving a correct value for the strength of the acid The catalytic method, however, is fundamentally unsound, since the *molecules* of a strong acid are now known to have a higher catalytic activity than their *ions* The methods of measuring the strengths of acids (i) by avidity methods, and (ii) by measurements of the concentration of hydrogen ions, are described below

**Avidity methods.**—The two most important methods for comparing the avidities of two competing acids for a base are set out below

(*a*) *Thomsen's thermal method*.—In dilute solution (about $N/5$) the heats of neutralisation of potash by hydrochloric and sulphuric acids are 13,700 cals and 15,700 cals It follows from Hess's law that if 1 equivalent of sulphuric acid, when added to 1 equivalent of potassium chloride, displaced all the hydrochloric acid, there should be an evolution of 2000 calories of heat It was found by experiment that only 700 calories were evolved, indicating that the reaction,

$$KCl + \tfrac{1}{2}H_2SO_4 \rightleftharpoons \tfrac{1}{2}K_2SO_4 + HCl,$$

reached an equilibrium when $700/2000 = 0\ 35$ of the sulphuric acid had combined with the base However, a correction had to be made to allow for the fact that some potassium acid sulphate, $KHSO_4$, was also formed Experiments with potassium sulphate and sulphuric acid indicated that the formation of the acid sulphate was responsible for the absorption of about 100 calories in the above experiment The proportion of the base combined with the sulphuric acid was therefore about $800/2000 = 0{\cdot}4$, which gave sulphuric acid a strength equal to about 0 4/0 6 or 67% of that of hydrochloric acid

(*b*) *Ostwald's volume method*.—This method depends upon measuring the changes of volume instead of the heat changes on neutralisation

A certain solution of copper nitrate had a volume of 3847 4 c c , and an equivalent solution of copper sulphate had a volume of 3840 3 c c Equivalent solutions of nitric and sulphuric acids had volumes of 1933 2 c c and 1936 8 c c respectively. If no action had occurred on mixing the solutions of copper sulphate and nitric acid, the volume would have been

$$3840\ 3 + 1933\ 2 = 5773\ 5\ c\ c$$

Complete conversion to copper nitrate and sulphuric acid would have given a volume of

$$3847{\cdot}4 + 1936\ 8 = 5784\ 2\ c\ c\ ,$$

or a total change of 10 7 c c The mean volume obtained by mixing copper sulphate with nitric acid, or copper nitrate with sulphuric acid, was 5781 0 c.c The nitric acid had therefore secured

$$\frac{5781\ 0 - 5773\ 5}{10\ 7} = \frac{7\ 5}{10\ 7} = 70\% \text{ of the base}$$

When corrections had been made to allow for the effect of the acids on their salts, the ratio of the strength of sulphuric acid to nitric acid was found to be 66 100

The relative strengths of acids deduced from avidity measurements such as the above are found to agree approximately with those which have been deduced from measurements of hydrogen ion concentration Some of the results are given in Table 86

TABLE 86.—RELATIVE STRENGTHS OF ACIDS IN $N/2$ SOLUTION

| Acid | Conductivity | Inversion of sugar | Avidity for bases |
|---|---|---|---|
| Hydrochloric - | 100 | 100 | 100 |
| Nitric - - - | 100 | 100 | 100 |
| Trichloracetic - | 88 | 75 | — |
| Sulphuric - - | 62 | 54 | 50 to 60 |
| Formic - - | 2 3 | 1 5 | — |
| Acetic - - - | 0 7 | 0 4 | — |

**Hydrion measurements.**—Two of the methods used to deduce the strength of an acid from the concentration of hydrogen ions, usually in an aqueous solution, are described below A third method is described on p 636

(*a*) *Conductivity methods*.—The simplest method of deducing the strength of an acid from the yield of hydrogen ions in solution is by means of measurements of conductivity (p 609) Table 87 shows the degree of dissociation of a number of acids in $N/2$ and $N/1000$ solutions as calculated from the ratio

$$\alpha = \frac{\Lambda_v}{\Lambda_\infty} = \frac{\text{equivalent conductivity at dilution } V}{\text{equivalent conductivity at infinite dilution}}.$$

Since the degree of dissociation increases with dilution, all acids tend to become equal in strength at very high dilutions Thus the figures in the last column of the table show that at a dilution of $N/1000$ all the strong acids are nearly equal in strength Although the results given by this method are in fair accord with those obtained by other methods, they can only be approximately correct, because the ratio $\Lambda_v/\Lambda_\infty$ is not an exact measure of the degree of dissociation (see p 624).

TABLE 87 —DEGREE OF DISSOCIATION OF ACIDS AT 25°

| | Degree of dissociation at $N/2$. | Degree of dissociation at $N/1000$ |
|---|---|---|
| (*a*) *Strong acids.* | | |
| Hydrochloric acid | 0 862 | 0 993 |
| Nitric acid | 0 862 | 0 997 |
| Sulphuric acid | 0 536 | 0 960 |
| Trichloracetic acid | 0 760 | 0 990 |
| (*b*) *Weak acids* | | |
| Monochloracetic acid | 0 054 | 0 692 |
| Formic acid | 0 020 | 0 368 |
| Acetic acid | 0 006 | 0 126 |
| Carbonic acid | 0 0008 | 0 017 |
| Hydrocyanic acid | 0 00005 | 0 0011 |

(*b*) *Catalytic methods* —The hydrolysis of methyl acetate and the inversion of cane-sugar (p 574) can be used to determine the catalytic activity of an acid In dilute solutions of the same concentration, the catalytic activities of a series of acids fall into the same sequence as their conductivities, $\Lambda_v$, or degrees of ionisation, $\alpha$ (Table 87) It was, therefore, thought that the catalytic activity of the acids was due exclusively to the hydrogen ions formed from them, and that the undissociated molecules were completely inactive In concentrated solutions, however, the velocity of inversion of cane-sugar, in presence of a given weight of an acid, increases with the concentration of the acid, whereas the degree of dissociation of the acid as deduced from measurements of conductivity decreases This *reductio ad absurdum* of the catalytic method was "explained away" by Arrhenius with the help of an arbitrary "activity coefficient," which increased with the concentration of the acids, so that a much greater catalytic activity was attributed to hydrogen ions in concentrated than in dilute solutions , but it is now recognised that catalysis by acids depends on the transfer of a proton to the organic "substrate" on which the catalyst is operating, and that *the molecules of a strong acid are even more efficient "proton-donors" than the oxonium ions derived from them* This result is easy to understand in view of the fact that the separation of a proton from an oxonium ion is a strongly endothermic reaction :

$$H_3O \rightarrow H_2O + H^{\cdot} - 180{,}000 \text{ cals}$$

The undissociated molecules of *strong* acids are, however, much more ready than the oxonium ion to part with protons and are therefore more active catalysts. The catalysis of the inversion of sugar by acids may

then be represented by the following equations, of which the latter takes place the more readily

$$\overset{+}{O}H_3 + C_{12}H_{22}O_{11} + H_2O \rightarrow C_{12}H_{22}O_{11}\overset{+}{H} + 2H_2O \rightarrow C_6H_{12}O_6 + C_6H_{12}O_6 + \overset{+}{O}H_3,$$

$$HCl + C_{12}H_{22}O_{11} + H_2O \rightarrow C_{12}H_{22}O_{11}H^+ + Cl^- + H_2O \rightarrow C_6H_{12}O_6 + C_6H_{12}O_6 + HCl$$

On the other hand, the definition of a *weak* acid implies that these do not readily transfer their protons to a base, and are therefore equally reluctant to transfer them to the substrate They are therefore much weaker catalysts than the oxonium ions

**The strength of bases.**—A base is a substance which possesses the property of neutralising an acid It may therefore be defined as a "proton-acceptor," *i e* as a substance which can combine with or eliminate hydrogen ions According to this definition (p 46) a base need not be a hydroxide, since the definition includes nitrogenous bases such as ammonia, which do not contain oxygen , and the anion of a weak acid is classified as a base because of its readiness to unite with a proton to form a molecule of the acid In aqueous solutions, however, where hydrogen and hydroxyl ions are always in equilibrium with one another, union with hydrogen ions results in the liberation of hydroxyl ions from the water, in accordance with the laws of mass action as applied to the equation

$$H_2O \rightleftharpoons H + OH'$$

The STRENGTH OF A BASE in an aqueous solution can therefore be defined in terms of the alkalinity of the solution, as measured by the concentration of hydroxyl ions, just as the acidity of a solution is measured by the concentration of hydrogen ions, *e g*

$$NaOH \rightleftharpoons Na + OH', \quad Ba(OH)_2 \rightleftharpoons Ba + 2OH'$$

TABLE 88.—DEGREE OF DISSOCIATION OF BASES

| | $\Lambda/\Lambda\infty$ at $N/2$ | $\Lambda/\Lambda\infty$ at $N/1000$ |
|---|---|---|
| (*a*) *Strong bases* | | |
| Potassium hydroxide - KOH | 0 826 | 0 981 |
| Sodium hydroxide - NaOH | 0 795 | 0 966 |
| Barium hydroxide - $Ba(OH)_2$ | 0 90 (at $N/10$) | 0 977 |
| (*b*) *Weak bases* | | |
| Methylamine $CH_3NH_2 + H_2O \rightleftharpoons CH_3\overset{+}{N}H_3 + \overset{-}{O}H$ | 0 313 | 0 500 |
| Ammonia $NH_3 + H_2O \rightleftharpoons \overset{+}{N}H_4 + \overset{-}{O}H$ | 0 0068 | 0 141 |
| Aniline $C_6H_5NH_2 + H_2O \rightleftharpoons C_6H_5\overset{+}{N}H_3 + \overset{-}{O}H$ | 0 000030 | 0 00068 |

Table 88 gives the "degree of dissociation," $\Lambda/\Lambda_\infty$, of a number of bases as deduced from the electrical conductivity of their aqueous solutions It will be seen that there are again two well-marked groups, namely, **STRONG BASES**, which give large values for this ratio at all dilutions, and **WEAK BASES**, which give only small values even at relatively great dilutions

**Determination of strength of bases.**—The strength of bases can be determined by methods which are precisely similar to those described for acids, *e.g.* from measurements of conductivity, or from the depression of the freezing-point of an aqueous solution The " degree of dissociation " calculated by these methods has a real meaning, however, only in the case of weak bases, since strong bases such as NaOH or $[N(CH_3)_4]OH$ (p. 762) are probably ionised completely at all concentrations (p 602)

The strength of an alkali can also be deduced from the velocity of saponification of an ester, as represented by the equation

$$CH_3 \cdot COOCH_3 + OH' \rightarrow CH_3\ COO' + CH_3\ OH,$$

where the metallic ion of the alkali (which remains unchanged) is omitted from the equation and only the hydroxyl ion is shown This hydroxyl ion is used up as the reaction proceeds, so that the change follows a bimolecular law , but, if a large excess of ester is used, its concentration remains nearly constant, and the rate of hydrolysis gives a measure of the strength of the alkali

Finally, a weak base or acid can be detected by the hydrolysis of its salts Salts of strong acids and strong bases give neutral solutions whilst salts of strong acids and weak bases are acid, and salts of strong bases and weak acids are alkaline in solution This acidity can scarcely be detected in a solution of ammonium chloride, but it is very marked in the salts of very weak bases, *e g* in aluminium chloride and in aniline hydrochloride

**The basicity of acids and acidity of bases.**—(*a*) *Definition* —(i) The *basicity of an acid* may be defined as the maximum number of protons which one molecule of the acid can give to a base Thus hydrochloric acid is said to be a MONOBASIC ACID, because its molecule can give only *one* proton to a base

$$HCl \rightarrow H^+ + Cl', \quad e\,g\quad NaOH + HCl = NaCl + H_2O$$

On the other hand, sulphuric acid is a DIBASIC ACID because its molecule can give *two* protons to a base

$$H_2SO_4 \rightarrow 2H^+ + SO_4'', \quad e\,g\quad 2NaOH + H_2SO_4 = Na_2SO_4 + 2H_2O$$

The basicity of an acid is not necessarily equal to the number of hydrogen atoms in its molecule, *e g* acetic acid, $C_2H_4O_2$, is monobasic although its molecule contains no fewer than four hydrogen atoms

$$CH_3COOH \rightarrow CH_3COO' + H^+,$$

$$e\,g\quad NaOH + CH_3 \cdot CO\ OH = CH_3\ CO\ ONa + H_2O$$

(ii) The *acidity of a base* may be defined as the number of protons which one molecule of it can accept from an acid By this definition sodium hydroxide and ammonia are MONOACIDIC, sodium carbonate and calcium hydroxide DIACIDIC, and aluminium hydroxide TRIACIDIC The neutralisation of alkalis and other metal hydroxides may be represented by the general equation

$$nOH' + nH^+ = nH_2O,$$

where $n$ = the acidity of the base, *e g*

$$Al(OH)_3 + 3HCl = AlCl_3 + 3H_2O.$$

The neutralisation of ammonia and of the carbonate ion can be represented by the equations

$$NH_3 + H = NH_4 \ , \quad e\,g \quad NH_3 + HCl = NH_4Cl$$

$$CO_3'' + 2H^{\cdot} = CO_2 + H_2O \ , \quad e\,g \quad Na_2CO_3 + 2HCl = 2NaCl + CO_2 + H_2O$$

(*b*) *Measurement*—It is difficult to determine the basicity of an acid, because none of the methods in use is entirely reliable It is, therefore, necessary to measure the basicity by as many methods as possible before reaching a decision The more important methods are described below

(1) A given quantity of the acid is neutralised, preferably with a strong alkali such as caustic soda or caustic potash, using phenolphthalein as an indicator , but other bases can be used sometimes with advantage The same quantities of acid and alkali are then mixed in the absence of the indicator and evaporated to crystallisation The process is repeated, but with quantities of alkali which are twice, thrice, one-half, one-third and one-quarter of the original amount The crystals obtained on evaporation are compared with the first specimen, when there ought to be as many different salts as the numerical value of the basicity Thus, under these conditions, sulphuric acid would give only two different salts, viz normal sodium sulphate, $Na_2SO_4$, from the first three mixtures, and sodium acid sulphate, $NaHSO_4$, from the last three, where the acid is in excess The conclusion would be drawn, therefore, that sulphuric acid was a dibasic acid It is necessary to try the effect of excess of alkali because some "acid" salts are alkaline even to phenolphthalein, which actually indicates the neutral point on the alkaline side (see p 634) Thus only two of the hydrogen atoms in phosphoric acid, $H_3PO_4$, are "neutralised" when phenolphthalein is the indicator, and the "acid" salt, $Na_2HPO_4$, therefore crystallises out on evaporation The "normal" salt, $Na_3PO_4$, is obtained when one and a half times as much alkali is used, whilst the monosodium salt, $NaH_2PO_4$, is obtained with half as much alkali, or when methyl orange is used as the indicator in place of phenolphthalein

The results obtained by this method are not very reliable because an acid sometimes forms a "molecular compound" with its salt Thus although oxalic acid, $C_2H_2O_4$, is a dibasic acid, it apparently behaves as a tetrabasic acid in forming potassium quadroxalate, $KHC_2O_4, H_2C_2O_4$, since this salt contains three "acid" hydrogens in its molecule Similarly hydrochloric acid combines with platinic and cuprous chlorides to form compounds such as $PtCl_4, 2HCl$ and $Cu_2Cl_2, 2HCl$, but these are coordination compounds and not acid salts since the metals occur in solution as anions .

$$H_2PtCl_6 \rightarrow 2H + PtCl_6'', \quad H_2Cu_2Cl_4 \rightarrow 2H + Cu_2Cl_4''.$$

Finally the last acid hydrogen of a polybasic acid may be so weak that its alkali salt is largely hydrolysed and cannot be crystallised from solution This difficulty is sometimes avoided either by using a different base or by

preparing the salt by a different method, *e g* normal sulphides are most readily obtained by double decomposition

$$CuSO_4 + H_2S = CuS + H_2SO_4$$

(ii) The basicity of an acid can be obtained by dividing its molecular weight by its equivalent weight The molecular weight ought to be measured in aqueous solution, but this is only possible for weak acids since the large ionisation of a strong acid leads to an abnormally low value for the molecular weight, which cannot be corrected unless the basicity of the acid is known If determination in aqueous solution is excluded, the molecular weight should be obtained from measurements of vapour density This unfortunately involves the assumption that the undissociated acid molecule is the same in aqueous solution as it is in the vapour state, which is not always true The equivalent weight of the acid can be measured by finding what weight of the acid is required to neutralise one equivalent of caustic soda in the presence of an indicator such as phenolphthalein Here again the true value of the equivalent weight may not be obtained owing to the weakness of the " acid " hydrogens in a polybasic acid

(iii) An important check on the basicity of an organic acid is obtained by the analysis of its silver salt On ignition, silver is left, and the equivalent weight of the acid radical can be calculated as that weight of it which was combined with 108 grams of silver The molecular weight of the acid can then be determined by converting it into an *ester* (p 447), in which the acidic hydrogen of the acid or the silver of the salt is replaced by a METHYL OR ETHYL RADICAL, $CH_3$ or $C_2H_5$ (p 656), *e g* by the action of methyl or ethyl iodide on the silver salt The composition of the ester can then be determined by combustion (p 447) and its empirical formula deduced from the results of this analysis Since the esters are not ionised and can usually be vaporised without decomposition, their molecular weights can be deduced without ambiguity from cryoscopic measurements, or directly from measurements of vapour density From the molecular formula of the ester it is easy to deduce the molecular formula of the acid and hence its basicity Thus the basicity of oxalic acid can be determined with certainty from the composition and vapour density of its methyl ester

$$\underset{\text{Oxalic acid}}{H_2C_2O_4} + 2\underset{\text{Methyl alcohol}}{CH_3OH} \rightarrow \underset{\text{Methyl oxalate}}{(CH_3)_2C_2O_4} + 2H_2O.$$

(iv) If the molecular weight of an acid is known, its basicity can be deduced from measurements of the heat liberated when it is mixed with varying proportions of caustic soda or potash Thus the maximum quantity of heat will be liberated when one molecular proportion of a monobasic acid is mixed in dilute solution with one molecular proportion of caustic soda, because the acidic hydrogen will be completely neutralised On the other hand the addition of another molecular proportion of alkali to a dibasic acid should result in the liberation of a considerable quantity of heat (not usually equal to the first) and so on for polybasic acids Thus in the case of phosphoric acid in dilute aqueous solution the addition

of one, two, three and six gram-mols of caustic soda to one gram-mol of phosphoric acid results in the liberation of 14,800 cals , 27,100 cals , 34,000 cals , 35,300 cals These figures indicate that phosphoric acid contains two reasonably strong acid hydrogens and a third (which is very weak), since the last reading shows that the addition of another three molecular proportions of caustic soda has relatively little effect on the heat of neutralisation

This method is not reliable for very weak acids , for example, the heat evolved when one molecular proportion of caustic soda is added to one molecular proportion of aqueous hydrogen sulphide is almost identical to that evolved when double the quantity of caustic soda is used Since the second stage of neutralisation is represented by the equation

$$\overset{+}{\mathrm{N}}\mathrm{aS}\overset{-}{\mathrm{H}} + \overset{+}{\mathrm{N}}\mathrm{a}\overset{-}{\mathrm{O}}\mathrm{H} \rightarrow \mathrm{NaSNa} + \mathrm{H_2O}, \quad \text{or} \quad \overset{-}{\mathrm{S}}\mathrm{H} + \overset{-}{\mathrm{O}}\mathrm{H} \rightarrow \overset{--}{\mathrm{S}} + \mathrm{H_2O},$$

we may conclude that there is no substantial evolution of heat when a proton is transferred from SH′ to OH′, or, in other words, that the *second* proton removed from a molecule of $SH_2$ is bound with about the same energy as the *first* proton removed from a molecule of water

(v) Ostwald established the approximate empirical rule that the difference between the equivalent conductivities of the sodium salt in $N/32$ and $N/1024$ solutions is 10 for a monobasic acid, 20 for a dibasic acid and 10*n* for a polybasic acid of basicity *n* Thus sodium fluoride gives a difference of about 20, in harmony with the facts that the acid forms an acid potassium fluoride, $KHF_2$, and that its molecular weight in dilute solution corresponds with the formula $H_2F_2$

(vi) Finally use may be made of the fact that monobasic oxyacids, unlike many polybasic oxyacids, do not yield their anhydrides ($HIO_3$ is an exception) when they are heated alone, but have to be prepared either by heating with a dehydrating agent such as phosphoric oxide (see $N_2O_5$, p 195) or by special methods, as in the case of acetic acid On the other hand many polybasic oxyacids, *e g* sulphuric acid, decompose into their anhydrides on heating

(vii) The acidity of a soluble base can be measured by methods analogous to (ii) and (iv) for the basicity of an acid The acidity of an insoluble base has no real significance since it is impossible to establish its molecular formula Thus the acidity of aluminium hydroxide is inferred to be three because the element is tervalent, but it might equally well be six as represented by the formula $Al_2(OH)_6$

**Strong and weak electrolytes.**—Strong acids and strong bases resemble metallic salts in being largely dissociated at moderate dilutions These three classes of substances are therefore spoken of as STRONG ELECTROLYTES On the other hand, weak acids and bases, which are only feebly dissociated at moderate dilutions, are described as WEAK ELECTROLYTES. In the next section it will be shown that a significant difference between these two classes is disclosed when the effect of dilution upon the degree of dissociation is studied quantitatively

**Ostwald's dilution law.**—The law of mass action was applied by Ostwald to the dissociation of an electrolyte in the following manner.

Let us suppose that we are dealing with a binary electrolyte, that is, one that dissociates into two ions The electrolytic dissociation of an acid such as acetic acid may then be expressed conventionally as follows *

$$\underset{1-\alpha}{CH_3\,CO{\cdot}OH} \rightleftharpoons \underset{\alpha}{CH_3\,CO\,O'} + \underset{\alpha}{H^{\cdot}}$$

Let the fraction dissociated at a dilution $V$ be $\alpha$, the proportion of undissociated acid is then $1-\alpha$ By the law of mass action

$$\frac{[CH_3COO'][H\,]}{[CH_3\;COOH]} = K \qquad (1)$$

The concentration of $CH_3\;COO'$ and of H is, however, $\alpha/V$, and the concentration of $CH_3\;COOH$ is $(1-\alpha)/V$, so that

$$K = \frac{\alpha^2}{V(1-\alpha)} \qquad (11)$$

Formula (11) is usually described as OSTWALD'S DILUTION LAW

To test the accuracy of this formula it is necessary to determine $\alpha$ for a number of values of $V$ This can be done by measurements of freezing-point depression, but more accurate values are obtained from conductivity measurements Table 89 contains some of the data found by van't Hoff and Reicher for acetic acid

TABLE 89.—DISSOCIATION OF ACETIC ACID AT 14 1°

| $V$ | $\Lambda$ | $\alpha = \frac{\Lambda}{\Lambda_\infty}$ | $K = \frac{\alpha^2}{V(1-\alpha)}$ |
|---|---|---|---|
| 2 02 litres | 1 94 | 0 00614 | 1 88 × $10^{-5}$ |
| 15 9 ,, | 5 26 | 0 0166 | 1 76 ,, |
| 1500 ,, | 46 6 | 0 147 | 1 69 ,, |
| 3010 ,, | 64 8 | 0 205 | 1 76 ,, |
| 7480 ,, | 95 1 | 0 301 | 1 73 ,, |
| 15000 ,, | 129 0 | 0 408 | 1 87 ,, |
| ∞ | 316 0 | — | — |

It will be seen that the dilution law holds for acetic acid over a range of dilutions from 2 to 15,000 litres or more for each gram-molecule of acid In the same way it has been found that a large number of *weak acids* and *weak bases* in aqueous solution obey the dilution law with a high degree of accuracy

The numerical value of the constant $K$ in Ostwald's equation gives a very convenient measure of the strength of a weak acid From formula (11) it follows that

$$\alpha^2 = KV(1-\alpha)\,, \qquad (111)$$

* Since the ionisation of an acid can only take place in the presence of a base this equation should be written $CH_3C\,O\,OH + H_2O \rightleftharpoons CH_3\,CO\,O' + H_3O$ For the sake of simplicity the essential part played by the water, which does not affect the final equation, is ignored in the following paragraphs

but when $\alpha$ is very small, as in the case of a weak acid at moderate dilutions, this equation can be simplified to

$$\alpha = \sqrt{KV} \qquad \text{(iv)}$$

This formula is very useful for calculating the degree of dissociation at moderate dilutions Thus, when the dilution is 1 litre, so that

$$V = 1,$$
$$\alpha = \sqrt{K}$$

The " strength " of a weak acid in a normal aqueous solution is therefore proportional to the square root of its dissociation-constant

**Dissociation-constants of acids.**—Table 90 gives the values of $K$ for a number of organic acids, and in particular shows the effect of substitution upon the dissociation-constants of certain acids Thus the effect produced on the strength of the acids of the acetic series by substituting chlorine for hydrogen is remarkable (see p 714)

TABLE 90 —DISSOCIATION-CONSTANTS OF ACIDS

| Acid | $t$ | $k \times 10^5$ |
|---|---|---|
| Acetic acid - - - - | 25° | 1 86 |
| Monochloracetic acid - - | 25° | 155 |
| Dichloracetic acid - - - | 25° | 5,000 |
| Trichloracetic acid - - - | 18° | about 20,000 |
| Formic acid - - - - | 25° | 21 |
| Acetic acid - - - - | 25° | 1 86 |
| Propionic acid - - - | 25° | 1 4 |
| Benzoic acid - - - - | 25° | 6 6 |
| Carbonic acid - - - | 18° | 0 0304 |
| Hydrogen sulphide - - | 18° | 0 0057 |
| Hydrocyanic acid - - - | 18° | 0 00013 |

**Behaviour of strong electrolytes.**—Strong electrolytes do not obey Ostwald's dilution law Thus the values of $\alpha$, calculated from the conductivities of aqueous solutions of potassium chloride, give rise to the " dissociation-constants " shown in Table 91

TABLE 91 —ELECTROLYTIC DISSOCIATION OF POTASSIUM CHLORIDE

| $V$ | $\alpha$ | $K$ |
|---|---|---|
| 10 | 0 861 | 0 533 |
| 20 | 0 888 | 0 352 |
| 50 | 0 922 | 0 218 |
| 100 | 0 943 | 0 156 |
| 200 | 0 961 | 0 118 |

The third column shows a rapid increase in the values of $K$ calculated by formula (ii) as the dilution decreases, showing that the conductivity falls off much less rapidly in strong solutions than it should do according to the law of mass action.

Various empirical formulae for the conductivity of strong electrolytes have been suggested, the most successful is probably that of Kohlrausch, according to which $1-\alpha \propto C^{\frac{1}{2}}$ when $1-\alpha$ is small

**The theory of Debye and Huckel.**—A theoretical foundation for Kohlrausch's formula has been derived by Debye and Huckel On the assumption that strong electrolytes are completely ionised in solution, they attribute the variations of the molecular conductivity with dilution to changes in the *mobility* and not in the *number* of the ions They suppose that the forces of interionic attraction give rise to an unequal distribution of ions in a solution, so that there is an excess of negative ions in the neighbourhood of a positive ion, and conversely, just as there is in a crystal of rock salt Two effects follow from this unequal distribution

(i) When an ion moves through the solution, the atmosphere of oppositely charged ions lags behind, and produces a retarding electrostatic force, which opposes the E M F under which the ion is moving

(ii) Since the ion drags through the solution an atmosphere of oppositely charged ions, the frictional resistance to its migration is increased

By a difficult calculation, the details of which need not be quoted, Debye and Huckel show that in both (i) and (ii) *the retardation is proportional to the square root of the ionic concentration* Their conductivity equation may be written in a simplified form as follows

$$1-\frac{\Lambda_v}{\Lambda_o}=(K_1w_1+K_2w_2b)\sqrt{vm},$$

where

$K_1$, $K_2$ are constants depending upon the temperature and dielectric constant of the solvent,
$b$ is the average radius of the ions,
$v$ is the number of ions in the molecule,
$m$ is the molecular concentration of the electrolyte, and
$w_1$ and $w_2$ are universal constants, depending upon the valency of the ions

Debye and Huckel's equation can only be applied to dilute solutions of strong electrolytes, since the electrostatic forces between the ions have a much wider range than the van der Waals' forces between molecules, and even then the calculated conductivities are not very exact The equation has, however, the merit of providing, on the basis of the theory of complete ionisation, a rational explanation of Kohlrausch's dilution law for strong electrolytes, just as Arrhenius' theory of reversible ionisation provides the theoretical basis of Ostwald's dilution law for weak electrolytes

**The ionisation of water.**—When the equation for the neutralisation of a strong acid by a strong base is expressed in terms of the theory of electrolytic dissociation, the only chemical change is the union of hydrogen and hydroxyl ions to form water, *e g*

$$H^{\cdot}+Cl'+K^{\cdot}+OH'=H_2O+K^{\cdot}+Cl'.$$

This conception of the process of neutralisation affords an immediate explanation of the experimental fact, noted in Chapter XL (p 552), that the heat of neutralisation of a strong acid by a strong base in a dilute solution is always 13,700 calories

It is of interest to enquire whether this action is reversible, *i e* whether pure water itself is ionised to any extent into hydrogen and hydroxyl ions

$$H_2O \rightleftharpoons H + OH', \text{ or more precisely } 2H_2O \rightleftharpoons OH_3 + OH'$$

The electrical conductivity of ordinary distilled water (about $10 \times 10^{-6}$ mhos) cannot be cited as evidence, since this is obviously due for the most part to traces of impurities, chiefly dissolved carbon dioxide and ammonia When these are eliminated by distillation from alkaline potassium permanganate much lower conductivities are observed The lowest value yet recorded was obtained by Kohlrausch, by repeated distillation in a sealed vessel, in which the water was kept in contact with platinum electrodes for long periods of time, and then poured back again and redistilled In this way he reduced the specific conductivity of the water to $\kappa = 0\ 0384 \times 10^{-6}$ mhos at 18°, but he was not able to reduce the conductivity any further This residual conductivity may be attributed to the dissociation of water itself, it can only be regarded as an upper limit, however, since lower values might be recorded at any time as a result of more successful purification

Assuming, however, that Kohlrausch's value represents the real conductivity of pure water, it is easy to deduce from it a value for the dissociation-constant Thus, the mobilities $\Lambda_H$ and $\Lambda_{OH'}$ of the hydrogen and hydroxyl ions at 18° are 315 and 174 respectively The number, $c$, of gram-ions per 1000 c c is therefore given by

$$c = \frac{1000\kappa}{\Lambda_H + \Lambda_{OH'}} = \frac{38\ 4 \times 10^{-6}}{489} = 0\ 785 \times 10^{-7},$$

that is, the number of gram-ions of hydrogen or hydroxyl in a litre of pure water is $0\ 78 \times 10^{-7}$ By applying the law of mass action (since water is a weak electrolyte), it is evident that in water and in any aqueous solution

$$[H\ ][OH'] = K[H_2O]$$

Since water is so slightly ionised, the concentration of undissociated water is constant, the right-hand side of this equation is therefore a constant and may be written

$$[H\ ][OH'] = K_W,$$

where $K_W$ is the IONIC PRODUCT for water, *e g* at 18°,

$$[H\ ] = [OH'] = 0\ 78 \times 10^{-7},$$

whence $K_W^{18°} = 0\ 61 \times 10^{-14}$ This ionic product, $K_W$, must be distinguished clearly from the dissociation-constant $K$ of the balanced action, which would be 55 times smaller, since

$$[H_2O] = 1000 - 18 = 55 \text{ (approx)}$$

Kohlrausch found that the conductivity of pure water increased rapidly with temperature, so that at 25° $K_W = 1\ 06 \times 10^{-14}$ Since $K_W$ is a multiple

of the equilibrium-constant for the dissociation of water, we can use the equation of van 't Hoff (p 558) in order to calculate the heat of the dissociation, $H_2O = H + OH'$, from values of the equilibrium-constant at two temperatures van 't Hoff's equation may be written

$$2{\cdot}303 \log_{10} \frac{K_1}{K_2} = \frac{U}{2} \frac{T_2 - T_1}{T_1 T_2}$$

Inserting the values given above for $K_W$ at 18° and 25°,

$$U = \frac{2 \times 2\ 303 \times 291 \times 298 \log_{10} \frac{0\ 61}{1\ 06}}{298 - 291},$$

$$= -13{,}670 \text{ cals}$$

This is practically identical in magnitude, but opposite in sign to the value found experimentally for the heat of neutralisation of a strong acid by a strong base,—a reaction which, according to the ionic theory, consists only of the combination of hydrogen * and hydroxyl ions

Dissociation, $H_2O \rightarrow H + OH' - 13{,}670$ cals

Neutralisation, $H + OH' \rightarrow H_2O + 13{,}700$ cals

The good agreement between these numbers, calculated from very different experimental data, is strong evidence of the validity of the theory of electrolytic dissociation as applied to this particular case Similar values for the ionic product of water have been obtained by a variety of other methods Thus, from the measurement of the degree of hydrolysis of sodium acetate and the dissociation-constant of acetic acid, Shields obtained the value $1\ 15 \times 10^{-14}$ for $K_W$ at 25°

**Hydrolysis.**—(*a*) *The salt of a strong base and a weak acid* —The very small dissociation of water might perhaps be thought to be of little importance, but it provides an explanation of many of the properties of aqueous electrolytes which would otherwise be difficult to understand, and, in particular, of the hydrolysis of metallic salts Suppose we have a solution of a metallic salt, MA, derived from a strong alkali, MOH, and a weak acid, HA We may regard the metallic salt (at least in dilute solution) as being completely ionised as in (*a*) whilst the weak acid and the water of the solution are feebly ionised as in (*b*) and (*c*) *

(*a*) $MA \rightarrow M + A'$

(*b*) $H_2O \rightleftharpoons H + OH'$

(*c*) $HA \rightleftharpoons H + A'$

It is obvious that there will be a competition for the possession of hydrogen ions between the hydroxyl ions of the water and the anions of the acid, and this will ultimately reach a condition of equilibrium, depending upon the relative tendencies of water and the acid to dissociate Thus, if the acid is very weak, the anion A' of the salt will unite with a large proportion of the hydrogen ions of the water, the equilibrium $H_2O \rightleftharpoons H + OH'$

* The hydration of the ions is again ignored, since the results are not affected by writing H where $H_3O$ would be more correct

will therefore be disturbed and more molecules of water will dissociate, giving rise to a further supply of hydrogen and hydroxyl ions The net result is that the concentration of the hydroxyl ions in the solution will exceed that of the hydrogen ions, some of which have been used up to form undissociated molecules of the weak acid, so that the solution will therefore be *alkaline* in reaction

The hydrolysis of the salt may be represented by the equation,

$$MA + H_2O \rightleftharpoons MOH + HA$$

Since, however, the salt and base are almost completely ionised and the acid almost undissociated in the presence of its highly ionised salt, this equation may be rewritten thus

$$M + A' + H_2O \rightleftharpoons M + OH' + HA,$$

or
$$A' + H_2O \rightleftharpoons HA + OH' \qquad (1)$$

It is evident from this discussion that the extent of hydrolysis depends upon the relative degrees of dissociation of water and of the acid Salts of acids with dissociation-constants much greater than water will only be hydrolysed to a small extent, whilst those with smaller dissociation-constants will be largely hydrolysed This can be expressed quantitatively by applying the law of mass action to the hydrolysis-equation (1) This gives

$$\frac{[HA][OH']}{[A'][H_2O]} = \frac{[\text{free acid}][\text{free base}]}{[\text{unhydrolysed salt}][\text{water}]} = K, \qquad (11)$$

or, since the concentration of water is practically constant in a dilute solution,

$$K_H = \frac{[\text{free acid}][\text{free base}]}{[\text{unhydrolysed salt}]} = \frac{[HA][OH']}{[A']}, \qquad (111)$$

where $K_H$, the HYDROLYSIS CONSTANT, takes the place of the product $K$ [water] in equation (11) The concentrations [HA] and [OH'] in equation (111) are now obtained in terms of $K_A$, the dissociation-constant of the acid, and $K_W$, the ionic product of water, thus

$$\frac{[H][A']}{[HA]} = K_A, \quad \therefore [HA] = \frac{[H][A']}{K_A},$$

and
$$[H][OH'] = K_W; \quad \therefore [OH'] = K_W/[H]$$

Substituting these values in equation (111), we obtain the expression

$$K_H = \frac{K_W}{K_A} \qquad .. \qquad (1v)$$

The hydrolysis constant of the salt is therefore equal to the ratio of the ionic product of water and the dissociation-constant of the acid Table 92 contains details of the dissociation-constants of a few weak acids, together with the percentage hydrolysis of their sodium salts in normal and decinormal solution It will be seen from the table that the degree of hydrolysis of these salts depends not only upon the value of the dissociation-constant of the acid, but also on the dilution, *e g.* the hydrolysis of sodium acetate in decinormal solution is 3·16 times that in normal solution.

The effect of dilution on the degree of hydrolysis can be calculated from equation (iii) Thus, if one gram-molecule of the salt is dissolved in $V$ litres, and a fraction $x$ is hydrolysed, we may substitute $x/V$ for the concentrations of the free base and free acid, and $(1-x)/V$ for that of the unhydrolysed salt, whence

$$\frac{x^2}{V(1-x)} = K_H . \qquad (v)$$

When $x$ is small in comparison to 1, it is clear that the degree of hydrolysis is directly proportional to the square root of the dilution

TABLE 92 —DEGREE OF HYDROLYSIS OF SODIUM SALTS

| Salt | Dissociation-constant of acid | Hydrolysis of sodium salt in | |
|---|---|---|---|
| | | normal solution | decinormal solution |
| Sodium acetate - | $1\cdot8 \times 10^{-5}$ | 0·0024% | 0·0076% |
| Sodium carbonate - | $3\cdot0 \times 10^{-7}$ | 0·0185 | 0·058 |
| Sodium sulphide - | $5\cdot7 \times 10^{-8}$ | 0·042 | 0·13 |
| Sodium cyanide - | $1\cdot3 \times 10^{-9}$ | 0·28 | 0·88 |

(*b*) *The salt of a weak base and a strong acid* —Similar considerations apply to the hydrolysis of a salt MA, formed from a weak base and a strong acid In this case the cations of the salt and the hydrogen ions from the water compete for hydroxyl ions, *e g*

$$M^+ + OH' \rightleftharpoons MOH , \quad H^+ + OH' \rightleftharpoons HOH$$

The hydrolysis of the salt may therefore be represented by the equation,

$$M^+ + A' + HOH \rightleftharpoons MOH + H^+ + A',$$

or

$$M^+ + HOH \rightleftharpoons MOH + H^+ \qquad (vi)$$

The solution is acid because a portion of the hydroxyl ions produced by the dissociation of the water has been used up to form undissociated molecules of the weak base, MOH, whilst the hydrogen ions remain intact At equilibrium we can write

$$\frac{[\text{free acid}][\text{free base}]}{[\text{unhydrolysed salt}]} = \frac{x^2}{V(1-x)} = K_H = \frac{K_W}{K_B} \qquad (vii)$$

This equation is identical with equation (v) for the hydrolysis of a salt of a weak acid, except that $K_B$, the dissociation-constant of the weak base, has been substituted for $K_A$

The hydroxides of ammonium, aluminium, ferric iron, bismuth and zinc are well-known examples of weak bases, since with strong acids they form salts which are acidic in aqueous solution

(*c*) *The salt of a weak acid and a weak base* —The hydrolysis of the salt of a weak acid and a weak base may be expressed by the general equation,

$$M^+ + A' + HOH \rightleftharpoons MOH + HA \qquad \ldots\ldots\ldots (viii)$$

This differs from equations (i) and (vi) in that both the products of hydrolysis are weak and therefore almost unionised in the presence of

their salt If they are equally weak, the solution will be neutral, however great the degree of hydrolysis may be When the law of mass action is applied to this equilibrium, we obtain the following expression

$$\frac{[MOH][HA]}{[M^+][A^-]} = \frac{[\text{free acid}][\text{free base}]}{[\text{unhydrolysed salt}]^2} = \frac{x^2}{(1-x)^2} = K_H = \frac{K_W}{K_A K_B} \qquad (IX)$$

This differs from (v) and (vii) in that the degree of hydrolysis, $x$, is independent of the dilution, and in the fact that the hydrolytic constant, $K_H$, is inversely proportional to the product, $K_A K_B$, of the dissociation-constants of acid and base

**Determination of the degree of hydrolysis of salts.**—The determination of the degree of hydrolysis of a salt cannot be measured by titrating with an acid or alkali, since this would upset the equilibrium and cause progressive hydrolysis of the salt Thus borax is only 0 5% hydrolysed in $M/10$ solution, yet the whole of the base can be titrated with acid using methyl orange as indicator Some of the more important methods used in the measurement of the hydrolysis of salts are discussed below

(*a*) *Catalytic method*—The concentration of the $H^+$ or $OH'$ in the solution is measured by the rate at which it catalyses the inversion of cane-sugar or the hydrolysis of methyl acetate Thus in Expt 133 the degree of hydrolysis of urea hydrochloride is determined by measuring the rate at which it catalyses the hydrolysis of methyl acetate

(*b*) *Partition method*—This method depends upon finding the concentration of one of the products of hydrolysis by means of partition measurements Thus, if a solution containing a known weight of aniline hydrochloride is shaken with a known volume of benzene, only the free aniline (produced by hydrolysis) will dissolve in the layer of benzene This is estimated by titration with a standard solution of bromine, which reacts with the base to give tribromoaniline,

$$C_6H_5{\cdot}NH_2 + 3Br_2 = C_6H_2Br_3\,NH_2 + 3HBr$$

The end-point is indicated by the yellow colour of free bromine The concentration of free aniline in the aqueous solution is then deduced from the partition coefficient of aniline in water and benzene, which can be measured in an independent experiment The concentration of unchanged aniline hydrochloride is obtained by subtracting this from the total quantity of aniline hydrochloride, whilst the free hydrochloric acid is equal to the total quantity of free aniline The hydrolytic constant, $K_H$, may then be calculated from the relation .

$$K_H = \frac{[\text{free aniline}]\,[\text{free acid}]}{[\text{unhydrolysed aniline hydrochloride}]}.$$

(*c*) *Indirect method*—The hydrolytic constant can be calculated from the dissociation-constants of water, and of the acid or base, or both Thus, for the hydrolysis of the salt of a weak acid and strong base, we have shown that .

$$\frac{K_W}{K_A} = K_H = \frac{x^2}{(1-x)V}$$

The values of $K_A$ and $K_W$ can be determined by conductivity or other methods. Using the approximate value $1.0 \times 10^{-14}$ for $K_W$, the degree of hydrolysis in normal solution of some sodium salts of weak acids has been calculated and the results are given in Table 92

(*d*) *Other methods* —The hydrolysis of salts may also be deduced from measurements of conductivity, electromotive force and depression of freezing-point, but space does not permit of a discussion of these methods, which are admirably suited to certain cases of hydrolysis

**Neutralisation.**—It is readily seen from the ionic theory that the process of neutralisation consists of the combination of the hydrogen ions of an acid with the hydroxyl ions of a base, and that neutrality is attained when the concentrations of these two ions are equal Further, since we know the value of

$$K_W = 1 \times 10^{-14},$$

we can predict that in a strictly neutral solution the concentration of hydrogen ions will be $10^{-7}$ gram-equivalents per litre

**Hydrogen-ion concentration.**—In discussing problems of neutralisation, a special method is often employed for stating the concentration of hydrogen ion The acidity or alkalinity is defined by a quantity known as $p_H$, where

$$p_H = -\log_{10}[H] = \log_{10}\frac{1}{[H]} \qquad (1)$$

Thus a solution in which $[H] = 10^{-6}$ is said to have $p_H = 6$, and one in which

$$[H] = 2 \times 10^{-10} = 10^{+0.30} \times 10^{-10} = 10^{-9.7}$$

is said to have a $p_H$ of 9 7 The neutral point, at which $[H] = 10^{-7}$, is of course $p_H = 7$

TABLE 93 —CHANGES OF HYDROGEN-ION CONCENTRATIONS DURING NEUTRALISATION

| c c *N* NaOH | [H] | $p_H$ |
|---|---|---|
| 45 0 | $5 \times 10^{-3}$ | 2 3 |
| 49 0 | $1 \times 10^{-2}$ | 3 0 |
| 49 5 | $5 \times 10^{-4}$ | 3 3 |
| 49 9 | $1 \times 10^{-4}$ | 4 0 |
| 49 95 | $5 \times 10^{-5}$ | 4 3 |
| 50 0 | $1 \times 10^{-7}$ | 7 0 |
| 50 05 | $2 \times 10^{-10}$ | 9 7 |
| 50 1 | $1 \times 10^{-10}$ | 10 0 |
| 50 5 | $2 \times 10^{-11}$ | 10 7 |
| 51 0 | $1 \times 10^{-11}$ | 11 0 |
| 55 0 | $2 \times 10^{-12}$ | 11 7 |

It is instructive to calculate the changes in concentration of hydrogen ion around the neutral point when a strong base is titrated by a strong acid Let us assume complete dissociation of both acid and base, and suppose that normal alkali is being added to 50 c c of normal acid, the volume in all cases being made up to 1000 c c When 49 5 c c of alkali have been added, the residual acid has a concentration of $0.5 \times 10^{-3} = 5 \times 10^{-4}$ gram-equivalents per litre, and (assuming complete dissociation) this number

also gives the concentration of hydrogen ions remaining in the solution On the alkaline side, when 50 5 c c of alkali have been added, the concentration of hydroxyl ions is also $5 \times 10^{-4}$, and since $[H^{\cdot}][OH'] = K_W$,

$$[H^{\cdot}] = 1 \times 10^{-14} - 5 \times 10^{-4} = 2 \times 10^{-11}$$

Table 93 is calculated in this way In this table the second column shows the change in [H ] as the neutral point is reached and passed , the last column shows the corresponding changes in $p_H$

In the first place it should be noticed that there is a very rapid change in the concentration of hydrogen ions in the neighbourhood of the neutral point, where a variation of $\pm 0$ 1 c c produces a million-fold change in the concentration of hydrogen ions from $10^{-4}$ to $10^{-10}$ gram-equivalents per litre It is evident that solutions with hydrogen-ion concentrations between $p_H = 4$ and $p_H = 10$ cannot be prepared with accuracy by mixing strong acids and bases, since slight errors of concentration or the presence of traces of acid or alkaline impurities would have an enormous effect on the acidity of the solution

**Influence of neutral salts.**—We have neglected so far the influence, upon the dissociation of the acid or base, of the salt formed by their neutralisation This is justifiable when strong acids and bases are concerned, but not when weak acids and bases are used. As an example we may discuss the neutralisation of a weak acid (*e g* acetic acid) by a strong base (*e g* caustic soda) As before, we will commence with 50 c c of normal acid and add normal NaOH from a burette, the solution in each case being made up to 1000 c c Since the dissociation of the weak acids obeys the law of mass action, as expressed by Ostwald's " dilution law," we have

$$\frac{[H][A']}{[HA]} = K_A = 1\ 8 \times 10^{-5} \qquad (ii)$$

Hence

$$[H] = K_A \frac{[HA]}{[A']}, \qquad (iii)$$

and

$$p_H = \log_{10} \frac{1}{[H]} = \log_{10} \frac{[A']}{K_A[HA]} \qquad (iv)$$

We may regard the sodium acetate as completely dissociated, so that [A'] corresponds to the amount of alkali added , also the acid is so feebly dissociated that we may suppose that [HA] corresponds to the whole of the residual acid. Thus, when 10 c c of alkali have been added,

$$[A'] = 10^{-2} \quad \text{and} \quad [HA] = 4 \times 10^{-2},$$

so that

$$p_H = \log_{10} \frac{10^{-2}}{1\ 8 \times 10^{-5} \times 4 \times 10^{-2}} = 4\ 14$$

Table 94 gives the values calculated in this way for the variation of $p_H$ during the titration It should be noted that there is a region in which the concentration of hydrogen ion changes only slowly, and that, when exactly half the acid is neutralised, the change of $p_H$ with added base is least. At this point, where [HA] = [A'], it will be seen from equation (iii)

that the concentration of hydrogen ions [H] is numerically equal to the dissociation-constant $K_A$ of the acid, namely, $1.8 \times 10^{-5}$ or $p_H = 4.74$

TABLE 94.—NEUTRALISATION OF A WEAK ACID BY A STRONG BASE

| Volume of normal acetic acid | Volume of normal sodium hydroxide | $p_H$ |
|---|---|---|
| 50 c.c. | 10 c.c. | 4.14 |
| ,, | 15 | 4.38 |
| ,, | 20 | 4.57 |
| ,, | 25 | 4.74 |
| ,, | 30 | 4.92 |
| ,, | 35 | 5.11 |
| ,, | 40 | 5.35 |
| ,, | 45 | 5.70 |
| ,, | 50 | 7.22 |
| ,, | 50.05 | 9.70 |
| ,, | 50.1 | 10.0 |
| ,, | 50.5 | 10.7 |

This characteristic behaviour of a mixture of a weak acid with an equivalent amount of one of its salts provides a ready means of preparing a solution of known hydrogen-ion concentration, since slight errors in the concentration of the acid or of the salt have very little effect on the concentrations of the hydrogen ions. Further, if small amounts of acid or alkali are added, the change in $p_H$ is very small. Such solutions, which resist a change in $p_H$ on the addition of acid or alkali, are termed **BUFFER SOLUTIONS**. Other mixtures used as buffer solutions are

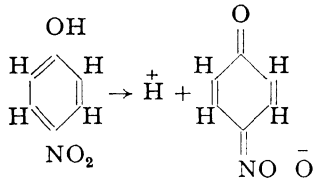
Citric acid + sodium citrate,
$Na_2CO_3 + NaHCO_3$,
$Na_2HPO_4 + NaH_2PO_4$,
Borax + boric acid

**The theory of indicators.**—The indicators used in titrating acids and alkalis are either weak acids or weak bases, and are therefore ionised only to a minute extent in pure water. In the presence of alkalis or acids they are converted into salts, which are highly ionised. The changes of colour which they undergo were therefore formerly attributed to ionisation, *i.e.* the ions were supposed to have a different colour from the undissociated molecules. Thus, the colourless molecule of phenolphthalein was supposed to yield a pink anion, since the indicator is colourless in the presence of acids, when it is not ionised, whilst it is pink in alkaline solutions, in which it is presumably present as an anion:

$$\underset{\text{colourless}}{HP} \rightleftharpoons H + \underset{\text{pink}}{P'}$$

This ionic explanation of the mechanism of an indicator is only partially correct, since the mere loss of a proton, $H^+$, is not sufficient to account for a fundamental change of colour. Moreover, phenolphthalein yields

an ester which is pink like the salts, although the esters are not ionised The change of colour is therefore attributed to a change of structure which accompanies the ionisation of the molecule as well as its conversion into an ester This change of structure may be illustrated in the simpler case of *p*-nitrophenol, which is colourless in acid and neutral solutions, but becomes orange in the presence of alkalis, owing to the change of structure shown in the following scheme



In alkaline solutions, the change proceeds from left to right owing to the removal of the hydrogen ions by the hydroxyl ions of the alkali It will be observed that the colourless "benzenoid" structure of the parent molecule, with three double bonds in a ring (p 780), has been replaced in the anion by a "quinonoid" structure (p 799), with a group of four parallel double bonds which is always associated with colour Similar changes occur in indicators of more complex constitution, but all these changes have as their essential characteristic the fact that it is the *concentration of hydrogen ions* in the solution which determines the change in constitution and therefore in colour

Like any other weak acid, an indicator is half-converted into anions when the concentration of hydrogen ions is numerically equal to its dissociation-constant For phenolphthalein this occurs at $p_H = 9\,5$ It can be shown that at $p_H = 8\,5$ only 10% of the indicator is in the form of anions, whilst at $p_H = 10\,5$ more than 90% of it is ionised Hence over a range from $p_H$ 8 5 to $p_H$ 10 5 phenolphthalein changes from an almost colourless solution to deep red In the same way, the change of colour in any other indicator takes place over a narrow working range on either side of the value of $p_H$ corresponding with its dissociation-constant. Table 95 gives the working range of a few common indicators

TABLE 95 —WORKING RANGE OF INDICATORS.

| | |
|---|---|
| Methyl orange | $p_H = 3\,1 - 4\,5$ |
| Methyl red | $4\,7 - 6\,4$ |
| Litmus | $5\,0 - 7\,0$ |
| Cresol red | $7\,2 - 8\,8$ |
| Phenolphthalein | $8\,5 - 10\,5$ |

**Choice of an indicator.**—From a knowledge of these values a decision can readily be made as to which indicator is most suitable for a particular titration

In Fig 165 the working range of the indicators is shown on the right-hand side of the diagram

(*a*) The continuous curve I shows the variation of $p_H$ during the titration of a strong acid by a strong base. This curve shows a rapid change

in $p_H$ from 4 to 10 for very small additions of base, so that all the indicators would give very nearly the same end-point and might be used with satisfactory results

(*b*) Curve II represents the titration of a weak acid by a strong base The $p_H$ is seen to change gradually until the neutral point is reached and then falls rapidly, following nearly the same course as curve I. It is evident immediately from the diagram that methyl orange and methyl red would be most unsatisfactory indicators for titrations of this type, because the $p_H$ at which their colour changes is reached long before the theoretical quantity of alkali has been added On the other hand, the $p_H$ at which phenolphthalein changes colour coincides with the theoretical neutral point, so that this indicator will give satisfactory results

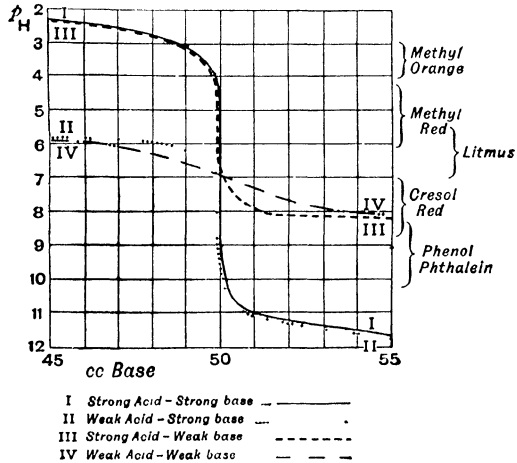



FIG 165 VARIATION OF CONCENTRATION OF HYDROGEN IONS DURING TITRATION

(*c*) Curve III represents the titration of a strong acid by a weak base It follows almost the same course as I up to the neutral point, but then diverges and shows only small changes in $p_H$ for a large excess of added base It is evident that methyl orange or methyl red would be satisfactory indicators for this titration, whilst phenolphthalein would give a very indefinite end-point, since it would only become coloured in presence of a large excess of weak base

(*d*) Curve IV shows the variation of $p_H$ when a weak acid is titrated with a weak base The curve is shallow on both sides of the neutral point and no indicator will give a satisfactory end-point

These conclusions may be summarised for practical purposes as follows

| Titration | Indicator |
|---|---|
| Strong acid – strong base | Any indicator |
| Weak acid – strong base | Phenolphthalein |
| Strong acid – weak base | Methyl red or methyl orange. |
| Weak acid – weak base | No indicator is satisfactory. |

**Measurement of hydrogen-ion concentration.**—The hydrogen-ion concentration of a solution can be determined with fair accuracy by adding a suitable indicator to the solution and comparing the colour produced with that given by the same indicator when added to buffer solutions of known $p_H$ (Expt 128) A more direct and accurate method depends upon measurements of electromotive force, using a hydrogen electrode

**The solubility-product of an electrolyte.**—The theory of electrolytic dissociation gives a very interesting explanation of the solubility relations of sparingly soluble substances, and in many cases enables us to determine the conditions under which a precipitate will be formed Thus, if we consider the equilibria which are set up in a saturated solution of a sparingly soluble substance such as silver chloride, we may express the main condition of equilibrium by a scheme such as

$$\underset{\text{(solid)}}{\text{Ag Cl}'} \rightleftharpoons \underset{\text{(dissolved)}}{\text{Ag Cl}'} \rightleftharpoons \underset{\text{(dissolved)}}{\text{Ag}^{\cdot} + \text{Cl}'}$$

The fact that the active mass of the solid is constant implies that the concentration of the ion-pairs in the solution is also constant, so that by applying the law of mass action we obtain the expression

$$[\text{Ag}^{\cdot}][\text{Cl}'] = K[\text{Ag Cl}' \text{ dissolved}] = S$$

The constant $S$ is named the SOLUBILITY-PRODUCT for silver chloride Its significance may perhaps be appreciated better if we now reverse our reasoning, since it is evident that, when silver ions and chloride ions are brought together in solution, *a precipitate will not form unless the product of the concentration of these ions is greater than the solubility-product S*

The solubility of silver chloride in water is $1 \times 10^{-5}$ gram-molecules per litre at room temperature In this very dilute solution we can assume that ionisation is complete, so that

$$[\text{Ag}^{\cdot}] = [\text{Cl}'] = 1 \times 10^{-5},$$

whence $S_{\text{AgCl}} = 1 \times 10^{-10}$

If the concentration either of silver ions or of chloride ions is increased, then the concentration of the other type of ion must fall until the product of the concentrations reaches the solubility-product. Since this can only occur by the removal of further silver chloride from the solution, it can be predicted that silver chloride will be less soluble in a solution containing silver nitrate or potassium chloride than in pure water

The amount of silver chloride precipitated in this manner can readily be calculated Suppose, to 1 litre of a saturated solution of silver chloride, sufficient silver nitrate is added to make the solution decinormal with respect to this salt The concentration of silver ions $[\text{Ag}^{\cdot}]$ is now $10^{-1}$, since the concentration of silver ion provided by the silver chloride is so small in comparison that it can be ignored. Hence, since

$$[\text{Ag}^{\cdot}][\text{Cl}'] = S = 10^{-10}, \quad \text{then} \quad [\text{Cl}'] = \frac{S}{[\text{Ag}^{\cdot}]} = \frac{10^{-10}}{10^{-1}} = 10^{-9}.$$

The amount of silver chloride in solution therefore falls from $10^{-5}$ to $10^{-9}$ gram-mols. per litre, and so $0{\cdot}9999 \times 10^{-5}$ gram-mol. is precipitated

Since the molecular weight of AgCl is 143 5 this amounts to 0 001435 gram per litre This amount is quite appreciable in determinations of atomic weight, a slight excess of silver nitrate is therefore always used in order to complete the precipitation of chloride ions by silver, or *vice versa*

**Applications to qualitative analysis.**—The theory of the solubility-product gives an interesting explanation of many of the reactions used in qualitative analysis (Part IV, p 377) The solubility-products of a number of the commoner sulphides in order of magnitude are

$$HgS,\ 4 \times 10^{-54},\quad CuS,\ 8 \times 10^{-45},\quad CdS,\ 5 \times 10^{-29},$$
$$ZnS,\ \text{about}\ 1 \times 10^{-20},\quad MnS,\ 1\ 4 \times 10^{-15}$$

When sulphuretted hydrogen is passed into a solution of the salts of these metals, precipitation will occur when

$$[M\ ][S''] > S,$$

where M is the ion of the metal

We cannot vary the concentration of the metallic ion very readily, since we are limited in one direction by the solubility of the salt, and, on the other hand, by the necessity of obtaining a sufficient amount of precipitate to handle and use for confirmatory tests We can, however, vary within wide limits the concentration of sulphide ion present Sulphuretted hydrogen is a weak acid, and the dissociation,

$$H_2S \rightleftharpoons 2H\ + S'',$$

is readily repressed by hydrogen ions If therefore the solution is acidified with hydrochloric acid, the concentration of sulphide ions [S''] is lowered so much that the solubility-product is only attained for the very insoluble sulphides, *e g* HgS, CuS, and CdS, whilst ZnS and MnS remain in solution If too much acid is added, CdS may not be precipitated, though here the reaction is complicated by the fact that an unstable orange form of CdS with a greater solubility-product is first produced

If $H_2S$ is passed into a neutral solution of a zinc salt, some ZnS is precipitated, but the reaction is never complete, as the acid liberated by the reaction rapidly lowers the concentration of sulphide ions and stops the precipitation If, however, ammonium acetate and acetic acid are added, so that only a weak acid is present, ZnS can be precipitated completely Under these conditions, the more soluble MnS is not thrown down and requires the addition of a soluble sulphide, *e g* ammonium sulphide, to give a supply of sulphide ions in excess of its solubility product

Another example, in which the dissociation of a base is controlled, is provided by the separation of iron, aluminium and chromium from zinc, manganese and magnesium Ammonium hydroxide is a weak base and its degree of dissociation is lowered markedly by the addition of ammonium chloride If, therefore, a dilute solution of ammonia is added to a solution containing salts of these metals, together with ammonium chloride, only those hydroxides with small solubility-products, namely, $Fe(OH)_3$, $Al(OH)_3$, $Cr(OH)_3$, are precipitated If, however, too much

ammonia is added, or if enough ammonium chloride is not present, or if the concentration of the metallic ions is too large, then the hydroxides of zinc, manganese, and magnesium will also be thrown down, since their larger solubility-products will be exceeded In this case, ammonium chloride is used to regulate the dissociation of ammonia, and to differentiate between hydroxides with different solubility-products

The conception of a solubility-product can also be used to account for the solubility relationships of the chromates and sulphates of calcium, strontium, and barium, and for the solubility of salts of weak acids, *e g* phosphates and cyanides, in strong acids In all such cases it must be remembered that the solubility-product can only be regarded as constant for *sparingly soluble* substances and for reagents in dilute solutions In stronger solutions of salts, with or without an ion common to the sparingly soluble substance, it has been found that the solubility-product is by no means constant Silver chloride, for example, is more soluble in concentrated solutions of potassium chloride than in pure water, although in dilute solutions of this salt it is much less soluble than in water, and gives a solubility-product which is nearly constant Similarly, the conception of a solubility-product cannot be applied to explain the precipitation of sodium chloride when hydrogen chloride is passed into a strong solution of brine In this case much of the precipitation is due to the fact that the nature of the solvent has been altered, owing to the conversion of a large number of water molecules into oxonium ions, $H_3O^+$

$$HCl + H_2O = H_3O^+ + Cl^-.$$

EXPT 127 **Preparation of buffer solutions.**

Prepare a litre of each of the following solutions

(1) $N/5$ Acetic acid
(2) $N/5$ Sodium acetate
(3) $M/20$ Borax (19 11 gm $Na_2B_4O_7$, $10H_2O$ in 1 litre)
(4) $M/5$ Boric acid + NaCl (12 40 gm $H_3BO_3$ + 2 93 gm NaCl in 1 litre)

Clean and dry six stoppered bottles of about 250 c c capacity and label them $p_H = 4$, $p_H = 5$, to $p_H = 9$ Run into the bottles from a burette the following quantities of the stock solutions

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| $p_H = 4$ | 164 c c | $N/5$ acetic acid | + | 36 c c | $N/5$ sodium acetate |
| $p_H = 5$ | 59 | ,, | ,, | ,, | + 141 | ,, | ,, | ,, | ,, | ,, |
| $p_H = 6$ | 9 | ,, | ,, | ,, | + 191 | ,, | ,, | ,, | ,, | ,, |
| $p_H = 7$ | 12 | ,, | $M/20$ borax | + 188 c c | $M/5$ boric acid + NaCl |
| $p_H = 8$ | 55 | ,, | ,, | ,, | + 145 | ,, | ,, | ,, | ,, | ,, |
| $p_H = 9$ | 160 | ,, | ,, | ,, | + 40 | ,, | ,, | ,, | ,, | ,, |

EXPT 128 **Working range of indicators**

Place 10 c c of these six buffer solutions in a series of six clean dry test tubes. Add three drops of methyl orange to each test tube Note in which of the tubes a marked change of colour occurs Repeat with other indicators, *e g* methyl red, litmus, cresol red, and phenolphthalein, and record the working range of each indicator.

EXPT. 129. **Measurement of the hydrolysis of sodium acetate.**

Prepare an $N/10$ solution of sodium acetate and place 10 c c. in a clean test tube. Add 0·5 c c B D H. "universal indicator" and compare the tint with those of a series of buffer solutions tinted with the same concentration of indicator From the colour of the solution, estimate its $p_H$ and compare with the value predicted from the dissociation-constant of acetic acid ($K_A = 1{\cdot}86 \times 10^{-5}$ at 18°).

EXPT 130 **Determination of the solubility-product of potassium bromate.**

(*a*) Prepare a saturated solution of potassium bromate by placing an excess (about 10 grams) of the salt in a 100 c c of water in a small flask Shake the latter at intervals and keep it for about 48 hours at a constant temperature (as near room temperature as possible) by immersion in a thermostat or large bath of water

(*b*) Withdraw 25 c c of the saturated solution with a pipette (fitted with a short tube with small cotton-wool plug to prevent fine suspended particles of bromate being drawn into the pipette) and dilute to 500 c c with water Titrate 25 c c portions of this solution with $N/10$ thiosulphate, after first adding about 20 c c of a 10% solution of potassium iodide and 20 c.c. of dilute (10%) sulphuric acid

$$BrO^-_3 + 6I^- + 6H^+ = Br^- + 3I_2 + 3H_2O$$

Repeat experiment (*a*) above, except that a saturated solution of the bromate is prepared in 100 c c $M/2$ potassium bromide solution, and then 25 c.c. of it is diluted to 250 c c , not 500 c c

(*c*) Assuming that both salts are completely dissociated, calculate the concentrations of the potassium and bromate ions in the saturated solutions, and hence deduce the solubility products. Comment on your results

EXPT 131 **Solubility-product of silver acetate.**

Prepare a saturated solution of silver acetate by leaving an excess (about 12 grams) of the salt in contact with 800 c c, of water in a flask for 48 hours, at constant temperature, as in Expt 130

Estimate the concentration of silver acetate in the clear saturated solution by withdrawing 25 c c portions with a pipette (fitted with a cotton-wool guard as in Expt 130) and titrating against $N/10$ potassium or ammonium thiocyanate, p 431

By means of a measuring cylinder place 160 c c portions of the above saturated solution in three flasks , to one add 40 c c of a $2N$ solution of sodium acetate (164 grams anhydrous salt per litre), to another 20 c c , and to the other 10 c c of the same solution Add respectively 20 c c and 30 c c of water to the last two flasks to make up the total volumes to 200 c c Shake the flasks vigorously, and again at intervals of a few hours,

and maintain them at the same temperature as the original solution. After 24 hours or so, withdraw 50 c c portions of the clear solutions with a pipette, fitted with a guard tube as before, and titrate against $N/20$ potassium thiocyanate solution

Assuming that the salts are completely dissociated into ions, calculate the concentrations of the silver and acetate ions in gram-ions per litre, and hence deduce the solubility-product of silver acetate for each solution Are the figures approximately constant?

EXPT 132 **Catalytic activity of acids of different strength.**

By the method outlined below, determine the velocity coefficients of the hydrolysis of methyl acetate by (i) $N/2$ hydrochloric acid, (ii) $N/2$ sulphuric acid, (iii) $N/2$ monochloracetic acid These velocity coefficients are roughly proportional to the strength of the acids

Place 100 c.c. of each acid in a corked flask and immerse in a thermostat at about 25°, together with a flask containing about 30 c c of methyl acetate When the contents of the flasks have reached the temperature of the thermostat, add 5 c c of methyl acetate to one of the acids and shake to mix the contents of the flask thoroughly The zero titration reading $C_o$, is obtained by withdrawing 5 c c of the mixture with a pipette, noting the time as this is run into 30 c c of boiled-out distilled water, and then titrating as quickly as possible with $N/10$ $Ba(OH)_2$ solution, using phenolphthalein as indicator The same operation is carried out with the other two acids in turn The mixtures are then left for two or three hours before another set of titrations, $C_t$, is taken, the latter should be confirmed by carrying out another titration immediately afterwards to make sure that no error has been made The final titration, $C_\infty$, is taken at the end of two days, when the hydrolysis is virtually complete The velocity coefficient for each mixture is calculated from the equation

$$k = \frac{2\ 303}{t} \log_{10} \frac{C_\infty - C_o}{C_\infty - C_t}$$

where $t$ = the interval of time in minutes between the first and second titrations

EXPT. 133 **Hydrolysis of urea hydrochloride.**

Prepare an $N/2$ solution of urea hydrochloride by dissolving the calculated amount of urea in $N/2$ HCl By the method outlined in Expt 132, determine the velocity coefficient for the hydrolysis of methyl acetate in this solution The ratio of this coefficient to that obtained for $N/2$ HCl gives the degree of hydrolysis, $x$, of the urea hydrochloride, so that the hydrolytic constant, $K_H$, may be calculated from equation (vii) (p. 629)

# CHAPTER XLVI

## THE COLLOIDAL STATE

**Crystalloids and colloids.**—The terms COLLOID and CRYSTALLOID were introduced by Graham in 1861 in order to distinguish between two important classes of dissolved substances, which differed widely in the rate at which they diffused into pure water Some substances, such as salts, sugar, urea, etc , were found to diffuse relatively fast in aqueous solution , these were described as CRYSTALLOIDS, in order to recall the fact that the solid substances are crystalline On the other hand, a large group of amorphous substances, including gelatin, starch, gum, etc , were found to diffuse very slowly in solutions , these were described as COLLOIDS (from the Greek κόλλα = glue), in order to recall the fact that the solids were generally obtained in the form of a sticky paste on evaporating the colloidal solutions Table 96 gives some of Graham's figures for the rates of diffusion of members of these two classes

TABLE 96 —RELATIVE RATES OF DIFFUSION IN WATER

| (*a*) Crystalloids | | (*b*) Colloids | |
|---|---|---|---|
| HCl - - - | 1 00 | Albumen - - | 0 02 |
| NaCl - - - | 0 43 | Caramel - - - | 0 01 |
| $MgSO_4$ - - | 0 14 | | |
| Sucrose - - | 0 14 | | |

It has also been found that many substances, such as metallic gold, which (unlike gelatin or gum) are quite insoluble in water can be brought into a colloidal condition by adopting special methods of treatment Thus, when gold is precipitated from an aqueous solution of auric chloride by the action of a suitable reducing agent, a red or purple " solution " is obtained which passes completely through filter paper, and contains no particles which are visible to the naked eye or even under a microscope These " solutions " of insoluble substances possess the characteristic property of very slow diffusion, but are usually unstable, since the " dissolved " substance is often precipitated on standing, on boiling, or on the addition of an electrolyte

Later workers have found that the colloidal state can also be produced in other media than water Thus it is possible to prepare a colloidal solution of rubber in benzene, or of nitro-cellulose in acetone or in a mixture of alcohol and ether Even common salt can be brought into a colloidal state in benzene , and soap, which gives colloidal solutions in water, behaves as a crystalloid when dissolved in alcohol In face of facts such as these, it appears probable that any substance may be obtained in a colloidal state if suitable conditions are employed It is therefore probably

more correct to speak of the COLLOIDAL STATE than to describe a particular substance as a colloid or a crystalloid The term COLLOID can, however, be applied without hesitation to substances such as gelatin or glue, which always give colloidal solutions, and do not even form a crystalline solid when dried by evaporation

**Classification of colloids.**—It is convenient to divide colloids into two main groups, of which *colloidal gold* and *gelatin* may be taken as typical examples Thus colloidal gold is readily precipitated by traces of electrolytes, and the precipitate cannot be redissolved again by mere contact with the pure solvent Since the colloid has very little affinity for the solvent it is said to be *lyophobic* (*i e* solvent-fearing), and the system is described as a COLLOIDAL SUSPENSION Colloidal metals and metallic sulphides belong to this group On the other hand, a solution of gelatin can only be precipitated by very strong solutions of electrolytes, such as saturated ammonium sulphate, and the precipitate dissolves again readily in moderately pure water Systems of this type may therefore be described as COLLOIDAL SOLUTIONS, whilst the colloid is said to be *lyophilic* (*i e* solvent-loving) Starch, albumen and gum arabic belong to this group It is suggested below that colloidal solutions (like true solutions) may be divided into two sub-groups, according to whether the colloidal material is an electrolyte or a non-electrolyte

(*a*) *Colloidal suspensions* —It has been established clearly by experiment that many colloidal solutions or SOLS are not solutions at all, but mere suspensions, in which an insoluble substance, such as gold, is reduced to such a fine state of subdivision that it behaves almost as if it were *dissolved* in a solvent, instead of being merely " dispersed " or scattered in the liquid medium A colloidal system of this type contains two phases, namely, (i) THE DISPERSING MEDIUM, which takes the place of the solvent in a true solution, (ii) THE DISPERSE PHASE, which takes the place of the solute The minute particles of the disperse phase are prevented from settling by the bombardment of the molecules of the solvent, and are prevented from coalescing by the fact that they carry electric charges of the same sign, either positive or negative

(*b*) *Colloidal electrolytes* —When a fatty acid of high molecular weight, *e g* palmitic acid (p 718), is added to water it spreads rapidly into a thin layer, which occupies a very large area on the surface of the water This spreading has been explained by the fact that the carboxyl radical of the acid is *hydrophilic* and has a definite affinity for water, whilst the oily hydrocarbon radical to which it is attached is *hydrophobic* and tends to separate itself from the water These two tendencies can only be satisfied simultaneously by allowing the acid radicals to come into direct contact with the water, whilst the hydrocarbon radicals form an outer layer on the surface Under these conditions, the thickness of the film is reduced to that of a single molecule, provided that there is enough surface available for this reduction of thickness to take place Incidentally, the striving of the molecules to take up a position at the water-air interface tends to stretch the surface and therefore reduces the surface tension of the liquid, in addition to causing the molecules to set themselves in a definite orientation

When alkali is added, the fatty acid is converted into a soap, which forms

a colloidal solution in the water The chemical change which takes place can be shown for the typical case of palmitic acid by the equation,

$$\underset{\text{Palmitic acid}}{C_{15}H_{31}\ CO\ OH} + \overset{+}{Na}\,\vdots\,\overset{-}{OH} \rightleftharpoons \underset{\text{Sodium palmitate}}{C_{15}H_{31}\ CO\ \overset{-}{O}\cdot\overset{+}{Na}} + H_2O,$$

where the sodium hydroxide and sodium palmitate are represented as pairs of ions The electrolytic dissociation of the salt then permits the sodium ions of the sodium palmitate to escape into the water, and thus creates such a strong pull upon the oppositely charged palmitate ions that they can no longer remain as an oily film on the surface of the water, but are dragged into the interior Even there, however, the palmitate ions retain their oily character, and, instead of breaking up into individual anions, they collect into oily aggregates which have been described by the term IONIC MICELLE The colloidal solution then consists of sodium ions which are in true solution and palmitate ions which are merely suspended in the medium without even being dispersed as individual ions Colloids of this kind are known as COLLOIDAL ELECTROLYTES They differ from colloidal suspensions on the one hand, and from non-conducting colloidal solutions on the other hand, in that *the molecules are ionised by the solvent* It is for this reason that the substance passes spontaneously into the colloidal state by mere contact with the solvent, without requiring any other special treatment

(*c*) *Non-conducting colloidal solutions* —By choosing a suitable solvent, it is sometimes possible to obtain solutions of non-electrolytes with very high molecular weights Thus rubber may be dissolved in benzene, and nitro-cellulose in acetone These solutions have colloidal properties, *e g* they diffuse slowly and give the Tyndall cone effect (p 644), evidently because of the very large size of the molecules of the solute However; unlike the solutions just considered, they do not conduct the electric current, and hence are called non-conducting colloidal solutions

## COLLOIDAL SUSPENSIONS

**Preparation of colloidal suspensions.**—Lyophobic colloids are generally unstable in the presence of electrolytes It is therefore usually necessary to prepare them in the absence of electrolytes, or to remove the latter at the end of the preparation The chief methods employed are as follows

(*a*) *Bredig's method*, which is used for the preparation of colloidal metals, consists in striking an electric arc between two wires of the metal immersed in a suitable solvent The metal is vaporised in the arc, and immediately condensed by the surrounding liquid into extremely fine particles, which form a colloidal suspension

(*b*) *Reduction* —A salt of a metal is reduced by a suitable reagent, which is usually a non-electrolyte, such as phosphorus in ether or aqueous formaldehyde Thus colloidal gold may be prepared by reducing a very dilute solution of auric chloride with yellow phosphorus dissolved in ether ; the colour of the colloidal suspension varies from violet through red to brown, depending upon the fineness of the particles

(*c*) *Double decomposition* —Colloids are sometimes prepared by double

decomposition in the absence of strong electrolytes Thus, when hydrogen sulphide is passed into a solution of arsenious chloride, a yellow precipitate of the sulphide is obtained, since the hydrogen ions from the hydrochloric acid largely prevent the formation of a colloidal suspension If, however, hydrogen sulphide is passed into an aqueous solution of arsenious oxide, a clear colloidal suspension of the sulphide is obtained (Expt 135) In the latter case there is only a small concentration of hydrogen ions, because both the arsenious oxide and the sulphuretted hydrogen are weak electrolytes

**Purification by dialysis.**—Since electrolytes differ considerably in their action on colloids, it is possible in some cases to prepare an insoluble substance in the colloidal state by mixing suitable electrolytes in the right order Thus, when hydrochloric acid is added to a solution of sodium silicate, a precipitate of silicic acid is formed,

$$Na_2SiO_3 + 2HCl = 2NaCl + H_2SiO_3,$$

owing to the powerful coagulating effect of the hydroxyl ions produced by the hydrolysis of the salt If, however, the silicate is poured slowly into excess of dilute hydrochloric acid, a clear solution is obtained, which contains colloidal silicic acid as well as sodium chloride The latter can be removed by the process of DIALYSIS This process depends upon the fact that crystalloids will diffuse rapidly through a diaphragm of parchment paper or of bladder, whilst the colloid is unable to pass through the membrane An early form of dialyser (due to Graham) consists of a shallow cylinder with the base closed by a bladder The solution to be dialysed is placed in the vessel, which is then suspended in a dish of water (Fig 166) A convenient modern form is a cup of parchment paper suspended in a vessel through which water flows slowly

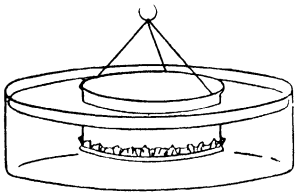


FIG 166 APPARATUS FOR DIALYSIS

**Properties of colloidal suspensions.**—(*a*) *Dimensions* —When a colloidal suspension (which has been filtered to remove coarse particles) is examined under the microscope, no particles can be detected, even with the most powerful objectives, and the solution appears to be homogeneous The size of particle which can be detected by the ordinary microscope is, however, limited by the wave-length of the light used Particles smaller than $2 \times 10^{-5}$ cm in diameter could not be seen with visible light, no matter how excellent the construction of the instrument

A method of detecting still smaller particles, which was discovered by Tyndall, depends upon their power of scattering light The path of a beam of light through pure water or through a solution of a crystalloid of small molecular weight is invisible when viewed at right angles to the beam ; if, however, a colloidal sol is substituted for pure water, the path of the beam is shown by a bright column or cone of scattered illumination which is often termed the TYNDALL CONE (Expt 138)

The ULTRAMICROSCOPE is a microscope with "dark-ground illumination," in which the objects in the field of view are illuminated laterally, so

that only scattered light from these objects enters the object glass and the remainder of the field of view is dark When a drop of a colloidal suspension is placed in the field of view, it is seen that the Tyndall cone is due to a number of scattered points of light which are moving about irregularly with considerable velocity on a dark background. Each little bright star is due to a colloidal particle which scatters the light falling upon it and so becomes visible In this way particles which are much too small to be distinguished under the microscope can be detected and counted

The shape and size of the particles cannot be determined directly, but X-ray analysis has established the fact that the particles of colloidal gold have the same crystalline character as the more ordinary forms of the metal

Moreover, by counting the number of particles in a given volume, by means of the ultramicroscope, and determining the weight of colloid in this volume, it is possible to calculate the average size of the colloid particles In this way it has been shown that the radii of colloidal suspensions vary from 20 to about 1000 A U , as compared with 1 A U for the hydrogen atom and 8 A U for the chloroform molecule The size of colloidal particles therefore readily explains why they diffuse slowly in solution and have as a rule negligible osmotic pressures

(*b*) *Brownian movement* —The particles seen under the ultramicroscope are in continual motion The irregular movement of small particles under the microscope was first described in 1827 by the botanist Brown, and is therefore known as the BROWNIAN MOVEMENT It can be accounted for by the irregular bombardment of a particle by molecules of the liquid in which it is suspended If the particle is large, it receives millions of blows per second on all sides, and the effect of these cancels out If, however, the particle is small enough, then at a particular instant it may receive a greater impulse on one side than on the other, and so move in a definite direction The amplitude of the Brownian movement is therefore greatest in the case of very small particles

This kinetic theory of the Brownian movement was developed mathematically by Einstein, on the assumption that the colloidal particles behave like molecules of very large dimensions, and was tested experimentally by Perrin By counting the number of particles in different layers of an emulsion of gamboge, when a column of the suspension was allowed to settle, Perrin was able to determine Avogadro's number $N$ (*i e* the number of molecules in a gram-molecule, p 461) with considerable accuracy. Other values of $N$ were obtained by measuring the average distance through which the particles moved in unit time, and also from the average rotation of a particle in unit time

Since all these observations led to similar values of $N$, and since these were in good agreement with the number determined by other methods, the correctness of this explanation of the Brownian movement is fully established The study of the Brownian movement has in fact provided the most convincing evidence for the real existence of molecules, and for the perpetual molecular motion which is postulated by the kinetic theory.

(*c*) *Electrification* —One of the most important properties of colloidal suspensions is that the particles carry an electric charge. Thus sols of

metallic hydroxides generally carry a positive charge, whilst most other sols (metals, $As_2S_3$, etc) carry a negative charge, but the sign of the charge on a given colloid can often be altered by changing the conditions of preparation The presence of the charge is proved by the fact that the particles move in a definite direction when the sol is placed in an electric field This phenomenon is known as CATAPHORESIS (Expt 139) The sign of the charge can be deduced from the *direction* of the motion of the particles, whilst their *velocity* in a given electric field can be used to determine the magnitude of the potential difference between the solid and liquid phases This velocity is practically constant for all the particles of a given colloid whatever their magnitude, since the frictional resistance and the charge carried by the particle are both proportional to its diameter and therefore to one another

(*d*) *Coagulation* —The sign of the charge on the particles is related closely to the sensitiveness of colloidal suspensions towards electrolytes, since the coagulation of a colloidal suspension is generally caused by the absorption of oppositely charged ions from the medium Table 97 shows the smallest amount of a number of salts which just caused coagulation of an arsenic sulphide sol

TABLE 97 —COAGULATION OF AN ARSENIOUS SULPHIDE SOL BY ELECTROLYTES

(Millimols per litre required to produce coagulation)

| | | | | | |
|---|---|---|---|---|---|
| KCl | 49 5 | $MgSO_4$ | 0 81 | $AlCl_3$ | 0 093 |
| NaCl | 51 0 | $CaCl_2$ | 0 65 | $Al(NO_3)_3$ | 0 095 |
| | | $BaCl_2$ | 0 69 | | |

It will be seen that, as the valency of the positive ion of the salt increases, its efficiency as a coagulant becomes very much greater Since the sol of arsenious sulphide carries a negative charge, *the valency of the ion of opposite sign* is the principal (but not the only) factor which determines the efficiency of the electrolyte as a coagulating agent

With a positively charged sol, such as ferric hydroxide, it is the valency of the negative ion which is important Thus it will be seen from Table 98 that barium chloride is no more efficient than potassium chloride in producing coagulation, whilst potassium sulphate is much more effective

TABLE 98 —COAGULATION OF A FERRIC HYDROXIDE SOL BY ELECTROLYTES

(Millimols per litre required to produce coagulation)

| | | | |
|---|---|---|---|
| NaCl | 9 3 | $K_2SO_4$ | 0 20 |
| KCl | 9 0 | $MgSO_4$ | 0 22 |
| $BaCl_2$ | 9 6 | | |

These results suggest that the coagulation of a lyophobic colloid by electrolytes is due to the neutralisation of the charge on the particles by the ions of opposite sign This is supported by the fact that, as increasing amounts of an electrolyte are added, the rate of movement in an electric field becomes smaller and smaller, and is practically zero in the neighbourhood of the point at which rapid coagulation occurs In addition, it is found that two oppositely charged colloids will coagulate each other if

mixed in such proportions that their charges are mutually neutralised (Expt 142) The stability of colloidal suspensions appears to be due, therefore, to the repulsion of the electrical charges, which prevents the small particles from coalescing, and so becoming too large to be maintained in suspension by the Brownian movement

## COLLOIDAL SOLUTIONS

**Preparation of colloidal solutions.**—Colloidal solutions are obtained by the direct action of the solvent on the lyophilic colloid Substances such as aluminium hydroxide, which are normally insoluble in water, can often be made lyophilic by the addition of a small quantity of an acid or alkali, which converts them partially into salts Thus aluminium hydroxide can be obtained in the form of a colloidal solution by the action of very dilute hydrochloric acid (Expt 136) A similar statement can be made in reference to gelatin, since highly-purified gelatin has been prepared as an insoluble powder, which acquires the characteristic property of swelling and dissolving in water only when contaminated with the anions or cations of a strong electrolyte

This process is sometimes described as PEPTISATION, and the electrolyte is described as a PEPTISING AGENT, but the action appears to be nothing more than a partial replacement of hydroxyl by chlorine, as a result of which an aggregate of molecules of aluminium hydroxide is converted into a colloidal electrolyte, just as a fatty acid can be converted into a colloidal soap by the action of a smaller quantity of sodium hydroxide than is required to convert the whole of the acid into its sodium salt A similar explanation can probably be given in other cases in which an acid acts as a " peptising agent " for a weak base, or conversely

**Properties of colloidal solutions.**—Colloidal solutions resemble colloidal suspensions in giving the Tyndall cone and Brownian movement, but differ in many other important respects

(*a*) *Electrification* —It has been mentioned already that colloidal solutions may be divided into two classes, viz non-electrolytes and electrolytes The former, of which starch and gum are good examples, give non-conducting solutions The latter, *e g* the soaps, often give solutions of high conductivity, although their osmotic pressures may indicate that the molecules are *associated* instead of being *dissociated into ions* This anomaly is explained by supposing that the molecules of a colloid such as soap, NaX, are dissociated into ions, $Na^{\cdot}$ and $X'$, in the ordinary way, the cations then scatter throughout the solutions, but the anions coalesce with one another, and with neutral molecules to form charged aggregates, termed IONIC MICELLES, which are hydrated $(NaX)_x(X')_y(H_2O)_z$ On account of the large size of these micelles the solutions have osmotic pressures which are usually less than that of a non-electrolyte, in spite of their relatively high electrical conductivity

(*b*) *Viscosity.*—A colloidal solution becomes very viscous as its concentration is increased. Indeed, in many cases, the liquid acquires the elasticity of a solid, and the solution sets to a jelly or GEL as it is commonly called.

(*c*) *Coagulation.*—Unlike colloidal suspensions, colloidal solutions are

usually quite insensitive to small amount of electrolytes, although they are often precipitated by the addition of a large quantity of a suitable electrolyte Thus soaps can be " salted out " from water by the liberal addition of salt, which represses the electrolytic dissociation of the soap micelles and so weakens the grip of the water on them Similarly albumen can be precipitated by the addition of ammonium sulphate Precipitation methods such as these are often used in the purification of lyophilic colloids, since, unlike lyophobic colloids, they can be redissolved by the mere addition of the solvent

(*d*) *Protective effect*—Lyophilic colloids also possess the important property of protecting lyophobic colloids from precipitation by electrolytes Thus, if a little gelatin is added to a gold sol, the latter is no longer precipitated on the addition of a little sodium chloride There is an enormous variation in the protective powers of different colloids Zsigmondy measured this by a GOLD NUMBER, which is the weight in milligrams of the protective colloid which will inhibit the coagulation of 10 c c of a given gold sol by 1 c c of a 10% solution of sodium chloride The gold numbers of a few colloids are given in Table 99 It will be seen that gelatin and egg albumen are much more effective than purified albumen and starch

TABLE 99—GOLD NUMBERS

| | | | |
|---|---|---|---|
| Gelatin | 0 005 | Crystalline albumen | 2–8 |
| Egg albumen | 0 08 | Starch | 3 |
| Gum arabic | 0 10 | Dextrin | 6–12 |

EXPT 134 **Preparation of colloidal platinum**

Weld two short pieces of platinum about 2 mm in diameter to the ends of stout copper wires passing through glass tubes which serve as insulating handles Connect to the lighting circuit (200 volts) through a resistance of 30–40 ohms capable of carrying 5 amperes Place 100 c c of conductivity water in a porcelain dish cooled in ice , bring the platinum wires together under the water and separate them about 2 mm to form an arc, which, however, soon dies out Repeat the formation of the arc for about 10 minutes, and finally filter the brown solution to remove the larger particles For use in Expt 120*c*, dilute until the hydrogen peroxide is half decomposed in about 20 minutes

EXPT 135 **Preparation of colloidal arsenious sulphide.**

Finely powder 0 5 gram of pure arsenious oxide, and boil with 500–600 c c of distilled water until all is dissolved Through the cooled solution pass a current of sulphuretted hydrogen which has been filtered from acid spray by means of a U-tube containing cotton wool

When no further deepening of colour occurs, expel the excess of hydrogen sulphide, which provides a small concentration of hydrogen ions, by blowing hydrogen (freed from acid spray) through the solution for half an hour The " solution " is filtered if any sulphide has been precipitated, and may be kept in a stoppered flask for several years without coagulation taking place Examine the effect of adding dilute hydrochloric acid to a portion of this solution

**EXPT 136 Preparation of colloidal aluminium hydroxide.**

Dissolve about 3 grams of aluminium sulphate in 300 c c of water and precipitate the aluminium hydroxide in the usual manner with ammonium chloride and ammonia Filter off the hydroxide on a large filter paper and wash with five or six lots of 200 c c of boiling water Towards the end of the process the precipitate will become slimy and filtration will be very slow When this occurs, transfer the precipitate to a clean flask and boil with 500 c c of water for 2–3 hours A few drops of $N/10$ HCl should be added from a burette every half hour After 3 hours, practically all the hydroxide will have passed into solution and the sol should be filtered and stored in a clean glass bottle

**EXPT 137 Experiments on dialysis**

Make a dialyser by soaking a large filter-cup (as used in a Soxhlet extraction apparatus) in a 5% solution of collodion in glacial acetic acid When the excess of collodion has drained off, immerse the cup in water and wash it free from acetic acid, when it will be ready for use Cups of parchment paper can also be purchased ready for use as dialysers Place within the cup a 2% solution of gelatin, to which a little sodium chloride has been added, and immerse in a beaker of water After 24 hours, test the water in the beaker for salt by adding silver nitrate, and for gelatin by adding a solution of tannic acid It will be found that the salt has passed through the membrane whilst the gelatin has been retained completely in the inner vessel

**EXPT 138 Observation of the Tyndall cone**

Set up an ordinary projection lantern in a dark room and prepare a series of round-bottomed flasks of about 20 c c capacity filled with (*a*) distilled water, (*b*) filtered salt solution, (*c*) colloidal arsenious sulphide, (*d*) colloidal aluminium hydroxide For the two latter flasks use the solutions prepared in Expts 135 and 136, diluted ten-fold with distilled water Hold each flask in turn in the narrow portion of the projected beam (about 6–8 inches in front of the protecting lens) The track of the beam will scarcely be visible in flasks (*a*) and (*b*), but will stand out vividly as a band of light in flasks (*c*) and (*d*)

**EXPT 139 Demonstration of cataphoresis**

The apparatus required consists of a U-tube ending in a bent capillary tube which carries a stopcock and funnel (Fig 167) Clamp the U-tube vertically, and run in distilled water through the stopcock till the limbs are rather less than half filled Then run in slowly a colloidal solution of arsenious sulphide so as to maintain a sharp interface until the level of the water is near the top of the U-tube Close the U-tube with stoppers carrying electrodes formed of flat spirals of platinum wire and place an opal glass scale behind each limb to show the position of the interface. Connect

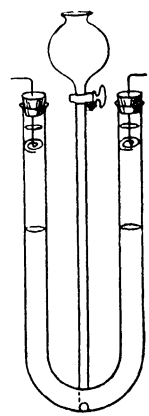


FIG 167
APPARATUS FOR DEMONSTRATION OF CATAPHORESIS

the electrodes to a direct-current electric supply at a potential of about 200 volts, and read the position of the interface every 15 minutes for an hour. Arsenious sulphide will be found to move towards the anode, thus showing that the particles are negatively charged

Repeat the experiment with colloidal ferric hydroxide, which will be found to move towards the cathode, since the particles carry a positive charge

EXPT 140 **Coagulation of colloidal arsenious sulphide.**

Prepare a $2N$ solution of sodium chloride and place 5 c c of this in the first of a row of clean test tubes From the same solution, by successive dilutions, prepare solutions of $N$, $N/2$, $N/4$, $N/8$, $N/16$, and $N/32$ concentration, and place 5 c c of each in successive test tubes To each tube add 5 c c of the arsenious sulphide sol, mix by inverting the tubes twice, and allow to stand After 2 hours note the concentration at which precipitation is just produced

Set up a similar experiment with barium chloride as precipitant, using concentrations of $N/10$, $N/20$, $N/40$, $N/80$, etc , and with aluminium sulphate, using concentrations $N/200$, $N/400$, $N/800$, $N/1600$, etc Calculate in each case the concentration in millimols per litre which just causes precipitation in 2 hours Remember that the added electrolyte is diluted to twice its bulk by the sol

EXPT 141 **Coagulation of colloidal aluminium hydroxide**

By the method described in the previous experiment, determine the minimum amounts of sodium chloride, of potassium sulphate, and of sodium phosphate which will just coagulate a sol of aluminium hydroxide Use the following concentrations as a start NaCl, $2N$, $N$, $N/2$, etc , $K_2SO_4$, $N/10$, $N/20$, $N/40$, etc , $Na_2HPO_4$, $N/200$, $N/400$, $N/800$, etc

EXPT 142 **Mutual coagulation of colloidal suspensions**

Prepare a series of mixtures of colloidal suspensions in pairs, *e g* $As_2S_3$ and $Fe(OH)_3$, and notice which pairs coagulate one another

EXPT 143 **Reversible precipitation of albumen**

Mix the white of an egg with about 100 c c of water and filter at the pump to remove fibrous matter To 30 c c of the clear solution add powdered ammonium sulphate and shake the mixture continuously As the solution approaches saturation, a white curdy precipitate of albumen is formed Allow this to settle and pour off the supernatant liquid Shake the precipitate with about 30 c c of water The precipitate will redissolve, showing that the precipitation of albumen by ammonium sulphate is readily reversible.

# *PART VI*

# PRINCIPLES OF ORGANIC CHEMISTRY

## CHAPTER XLVII

## GENERAL PRINCIPLES

**Natural and synthetic products.**—Organic chemistry was originally concerned with the natural products of vegetable and animal life Unlike the acids and alkalis, calces and salts, of inorganic chemistry, which were generally *artificial* products (made by man from the mineral ores and other raw materials of nature), these *natural* products were so far beyond the scope of his creative abilities that their production was at one time believed to depend on a " vital force," which operated in living matter, but was not available in the laboratory This formidable barrier was, however, broken down for the first time when Wohler in 1827 prepared **urea**, a typical product of animal metabolism, from materials derived from the stock of an ordinary chemical laboratory, namely, potassium cyanide, ammonium sulphate and litharge

$$KCN + PbO = Pb + KCNO \quad \text{(Potassium cyanate)}$$

$$2KCNO + (NH_4)_2SO_4 = K_2SO_4 + 2(NH_4)CNO \quad \text{(Ammonium cyanate)}$$

$$(NH_4)CNO = CON_2H_4 \quad \text{(Urea)}$$

Since that date the SYNTHESIS of organic compounds from simpler materials, and ultimately from the elements, has been a subject of constant research As a result, many organic products are now manufactured industrially by synthetic processes, *e g* methyl alcohol or methanol from water-gas

$$CO + 2H_2 = CH_3OH$$

Moreover, these researches have achieved even more remarkable success in the synthesis of complex compounds, such as tartaric and citric acids, uric acid and nicotine, and of many compounds of even greater complexity ; and in some instances the products of these difficult syntheses have actually superseded natural products, *e g.* madder (alizarin), and indigo

**Organic and inorganic carbon compounds.**—Since no sharp distinction can now be drawn between the natural products of vegetable and animal life, and the artificial products of the laboratory, it has become customary to define organic chemistry as *the chemistry of carbon and its compounds*, since this element is present (with hydrogen, oxygen, nitrogen, etc.) in all

the substances cited in the preceding paragraph Moreover, it plays a dominant part in the chemistry of these complex compounds, since it provides the framework or skeleton of atoms on which their structure rests A few of the simplest compounds of carbon, including some minerals and furnace-products, are, however, treated as exceptions and are still allocated to the field of inorganic chemistry, *e g*

carbonates, $CaCO_3$, $FeCO_3$, etc. ;
oxides and sulphides of carbon, CO, $CO_2$, $CS_2$, etc ;
carbides, $Fe_3C$, $CaC_2$, etc.

On the other hand, the hydrocarbons are generally regarded as organic compounds, even when they can be produced, like methane, $CH_4$, and acetylene, $C_2H_2$, by so simple a process as the action of water upon a metallic carbide

**The chemistry of carbon.**—It is natural to ask why carbon, with a few associated elements, such as hydrogen, oxygen and nitrogen, should play so unique a rôle in the chemistry of living organisms, whereas every one of the 90 elements of the periodic classification has a place in mineral chemistry The principal characteristic which confers this unique ability on the element carbon is easily disclosed We have already seen that inorganic chemistry is concerned primarily with the union of *unlike* elements and compounds, *e g* with the combination of metals and non-metals to form salts, in which the presence of acidic and basic radicals can easily be recognised In more modern terms, inorganic chemistry is largely (but not exclusively) *the chemistry of ions* Thus, the group-tests of qualitative analysis are concerned primarily with the identification of the ions which are present in an aqueous solution, Ag , Pb , Hg , Hg , Cl′, $NO_3'$, $SO_4''$, etc , and only indirectly with the elements of which these ions are composed We may also note that the simplest ions are formed from their elements by a process of electron transfer, *e g*

$$Na + Cl \rightarrow Na^+Cl^-,$$

and that the immediate neighbours of the inert gases are the most ready to interact in this way , they therefore play the most heroic part in inorganic chemistry and provide many of its most powerful reagents Carbon, however, is equally distant from the inert gases, helium and neon, which precede and follow it in the periodic classification of the elements It is therefore too remote to acquire the electronic configuration of either of these gases by a process of electron transfer, and the ions $C^{-4}$ and $C^{+4}$, which would be produced in this way, are both unknown to chemists The factors which thus impede the formation of salt-like compounds by electron transfer are, however, entirely favourable to the formation of compounds of *like* elements by electron sharing In particular, carbon is unique in its ability to form giant molecules by the direct linkage of carbon atoms to one another by covalent bonds, as in *diamond* (Fig 28, p 140), where the linkages extend indefinitely in three dimensions, and in *graphite* (Fig 29, p 140), where the giant molecules extend indefinitely in two dimensions only This ability of carbon, to combine without limit with itself, enables it to form compounds which are almost

unique in their complexity, and which alone provide a basis for the complex chemistry of vegetable and animal life.

*** Reagents used in organic chemistry.**—The rupture of covalent bonds, which is characteristic of nearly all organic reactions, calls for the use of reagents which sometimes differ from those used in inorganic chemistry The principal reagents used in organic chemistry are therefore indicated below ·

(*a*) *Sulphuric acid* is used (i) to remove water, as in the conversion of alcohol into ether or into ethylene (p 668) and in the preparation of ethyl acetate (p 729),

(ii) to reinforce the action of nitric acid by removing water, as in (*b*) (ii) and (iii),

(iii) to prepare the sulphates of organic radicals (pp 727 and 728),

(iv) to prepare sulphonates, R $SO_2OH$, in which sulphur is linked directly to carbon (pp 777 and 778),

(v) as a catalyst to promote the addition and removal of water in hydrolysis and esterification (pp 592 and 720)

(*b*) *Nitric acid* is used (i) as an oxidising agent, as in the preparation of oxalic acid from sugar (p 749),

(ii) as a nitrating agent, to produce organic nitrates, such as nitroglycerine (p 736) or gun-cotton (p 736), in which the nitrogen is linked to carbon through oxygen,

(iii) as a nitrating agent, to produce nitro-compounds (p 777) in which nitrogen is linked directly to carbon

(*c*) *Hydrochloric acid* is used (i) to prepare organic chlorides (p. 724), often with *zinc chloride* as a catalyst and dehydrating agent,

(ii) as a catalyst in esterification and hydrolysis (pp 729 and 731)

(*d*) *Hydrobromic acid* is used to prepare organic bromides (p 725)

(*e*) *Hydriodic acid* is used (i) to prepare organic iodides (p 724),

(ii) as a reducing agent, *e g* to reduce an alcohol (through the iodide) to a hydrocarbon by heating in a sealed tube with hydriodic acid and phosphorus

(*f*) *Chromic acid*, or a mixture of a dichromate and sulphuric acid, is used as an oxidising agent, *e g* to convert alcohol to aldehyde (p 689)

(*g*) *Nitrous acid* and its salts are used (i) to convert primary amines into alcohols (p 762),

(ii) to convert primary aromatic amines into diazo-compounds (p 799) and thence into many other derivatives,

(iii) to convert secondary amines into nitroso-compounds (p 762),

(iv) to prepare organic nitrites and nitro-compounds (p 768),

(v) to prepare oximes from methylene compounds (p 708)

(*h*) *Sulphurous acid and the sulphites* are used (i) as reducing agents,

(ii) to prepare addition-compounds with aldehydes and ketones (p 694)

* This summary may be read *after* the chapters in which the use of these reagents is described in detail.

(*i*) *Hydrocyanic acid* and its salts are used (i) to prepare organic cyanides, *e g* from the iodides, usually with a view to conversion into a carboxylic acid as in the synthesis of acetic acid (p 709) and in the conversion of chloracetic acid into malonic acid (p 751),

(ii) to prepare cyanhydrins from aldehydes and ketones, again often with the object of preparing carboxylic acids such as lactic acid (p 745);

(iii) as a catalyst (KCN) in the polymerisation of benzaldehyde to benzoin (p 787)

(*j*) *Alkalis* are used (i) to prepare salts of organic acids;

(ii) to saponify fats (p 717) and other esters,

(iii) to liberate organic bases from their salts and to split off ammonia from amides (p 712),

(iv) to eliminate $CO_2$, as in the preparation of methane from acetic acid (p 662),

(v) to eliminate $SO_2$, as in the preparation of phenol from benzenesulphonic acid (p 791)

(*k*) *Sodium* is used (i) as a reducing agent, *e g* in the form of sodium amalgam it is employed for the reduction of ketones (p 704), etc

(ii) to eliminate halogens, as in the conversion of methyl iodide into ethane (p 663),

(iii) to prepare sodium-derivatives from hydrides, such as alcohol, ethyl acetoacetate and ethyl malonate, which are not sufficiently acidic to form salts with alkalis, these metallic-derivatives interact with organic halides, and are extensively used in organic synthesis,

(iv) to remove the last traces of water from substances such as ether, which are not attacked by sodium

(*l*) *Iron*, *tin* and *zinc* are used as reducing agents (pp 796 and 663), and ZINC-DUST DISTILLATION is used as a general method of reducing an organic compound to the parent hydrocarbon, *e g* phenol to benzene (p 793) *Nickel*, *palladium* and *platinum* are used as catalysts in hydrogenation (p 718) and dehydrogenation, whilst *copper powder* and *cuprous salts* are used to promote the elimination of nitrogen in the Gatterman and Sandmeyer reactions (p 800)

(*m*) *Potassium permanganate* is used, especially in alkaline solution, as a powerful oxidising agent Thus the presence of a double or triple bond between carbon atoms is indicated by the decolorisation of bromine water (see Expt 148), and is confirmed by the reduction of a dilute solution of potassium permanganate made alkaline with sodium carbonate The purple permanganate is reduced to give either a green solution of a manganate or a brown precipitate of manganese dioxide

Atmospheric *oxygen* also serves, not only for complete combustion to carbon dioxide and water, but (in presence of platinum or copper as a catalyst) to oxidise methyl alcohol to formaldehyde (p 698) and ethyl alcohol to acetaldehyde (p 709), and (in presence of manganous acetate) to oxidise acetaldehyde to acetic acid (p 709).

(*n*) *Chlorine*, *bromine* and *iodine* are used in the formation of addition-compounds, and (less readily) to replace hydrogen by a halogen in sunlight, or in presence of a halogen-carrier, as when chlorination is carried out in presence of $SbCl_5$ or $I_2$ (p 779) Bleaching powder is also used as an oxidising and chlorinating agent, *e g* in the preparation of chloroform (p 702) and for the preparation of chlorhydrins (p 734)

(*o*) *Phosphorus trichloride*, *phosphorus tribromide*, *red phosphorus* and *iodine*, *thionyl chloride* and *sulphuryl chloride* are used to replace hydroxyl by a halogen, whilst *phosphorus pentachloride* and *phosphorus pentabromide* are used for this purpose and also to replace a doubly-bound atom of oxygen by two atoms of halogen (p 692)

(*p*) *Zinc chloride* and *aluminium chloride* are used to promote condensations (p 775) in which hydrogen chloride is eliminated, just as sulphuric acid is used to promote the elimination of water

(*q*) *Ammonia* is used to replace $-Cl$, $-OCH_3$ or $-OC_2H_5$ by $-NH_2$, as in the conversion of ethyl oxalate to oxamide, $(CO\ OEt)_2 \rightarrow (CO\ NH_2)_2$ Substituted ammonias, including hydroxylamine and hydrazine, are used to replace the doubly-bound oxygen of aldehydes and ketones by radicals of the type $=NX$ (pp 696 and 705)

(*r*) Finally, amongst ORGANIC REAGENTS, *methyl alcohol*, *methyl iodide*, *methyl sulphate* and *magnesium methiodide*, $CH_3MgI$, are used to replace hydrogen by the METHYL RADICAL, $CH_3$, in organic compounds *Alkyl iodides*, RI, and GRIGNARD REAGENTS, R Mg I, formed by the interaction of magnesium with organic halides, are also used very widely in order to introduce, not only methyl, but many other organic radicals into organic compounds *Carbon monoxide*, *carbon dioxide*, *chloroform* and *carbon tetrachloride* are also cited as reagents in the following chapters, together with compounds such as *acetyl chloride* (p 711), *acetic anhydride* (p 712) and *benzoyl chloride* (p 789)

**Compound radicals in organic chemistry.**—Berzelius in 1817 recognised that organic compounds are made up of COMPOUND RADICALS, which take the place of the SIMPLE RADICALS of inorganic chemistry To this conception we must add, however, that the compound radicals of organic chemistry are held together by covalent bonds, whereas the simple radicals of inorganic chemistry often form only ionic aggregates, organic compounds therefore tend to form volatile oils, whilst the corresponding inorganic compounds are often crystalline solids, which dissolve in water to form conducting solutions This point of view can be justified by many examples, *e g*

| *Organic compounds* (Volatile liquids, non-electrolytes) | | *Inorganic compounds* (Crystalline solids, electrolytes) | |
|---|---|---|---|
| Methyl iodide | $CH_3I$ | Potassium iodide | KI |
| Methyl alcohol or methyl hydroxide | $CH_3OH$ | Potassium hydroxide | KOH |
| Ethyl ether or diethyl oxide | $(C_2H_5)_2O$ | Potassium oxide | $K_2O$ |

Some of the principal types of organic radicals are set out in Table 100

TABLE 100.—COMPOUND RADICALS.

(*a*) Univalent ALKYL RADICALS

| | | | |
|---|---|---|---|
| METHYL | $-CH_3$ | or | Me |
| ETHYL | $-C_2H_5$ | or | Et |
| PROPYL | $-C_3H_7$ | or | Pr |
| BUTYL | $-C_4H_9$ | or | Bu |
| AMYL | $-C_5H_{11}$ | | |
| HEXYL | $-C_6H_{13}$, etc | | |

The isomerism of the alkyl radicals from $C_3H_7$ and onwards is illustrated on p 677

(*b*) Bivalent ALKYLENE and ALKYLIDENE RADICALS·

| | |
|---|---|
| METHYLENE | $-CH_2-$ |
| ETHYLENE | $-CH_2CH_2-$ |
| ETHYLIDENE | $CH_3CH<$ |

(*c*) The bivalent CARBONYL RADICAL, $>C=O$ in

(i) Aldehydes as $\begin{matrix}R\\H\end{matrix}\!>\!C=O$

(ii) Ketones as $\begin{matrix}R\\R\end{matrix}\!>\!C=O$

(iii) Acids as $\begin{matrix}R\\HO\end{matrix}\!>\!C=O$

(iv) Amides as $\begin{matrix}R\\H_2N\end{matrix}\!>\!C=O,$

where R is an alkyl radical

(*d*) The univalent ACYL RADICALS

| | |
|---|---|
| FORMYL | $HCO-$ |
| ACETYL | $CH_3CO-$ |
| PROPIONYL | $C_2H_5CO-$ |
| BUTYRYL | $C_3H_7CO-$ |
| VALERYL | $C_4H_9CO-$ |
| HEXOYL | $C_5H_{11}CO-$ |

(*e*) The univalent ARYL RADICALS

| | |
|---|---|
| PHENYL | $C_6H_5-$ |
| BENZYL | $C_6H_5CH_2-$ |
| TOLYL | $CH_3C_6H_4-$ |

These organic radicals are often linked to simple or compound inorganic radicals, *e g*

| *Univalent radicals* | | *Bivalent radicals.* | |
|---|---|---|---|
| (*a*) HALIDES | $-F$, $-Cl$, $-Br$, $-I$ | (*e*) OXIDE | $-O-$ |
| (*b*) HYDROXYL | $-OH$ | (*f*) SULPHIDE | $-S-$ |
| (*c*) AMINO-GROUP | $-NH_2$ | (*g*) SULPHATE | $-OSO_2O-$ |
| (*d*) NITRO-GROUP | $-NO_2$ | (*h*) IMINO-GROUP | $-NH-$ |

Thus in **methyl sulphate**, $CH_3\ O\ SO_2\ O\ CH_3$, two univalent methyl radicals are linked by a sulphate radical, but the product is a liquid boiling at 188°, and *not* a crystalline salt

The orderliness of organic chemistry results from the fact that each radical possesses a series of characteristic physical and chemical properties Complexities arise from the fact that the functions of a given radical may be influenced more or less profoundly by its neighbours Thus (i) The *hydroxyl radical* has a constant dipole moment (p 665) in all the alcohols, and its reactions are very similar throughout, so long as only the hydroxyl group is involved , but when it is associated with a *carbonyl radical* to form a CARBOXYL GROUP, $-CO\ OH$, as in acetic acid, $CH_3\ CO\ OH$, its properties are altered profoundly, and it acquires acid properties which are lacking in the simple alcohols (ii) In the same way the *carbonyl radical* has an almost constant dipole moment and gives the same characteristic ultra-violet absorption (*i e* it has a similar absorptive power for light of the same wave-length), whatever the nature of the alkyl radicals to which it is linked It also exhibits similar (but not identical) chemical properties in the *aldehydes*, where it is linked to one alkyl radical and one atom of hydrogen, and in the *ketones*, where it is linked to two alkyl radicals When, however, it is linked to a hydroxyl radical in the carboxyl group, $-CO\ OH$, its dipole moment and absorption-spectrum are modified profoundly, and its chemical properties are so changed that the characteristic reactions of an aldehyde or ketone are eliminated almost completely in the carboxylic acids and their derivatives

In studying the principles of organic chemistry, it is clear that we must first recognise the existence and determine the characteristic properties of the principal radicals which are found in organic compounds , but we must also record and investigate those phenomena which depend on the mutual influence of the radicals upon one another This influence is strongest when the radicals are contiguous, and becomes weaker when other radicals are interposed , but in some cases an attenuated effect can be detected even when the interacting radicals are separated by a chain of three or four methylene radicals, as in

δ-chlorovaleric acid, $Cl\ CH_2\ CH_2\ CH_2\ CH_2\ CO\ OH$,

which is appreciably stronger than

valeric acid, $H\ CH_2\ CH_2\ CH_2\ CH_2\ CO\ OH$

**Directed valencies.**—The quadrivalency of carbon was recognised by Kekulé in 1858 The fact that the four valencies are not laid out in one plane, but are distributed symmetrically in space of three dimensions was probably also a familiar idea to him, since Pasteur had already demonstrated the importance of three-dimensional models in chemistry but drawings, which show the four valencies of an atom of carbon pointing to the four apices of a tetrahedron, were published by his pupil Paterno in 1869 , and in 1874 le Bel and van 't Hoff, simultaneously and independently, showed how the tetrahedral model of the carbon-atom could be used to account for the phenomenon of stereoisomerism (p 757), *i e* isomerism depending on the *different orientation in space* of the same

sequence of radicals in a molecule of given structure, including (i) optical rotatory power (p 743), and (ii) geometrical isomerism (p 758)

The tetrahedral arrangement of the four valencies of a carbon atom is shown clearly in the model of the diamond (Fig 28, p 140), and van 't Hoff's use of tetrahedral models to represent a single, double and triple bond between two atoms of carbon is illustrated in Fig 7 (p 40)

The directed character of the four *covalences* of carbon is in striking contrast to the undirected character of the *electrovalences* of an ionised salt, such as sodium chloride, since the electrostatic forces around an isolated ion are necessarily distributed uniformly in all directions, although in a crystal of rock-salt (Fig 129, p 493) they are mainly concentrated on six contiguous ions of opposite sign

The quadrivalency of carbon and the directed character of the valences are of fundamental importance in the three-dimensional chemistry of organic compounds

**Ionisation of organic compounds.**—Although organic chemistry is concerned primarily with covalent bonds, it must not be assumed that ions are not found amongst organic compounds or that they play no part in organic reactions On the contrary, organic acids yield ionised salts, just like mineral acids, and are themselves ionised to a greater or lesser degree in aqueous solutions

$$\underset{\text{Acetic acid}}{CH_3\,CO\,OH} + \overset{+}{N}a\overset{-}{O}H \rightarrow \underset{\text{Sodium acetate}}{CH_3\,CO\,\overset{-}{O}\overset{+}{N}a} + H_2O$$

This ionisation of *organic* compounds is a converse to the familiar proposition that covalent bonds are present, not only in organic molecules, but also in *inorganic* molecules and ions such as

$$H_2,\ Cl_2,\ ClO_4^-,\ CO_2,\ CO_3^{--},\ SO_2 \text{ and } SO_4^{--}$$

Equally important is the fact that the breakage of a covalent bond often gives rise to a pair of ions This phenomenon is already a familiar commonplace, since it is characteristic of all cases of reversible ionisation, *e g*

$$H{-}O{-}H + H\ Cl \rightleftharpoons \overset{+}{O}H_3 + \overset{-}{Cl}$$

$$Cl\ Hg\ Cl \rightleftharpoons \overset{-}{Cl} + \overset{++}{Hg} + \overset{-}{Cl}$$

Organic compounds, however, are usually non-electrolytes, which are not ionised appreciably even in ionising solvents at high dilutions Thus there is no direct evidence of ionisation in solutions of methyl iodide, $CH_3I$, although **tetramethylammonium iodide**, $[N(CH_3)_4]I$, is a strong electrolyte like potassium iodide Spontaneous ionisation of a bond between carbon and an acid radical appears indeed to be limited to a few extreme cases, such as **triphenylmethyl chloride**, which behaves as a fairly strong electrolyte * ·

$$C(C_6H_5)_3Cl \rightleftharpoons \overset{+}{C}(C_6H_5)_3 + \overset{-}{Cl}$$

* In this compound, the large size of the three phenyl radicals may perhaps impede the access of the negatively charged halogen ion to the positively charged carbonium ion, although factors of a more chemical character may also be at work to promote the ionisation

When, however, methyl iodide is boiled with potash, it gives potassium iodide and methyl alcohol as products of double decomposition

$$\underset{\text{Methyl iodide}}{CH_3I} + \overset{+-}{K}OH \rightarrow \underset{\text{Methyl alcohol}}{CH_3OH} + \overset{+-}{K}I$$

In this process, the neutral molecule of methyl iodide yields an iodide ion We may, therefore, suppose that the rending apart of the molecule is really a process of ionisation,

$$CH_3\ I \rightarrow \overset{+}{C}H_3 + \overset{-}{I},$$

like the conversion of hydrogen iodide into potassium iodide

$$H\ I + \overset{+-}{K}OH \rightarrow HOH + \overset{+-}{K}I$$

The *slowness* of organic reactions is perhaps a measure of the resistance which the covalent bond, *e g* between carbon and iodine, offers to this type of rupture, as compared with the ease with which hydrogen iodide is ionised even by so weak a base as water

**Ionic and non-ionic decomposition of organic compounds.**—With the reservation that ionisation of an organic compound usually takes place only under the drastic persuasion of an ionised reagent, we may formulate the interaction of methyl iodide and potassium hydroxide as follows

$$\overset{+}{K} + [I\ CH_3] + \overset{-}{O}H \rightarrow \overset{+}{K} + [\overset{-}{I} + \overset{+}{C}H_3] + \overset{-}{O}H \rightarrow \overset{+-}{K}I + CH_3OH$$

In these equations a covalent bond between $CH_3$ and I is ruptured by ionisation, whilst a covalent bond between $CH_3$ and OH is created by a reversal of this process, *i e* by the union of two ions to form a neutral molecule of methyl alcohol On the other hand, when methyl iodide is decomposed by exposure to light, it appears to yield free *atoms* (not ions) of iodine, which unite to form iodine molecules, together with the neutral

FREE RADICAL **methyl,** $CH_3$

$$CH_3I \rightarrow CH_3 + I$$

This radical is too unstable to persist in solution , but it has been prepared by the action of heat on the vapour of **lead tetramethyl,** $Pb(CH_3)_4$, and its transient existence as a product of decomposition has been demonstrated by its ability to reproduce this compound by direct attack on metallic lead at atmospheric temperatures,

$$Pb(CH_3)_4 \rightleftharpoons Pb + 4CH_3$$

From the point of view of the electronic theory of valency the two methods of decomposition of methyl iodide may be represented as follows

*Ionic decomposition*, under the influence of potash

$$CH_3I \rightarrow \overset{+}{C}H_3 + \overset{-}{I} \quad \text{or} \quad H\ C\ I \rightarrow H\ C + I:$$

*Non-ionic decomposition*, under the influence of light:

$$CH_3I \rightarrow CH_3 + I \quad \text{or} \quad \begin{matrix} H \\ H \end{matrix} \!\!>\!\! C \!\!<\!\! \begin{matrix} I \\ H \end{matrix} \rightarrow \begin{matrix} H \\ H \end{matrix} \!\!>\!\! C \!\!<\!\! \begin{matrix} \cdot \\ H \end{matrix} + \ddot{I}:$$

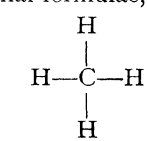
In the former, the iodine takes away the duplet which bound it to carbon, and forms a stable iodide ion, but leaves behind an unstable $CH_3^+$ residue with only a sextet of electrons; in the latter, the duplet is broken, giving a free atom and a free radical, each with a septet of electrons, and therefore both of them highly reactive.

# CHAPTER XLVIII

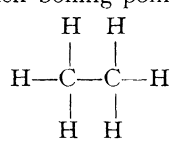
## PARAFFINS

**General properties of hydrocarbons.**—The most characteristic compounds of carbon are those in which it is united exclusively with *hydrogen* This element, with one planetary electron, possesses the same neutral character as carbon itself Thus under rather extreme conditions it can either (i) lose an electron and yield a free proton, $H^+$, or (ii) gain an electron, as in $Li^+H^-$, and give an ionised hydride in which the anion has two planetary electrons with the electronic configuration of helium As we have already seen (p 68), however, neither of these relationships expresses the real behaviour of the element, which is neither a metal, like sodium or potassium, nor an oxidising agent like chlorine The chemistry of hydrogen is therefore dominated, like that of carbon, by its covalency and not by its ability to form either positive or negative ions

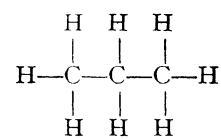
This neutral character makes hydrogen an ideal partner for carbon in the building up of complex structures, since the unused valencies of the carbon skeleton can always be "saturated" with hydrogen When the carbon skeleton is free from rings, and consists entirely of open chains of atoms (either straight or branched), the saturation of the spare valencies, by hydrogen gives rise to members of the series of PARAFFINS, so-called because of their inertness or lack of chemical affinity (Latin, *parvum*, little, *affinitas* from *affinis*, related by marriage) The *composition* of these paraffins can be represented by the general formula $C_nH_{2n+2}$ The *structures* of some of the simplest paraffins may be set out in two-dimensional formulae, with their boiling-points, as follows



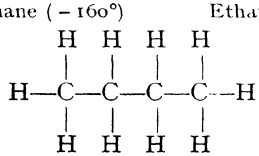
Methane ( − 160°)



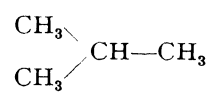
Ethane ( − 93°)



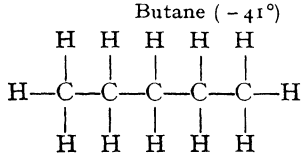
Propane ( − 45°)



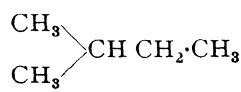
Butane ( − 41°)



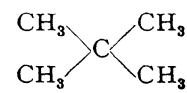
*iso*-Butane ( − 17°)



*n*-Pentane ( + 38°)



*iso*-Pentane ( + 30°



*neo*-Pentane ( + 10°)

**Isomerism of the paraffins.**—It will be seen that the structure of the first three members, $CH_4$, $C_2H_6$, $C_3H_8$, of the homologous series* is unambiguous, but that the fourth and fifth members, $C_4H_{10}$ and $C_5H_{12}$, can contain either (i) a straight chain of carbon atoms, giving rise to a "normal" hydrocarbon, or (ii) a branched chain, giving rise to hydrocarbons of the "iso" series, which are isomeric (p 248) with those of the normal series, (iii) the fifth member, $C_5H_{12}$, can also exist in a third form with four methyl groups attached directly to a central carbon atom It may be noticed in passing that this compact molecule has the lowest boiling-point, whilst the straight-chain hydrocarbon has the highest boiling-point of this group of three isomers The higher members of the series are described as

| | | |
|---|---|---|
| Hexane, $C_6H_{14}$ | Heptane, $C_7H_{16}$ | Octane, $C_8H_{18}$. |
| Nonane, $C_9H_{20}$ | Decane, $C_{10}H_{22}$ | Undecane, $C_{11}H_{24}$, etc. |

**Alkyl radicals.**—When one hydrogen atom in the molecule of a paraffin is replaced by another atom or group of atoms, the remainder of the paraffin molecule, viz $C_nH_{2n+1}$ is called an alkyl radical The name of an alkyl radical is usually derived from its parent paraffin by substituting "*yl*" for "*ane*", *e g* methyl, $CH_3$, ethyl, $C_2H_5$, propyl, $C_3H_7$, from methane, ethane and propane, respectively

**Preparation of the paraffins.**—(*a*) **Methane** is given off from decaying vegetation in the bottom of stagnant ponds and marshes, hence the original name MARSH GAS It also occurs in coal seams as "fire damp," and is responsible for many pit disasters, since it forms an explosive mixture with air An enormous amount of methane, mixed with higher paraffins, issues out of the ground in various parts of the world, notably in the American oilfields, from which it is often transported many miles in pipes and used in cities as "natural gas" for heating and lighting purposes Coal gas, prepared by the distillation of coal (p 149), contains approximately 30% of methane by volume.

Methane can be prepared by the following methods.

(i) by the action of water on aluminium carbide:

$$Al_4C_3 + 12H_2O = 4Al(OH)_3 + 3CH_4;$$

(ii) by the action of red-hot copper on a mixture of sulphuretted hydrogen with the vapour of carbon disulphide.

$$CS_2 + 2H_2S + 8Cu = CH_4 + 4Cu_2S;$$

(iii) by heating sodium acetate with barium hydroxide or soda-lime (*i e* quicklime slaked in caustic soda), but the former yields a purer product:

$$CH_3{\cdot}CO{\cdot}ONa + NaOH = Na_2CO_3 + CH_4;$$

* The term HOMOLOGOUS SERIES is used to describe any group of organic compounds in which each successive member differs from the one before by $CH_2$

(iv) by reducing a solution of methyl iodide in methyl alcohol with a moist zinc-copper couple (see Expt 145, below).

$$CH_3I + 2H = CH_4 + HI.$$

EXPT 144 **Preparation and properties of methane.**

Heat about 20 grams of crystallised sodium acetate, $NaOOCCH_3,3H_2O$, cautiously in an evaporating basin, stirring with a glass rod The solid first melts in its own water of crystallisation and then solidifies as the water is expelled Continue heating until this solid remelts, then allow to cool in a

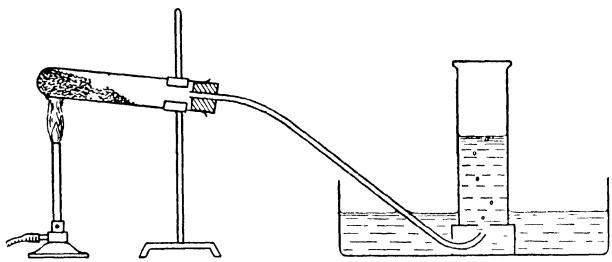


FIG 168 PREPARATION OF METHANE

desiccator Powder 10 grams of the anhydrous acetate, and mix it thoroughly with about 25 grams of barium hydroxide Introduce the mixture into a hard-glass boiling tube and then fit up the latter as depicted in Fig 168 Heat the tube strongly and, as soon as the air has been expelled, collect three jars of the gas and test them in turn with—(i) a lighted taper, (ii) 4 c c of dilute permanganate alkaline with sodium carbonate, (iii) 2 to 3 c c bromine water Comment on the flame in (i), and shake (ii) and (iii) for two or three minutes before deciding whether any change has occurred

(*b*) **Ethane** can be prepared,

(i) by the action of sodium on methyl iodide, when two methyl radicals unite to form a molecule of ethane

$$2CH_3I + 2Na = CH_3\,CH_3 + 2NaI,$$

(ii) by reducing a mixture of ethyl iodide and ethyl alcohol with a zinc-copper couple

$$C_2H_5I + 2H = C_2H_6 + HI,$$

(iii) by the action of finely-divided nickel on a mixture of ethylene and hydrogen at 450°

$$C_2H_4 + H_2 = C_2H_6$$

EXPT 145 **Preparation of a zinc-copper couple.**

Immerse some granulated zinc in a solution of copper sulphate until the zinc has become coated with a film of copper Wash the metal well with water, and then remove the water by successive rinsings with small quantities of ethyl alcohol

EXPT 146 **Preparation of ethane**

Fit up the apparatus shown in Fig 169 The dropping funnel passes to the bottom of one limb of the U-tube A mixture of ethyl alcohol and ethyl iodide is dropped from the funnel on to a zinc-copper couple in the

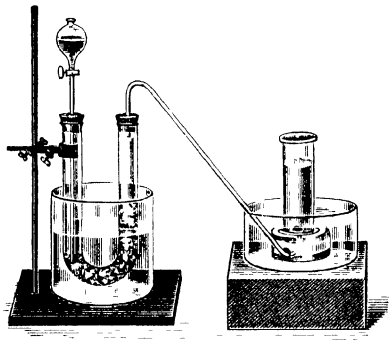


FIG 169 PREPARATION OF ETHANE

U-tube A bent delivery tube attached to the other end of the U-tube enables one to collect the ethane over water The U-tube is kept cool by immersion in water The whole apparatus must be dry Collect the ethane after the air has been displaced Notice how ethane burns

(*c*) The **higher homologues** are prepared,

(i) from the homologues of acetic acid by removal of carbon dioxide as in (*a*) (iii)

$$C_nH_{2n+1}\,CO\,OH \rightarrow C_nH_{2n+2} + CO_2\,,$$

(ii) from the alcohols by conversion into iodides and subsequent reduction with sodium or with a hydrogenating agent as in (*b*) (i) and (ii) above

$$2C_nH_{2n+1}I + 2Na = C_{2n}H_{4n+2} + 2NaI,$$
$$C_nH_{2n+1}I + 2H = C_nH_{2n+2} + HI\,,$$

(iii) from " unsaturated hydrocarbons " (p 668) by combination with hydrogen as in (*b*) (iii), *e g*

$$C_nH_{2n} + H_2 = C_nH_{2n+2}$$

EXPT. 147 **Preparation of butane**

Drop a tiny pellet of sodium into a dry test tube containing a few c c of ethyl iodide Notice that a vigorous action takes place and that a colourless inflammable gas is evolved

Both gaseous and liquid paraffins are present in petroleum and can be separated from it by fractional condensation of the gases or by fractional distillation of the liquid , but the number of isomers increases so rapidly in the homologous series that only the lowest members can be separated as pure chemical compounds Propane and butane are sold as com-

pressed gases, and the higher homologues as petrol, kerosene or lamp oil, paraffin wax, etc

**Properties of the paraffins.**—(*a*) *Physical properties* —The lowest homologues are gases, which are almost insoluble in water, but dissolve in organic solvents *n*-Pentane is a liquid boiling at 38°, the boiling-points of the normal paraffins then rise to about 100° at $C_7H_{16}$ and to 200° at $C_{12}H_{26}$ Solid paraffins begin to appear at about $C_{16}H_{34}$, and the normal hydrocarbon $C_{60}H_{122}$, melts above 100° All the liquids are oils of density about 0 8, which mix freely with one another but are insoluble in water

(*b*) *Chemical properties* —The paraffins are so inert that they resist the action of acids and alkalis, and of the common oxidising and reducing agents The only three important reactions of the paraffins are set out below

(i) Combustion in air or oxygen, *e g*

$$CH_4 + 2O_2 = CO_2 + 2H_2O.$$

In a limited supply of air, carbon monoxide is produced, this is responsible for the poisonous character of the "after damp" from explosions in coal mines

(ii) Decomposition by heat or "cracking," *e g*

$$\underset{\text{Ethane}}{C_2H_6} = \underset{\text{Ethylene}}{C_2H_4} + H_2$$

This operation is carried out on a large scale in the petroleum industry, in order to produce low-boiling "petrol" from higher-boiling hydrocarbons

(iii) Halogenation by chlorine or bromine, but not by iodine, *e g*

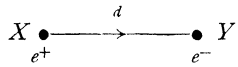
$$CH_4 + Cl_2 = CH_3Cl + HCl,$$
$$CH_3Cl + Cl_2 = CH_2Cl_2 + HCl, \text{ etc},$$

until all the hydrogen has been replaced by halogen The ADDITION of halogens is not possible, since all the four valencies of carbon are already saturated The SUBSTITUTION of halogen for hydrogen is promoted by the action of light, but is very slow, especially in the case of bromine The inability of iodine to act upon the paraffins can be attributed to the fact that hydrogen iodide is a reducing agent, alkyl iodides are therefore reduced to hydrocarbons by the action of hydrogen iodide, especially in presence of red phosphorus (p 738), which removes the free iodine as fast as it is formed

$$CH_3I + HI \rightarrow CH_4 + I_2$$

(*c*) *Dipole moments* —The characteristic inertness of the paraffins has its origin in the symmetry of the four valencies of the carbon atom, which are directed to the four apices of a regular tetrahedron Thus, if the four hydrogen nuclei in methane, $CH_4$, are situated at the apices of a regular tetrahedron, the centre being occupied by the carbon nucleus, it is clear that the electrical centre of the positively charged nuclei will coincide with the geometrical centre of the tetrahedron Similarly, if the negatively

charged electrons are also distributed symmetrically, their electrical centre will coincide not only with the geometrical centre but also, of course, with the positive electrical centre Under these conditions the methane molecule should be non-polar, as indeed it is When, however, a chlorine atom is substituted for one of the hydrogen atoms, the resulting methyl chloride molecule, $CH_3Cl$, loses its electrical symmetry because there is a drift of electrons towards the intensely electronegative chlorine atom, $\overset{+}{C}H_3Cl$, *i e* the negative electrical centre no longer coincides with the positive electrical centre, as is indicated by the diagram




where $d$ is the distance between the positive and negative electrical centres, $X$ and $Y$, and $e$ is the value of the charge The product, $de$, is called the dipole moment of the molecule and is represented by the symbol, $\mu$ In general, organic compounds tend to have a dipole moment when they contain a halogen, oxygen or sulphur atom, since these elements are so intensely electronegative that they cause a drift of electrons towards their nuclei, but the value of these dipole moments seldom exceeds one-fifth of the dipole moment that would exist in a sodium chloride molecule, $Na^+Cl^-$, if one were able to pick this out of a crystal of rock-salt

The presence of dipoles sets up an attraction between the positive pole of one molecule and the negative pole of another molecule, and this has important effects on the physical and chemical properties of a substance Thus the electrical attraction will lower the volatility of a substance and tend to increase its chemical activity, since it will assist in the preliminary locking together of the molecules, which must precede chemical change

The molecules of the paraffins are known to have no dipole moment, and this accounts for their relatively low boiling-points and non-miscibility with water (a polar substance) It also provides an explanation of the difficulty of attacking them with all the ordinary chemical reagents, except oxygen, chlorine and bromine On the other hand most of their halogen derivatives have fairly large dipole moments, and the effects of these are discussed on the opposite page

Before leaving this subject it is interesting to note that the existence of a dipole moment in a water molecule can only be explained by assuming that the atoms of hydrogen and oxygen are not joined in a straight line but are kinked,




for if the molecule was linear, $\overset{\delta+}{H}—\overset{\delta-}{O}—\overset{\delta+}{H}$, the electrical charges on either side of the atom would cancel out, *i e* the positive and negative electrical centres would coincide at the mass-centre of the molecule, and there would be no resultant dipole moment It is for this very reason that carbon dioxide is given the linear structure O=C=O.

**Halogen-derivatives of the paraffins.**—(*a*) *Preparation* —(i) The substitution of hydrogen by chlorine in methane gives rise to the following products:

$CH_4 + Cl_2 = HCl + CH_3Cl$ (Methyl chloride),
$CH_3Cl + Cl_2 = HCl + CH_2Cl_2$ (Methylene chloride),
$CH_2Cl_2 + Cl_2 = HCl + CHCl_3$ (Chloroform),
$CHCl_3 + Cl_2 = HCl + CCl_4$ (Carbon tetrachloride)

These *substitutions* are not of practical use as methods of preparation, but substituted paraffins are often prepared by the *addition* of halogens to the unsaturated hydrocarbons described in Chapters XLIX and L, *e g*

$C_2H_4 + Cl_2 = C_2H_4Cl_2$ (Ethylene dichloride or dichloroethane),
$C_2H_2 + 2Cl_2 = C_2H_2Cl_4$ (Acetylene tetrachloride or tetrachloroethane)

(ii) Halogenated paraffins are produced when alcohols (Chapter LI) are acted on by HCl, HBr or HI, *e g*

$CH_3OH + HI = H_2O + CH_3I$ (Methyl iodide or iodomethane),
$C_2H_5OH + HBr = H_2O + C_2H_5Br$ (Ethyl bromide or bromoethane),
$C_3H_7OH + HCl = H_2O + C_3H_7Cl$ (Propyl chloride or chloropropane)

(iii) Halogenated paraffins are also produced by a number of special methods, *e g*

Carbon tetrachloride, $CCl_4$, from $CS_2 + 2S_2Cl_2$ (p 148),
Chloroform, $CHCl_3$, from alcohol or acetone (p 702),
Iodoform $CHI_3$, from alcohol or acetone (p 703),
Ethylidene chloride, $CH_3CHCl_2$, from aldehyde (p 692)

(*b*) *Properties* —(i) In contrast to the hydrocarbons, the halogen-derivatives have fairly large dipole moments, *e g*

$$\overset{+}{CH_3}\longrightarrow Cl \quad 1.86 \times 10^{-18} \text{ e s u}$$

Carbon tetrachloride, however, has the same symmetry as methane, and the dipole moments associated with the four C—Cl bonds therefore cancel out completely

(ii) These dipole moments do not produce marked association of the molecules, perhaps because the negative halogen of one molecule cannot get very near to the electrical centre of the positive charges in the middle of the alkyl group of another molecule The halogenated paraffins are therefore not merely liquids, but are also quite volatile, though less volatile than the parent hydrocarbons

(iii) The presence of a dipole moment is responsible, in part at any rate, for the fact that the halogenated paraffins are chemically much more reactive than the parent hydrocarbons, *e g* they are usually easily hydrolysed by dilute acids or alkalies

$$C_2H_5Cl + KOH = C_2H_5OH + KCl$$

Their other chemical properties are described in some detail on pp **702, 703, 724.**

# CHAPTER XLIX

## OLEFINES

**General considerations.**—The OLEFINES are a series of hydrocarbons having the general formula $C_nH_{2n}$, as compared with $C_nH_{2n+2}$ for the paraffins They can be derived from the paraffins by removing two atoms of hydrogen, *e g* by " cracking " a paraffin by exposure to a high temperature , and they can be converted into paraffins by the addition of two atoms of hydrogen, *e g* in presence of nickel, as in the reaction

$$\underset{\text{Ethane}}{C_2H_6} \rightleftharpoons \underset{\text{Ethylene}}{C_2H_4} + H_2$$

They are described as UNSATURATED HYDROCARBONS, because, instead of being " saturated " with hydrogen, each molecule can take up two more atoms of hydrogen They also form ADDITION COMPOUNDS with $Cl_2$, $Br_2$, ClOH, $H_2SO_4$, etc , and can polymerise without change of composition to olefines of higher molecular weight, *e g* *iso*-butylene, $C_4H_8$, is readily polymerised by sulphuric acid to *iso*-dibutylene, $C_8H_{16}$

$$2\ \underset{\text{}}{\overset{CH_3}{\underset{CH_3}{\rangle}}C{=}CH_2} \rightarrow \underset{\text{}}{\overset{CH_3}{\underset{CH_3}{\rangle}}C{=}CH{-}C\overset{CH_3}{\underset{CH_3}{\overset{CH_3}{\langle}}}}$$

*iso*-Butylene — *iso*-Dibutylene

**Ethylene** or " olefiant gas," $C_2H_4$, the simplest of the olefines, was prepared in 1794 by a group of four Dutch chemists as a product of the dehydration of alcohol by concentrated sulphuric acid

$$\underset{\text{Alcohol}}{C_2H_6O} = \underset{\text{Ethylene}}{C_2H_4} + H_2O$$

It had the characteristic property of combining with chlorine to form an oil, known as " Dutch liquid," and was therefore distinguished as " olefiant " or oil-forming gas,

$$C_2H_4 + Cl_2 = C_2H_4Cl_2 \quad \text{(Ethylene chloride)}$$

**Preparation of ethylene.**—Ethylene can be prepared by three principal methods

(*a*) *By dehydrating alcohol* with concentrated sulphuric acid at 170° Since alcohol is also oxidised by sulphuric acid, dehydration is often effected by the action of phosphoric acid at 230°, or by passing the vapour over alumina at 450°

(*b*) *By removing hydrogen bromide from ethyl bromide* with a strong *alcoholic* solution of potassium hydroxide

$$C_2H_5Br + KOH = C_2H_4 + KBr + H_2O$$

If aqueous potash is used, the alkyl bromide is hydrolysed to alcohol :

$$C_2H_5Br + KOH = C_2H_5\,OH + KBr.$$

(*c*) *By electrolysing a solution of potassium or sodium succinate*, when ethylene and carbon dioxide are produced at the anode and potassium hydroxide and hydrogen at the cathode

$$\begin{array}{l} CH_2\,COO\;\overset{-}{}\;\overset{+}{K} \\ | \\ CH_2\,COO\;\overset{-}{}\;\overset{+}{K} \end{array} \rightarrow \begin{array}{l} CH_2\cdot CO\,O \\ | \\ CH_2\cdot CO\,O \end{array} \xrightarrow{+2H_2O} \begin{array}{l} CH_2 \\ \| \\ CH_2 \end{array} + 2CO_2 + 2KOH + H_2$$

The homologues of ethylene can be prepared by similar methods

EXPT 148 **Preparation of ethylene dibromide**

Fit up a round-bottomed litre flask as shown in Fig 170, being careful to arrange the wash-bottles back to back in pairs so as to avoid sucking back Pour (i) 250 c c of concentrated sulphuric acid into the flask, *A*, (ii) 30 c c of 20% sodium hydroxide solution into the wash-bottle, *C*, and (iii) 10 c c of bromine + 20 c c of water into the wash-bottle, *E* Now add cautiously 100 c c of rectified spirit to the acid in the flask, and heat the mixture to 170° The crude ethylene that is evolved is freed from acid impurities ($SO_2$, etc ) by the dilute alkali in *C* before it unites with the bromine in *E* Continue the heating until the colour of the bromine has disappeared, obtaining more ethylene, if necessary, by adding a mixture of equal volumes of acid and alcohol from the tap funnel Shake the ethylene dibromide in a tap funnel with dilute sodium carbonate, then dehydrate it with calcium chloride and distil, collecting the fraction which boils at about 131°

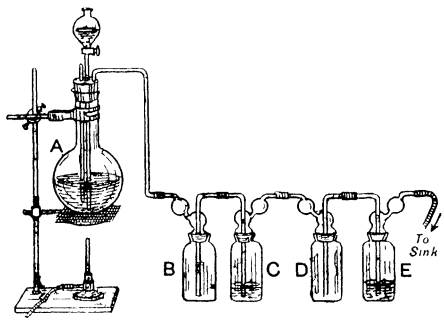


FIG 170 PREPARATION OF ETHYLENE DIBROMIDE

*N B* —The unsaturated character of ethylene can be confirmed by detaching the wash-bottles *D* and *E* and passing the gas into a test tube containing a dilute solution of potassium permanganate made alkaline with sodium carbonate (see p 654)

**Properties of olefines.**—Ethylene is a colourless gas with a faint sweetish smell It is sparingly soluble in water (6% at 0°) It condenses at − 103° to a colourless liquid Its homologues are similar in their general physical properties, but their boiling-points and melting-points rise with increasing molecular weight, just as in the homologous series of paraffins

(*a*) *Addition compounds* —The olefines differ fundamentally from the paraffins in that they do not carry the maximum complement of hydrogen They are therefore UNSATURATED and readily form ADDITION COMPOUNDS, *e.g.* with the halogens, halogen acids (HCl only under special conditions),

hypochlorous acid, sulphuric acid, etc Thus ethylene at room temperatures combines with

(i) chlorine and bromine (but only in presence of a polar catalyst),

$$C_2H_4 + Br_2 = C_2H_4Br_2 \qquad \text{(Ethylene dibromide)},$$

a similar addition product is formed with iodine at 100°,

(ii) hydriodic and hypochlorous acids

$$C_2H_4 + HI = C_2H_5I \qquad \text{(Ethyl iodide)},$$
$$C_2H_4 + Cl\ OH = Cl\ C_2H_4\ OH \qquad \text{(Ethylene chlorhydrin)},$$

(iii) concentrated sulphuric acid

$$C_2H_4 + H_2SO_4 = C_2H_5HSO_4 \qquad \text{(Ethyl hydrogen sulphate)},$$

(iv) sulphur dichloride to form the toxic liquid called " mustard gas "

$$2C_2H_4 + SCl_2 = S(C_2H_4Cl)_2 \qquad \text{(Dichloroethyl sulphide)}$$

(*b*) *Oxidation* —(i) The olefines burn in air with a smoky luminous flame, *e g*

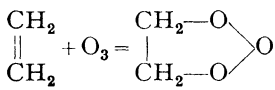
$$C_2H_4 + 3O_2 = 2CO_2 + 2H_2O$$

(ii) Unlike the paraffins, the olefines are readily oxidised by reagents such as potassium permanganate Thus ethylene is oxidised by a cold dilute alkaline solution of potassium permanganate to **ethylene glycol**, $C_2H_4(OH)_2$ (p 734)

$$C_2H_4 + H_2O + \tfrac{1}{2}O_2 = C_2H_4(OH)_2 \qquad \text{(Ethylene glycol)}$$

This oxidation can be regarded as an addition reaction, in which two univalent hydroxyl-groups are added to the double bond The product is therefore a " dihydric alcohol," and is described as " ethylene glycol," because the term " glycol," originally used to describe this compound only (p 734), is now used (like " aldehyde," p 689) as a generic term to describe all compounds of this class, *e g* methylene glycol (p 698)

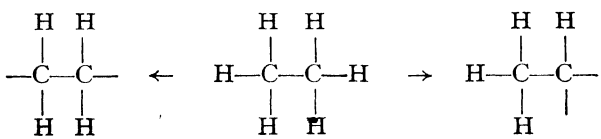
(iii) Ethylene and its homologues form addition compounds with ozone, *e g*



(Ethylene ozonide)

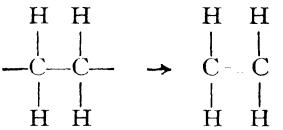
The OZONIDES thus produced are, however, very unstable, and break down into simpler oxidation products, this action is therefore often used in order to determine the position of a double bond in an unsaturated compound

**Structure of ethylene.**—Ethylene can be formed from ethane by removal of two atoms of hydrogen In theory these might be taken from both or from only one of the two atoms of carbon



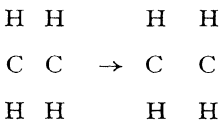
In practice the former process yields ethylene gas, whilst the latter product is described as the **ethylidene radical** and can be distinguished by the fact that it contains an intact methyl radical, $CH_3$ (p 692)

Assuming then that ethylene is formed from ethane by a symmetrical removal of two atoms of hydrogen, we may enquire how its properties may be correlated with its molecular structure We have seen (p 659) that the methyl radical, $CH_3$, with a single odd unpaired electron, is an intensely active " free radical," which attacks metallic lead instantly and in the cold If we take the relationship of methyl to methane as a precedent for the relation of ethylene to ethane, we should expect ethylene to be even more active, since it would carry two free valencies instead of one, and two unpaired electrons instead of one This analogy, however, gives an entirely wrong impression of the reactivity of ethylene It is true that the gas combines with bromine and chlorine, but it appears to do so only in presence of a polar catalyst, such as wet glass, and in general it must be " activated " in some way before it will react This relative inertness is a uniform characteristic of free valencies *on contiguous carbon atoms* It may be explained by saying that the two free valencies of the BIRADICAL unite to form the second link of a DOUBLE BOND.

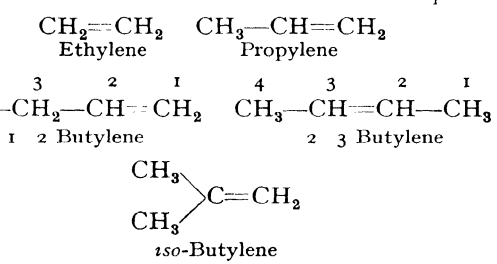


Single bond and two free valencies  Double bond

In terms of the electronic theory of valency, we can conclude that the odd electrons on the two contiguous carbon atoms are no longer free, but have become coupled with one another to form a second shared duplet or covalent link



**Isomerism of the olefines.**—The structures of the simplest olefines are set out below



Ethylene  Propylene

1 2 Butylene  2 3 Butylene

*iso*-Butylene

It is seen that three isomers of the formula $C_4H_8$ are possible. Two of these have a straight chain, whilst the other is branched

**Reactivity of olefines.**—(*a*) Spectroscopic observations show that a double bond is approximately twice as strong as a single bond, *i e* the force which resists the stretching of the molecules, and which governs its vibrations after stretching, is nearly twice as great Thus the frequencies of vibration are Ethane 990 Ethylene 1625

and the work required to break the central bonds is

Ethane 71,000 cal Ethylene 125,200 cal

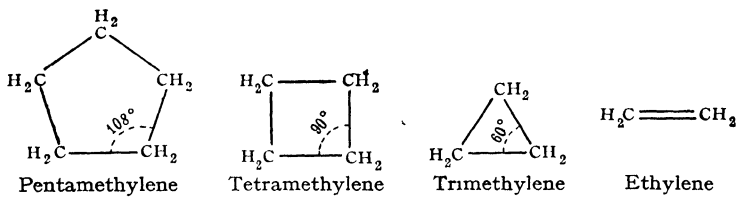
Nevertheless, from the chemical point of view, a double bond is a source of weakness and not of strength in the molecule, since it is far easier to add a molecule of chlorine to ethylene than to ethane, the single bond of which can only be ruptured after all the atoms of hydrogen have first been replaced by chlorine

$$H_2C{=}CH_2 + Cl_2 \rightarrow Cl - CH_2{-}CH_2 - Cl,$$
$$Cl_3C{-}CCl_3 + Cl_2 \rightarrow 2CCl_4$$

(*b*) The reactivity of the double bond finds a simple explanation in von Baeyer's STRAIN THEORY According to this theory the natural angle between the directed valencies of the tetrahedral carbon atom is $109\frac{1}{2}°$ This is very nearly the angle that is found in a regular pentagon, namely,

$$\pi - 2\pi/5 = 108°$$

A ring of five carbon atoms is therefore almost strainless , and rings of larger size are completely strainless, if not compelled to remain in a plane, since the strain can be removed completely by " buckling " or " puckering " of the ring, which thus assumes a zig-zag configuration The formation of a 4-atom ring, with the four carbon atoms at the corner of a square, reduces the angle subtended by neighbouring atoms from $109\frac{1}{2}°$ to 90°, and produces a definite element of strain in the ring, so that it is harder to form (and easier to break) a 4-atom than a 5-atom ring The strain is even greater in a 3-atom ring, with the three carbon atoms at the corners of an equilateral triangle, since the angle subtended is reduced from $109\frac{1}{2}°$ to 60° In a double bond, however, the ends of the two links meet *in the same atom*, so that the angle subtended is reduced from $109\frac{1}{2}°$ to 0° It is therefore easy to understand why the olefines behave as unsaturated hydrocarbons, whereas the cyclic **polymethylenes**, $(CH_2)_n$, only form addition compounds when the ring is small




Pentamethylene Tetramethylene Trimethylene Ethylene

(*c*) Addition of a hydride to an olefine takes place mainly (but not exclusively) in accordance with MARKOWNIKOFF'S RULE, which postulates that " *the negative constituent attaches itself to the carbon atom which*

*carries the smallest number of hydrogen atoms"* This implies that *the hydrogen is used preferentially to complete a methyl group, if possible* Thus propylene gives mainly *iso*-propyl and not *n*-propyl alcohol,

$$\underset{\text{Propylene}}{CH_3\,CH{=}CH_2} \rightarrow \underset{\textit{iso}\text{-Propyl alcohol}}{CH_3\,CH(OH)\,CH_3} \quad \text{not} \quad \underset{\textit{n}\text{-Propyl alcohol}}{CH_3\,CH_2\,CH_2\,OH},$$

butylene gives mainly *sec-* and not *n*-butyl alcohol,

$$\underset{\text{Butylene}}{CH_3\,CH_2\,CH{=}CH_2} \rightarrow \underset{\textit{sec}\text{-Butyl alcohol}}{CH_3\,CH_2\,CH(OH)\,CH_3}$$

$$\text{not} \quad \underset{\textit{n}\text{-Butyl alcohol}}{CH_3\,CH_2\,CH_2\,CH_2\,OH},$$

and, finally, *iso*-butylene and hydrogen bromide give mainly *tert*-butyl bromide and not *iso*-butyl bromide

$$\underset{\textit{iso}\text{-Butylene}}{\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!C{=}CH_2} \xrightarrow{+HBr} \underset{\textit{tert}\text{ Butyl bromide}}{\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!CBr-CH_3} \quad \text{not} \quad \underset{\textit{iso}\text{-Butyl bromide}}{\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!CH-CH_2Br}$$

In the case of acrylic acid (p 747), addition to the double bond takes place quantitatively in the opposite direction to that indicated by Markownikoff's rule, for reasons that are indicated in Chapter LIX (p 784)

# CHAPTER L

## ACETYLENE

**General considerations.**—The hydrocarbons of the ACETYLENE SERIES can be derived from the paraffins by removing *four* atoms of hydrogen, or from the olefines by removing *two* atoms of hydrogen from each molecule They are therefore unsaturated like the olefines, but form a longer series of addition products, since they can combine either with *two* or with *four* univalent radicals

**Preparation of acetylene.**—(*a*) *From calcium carbide* by the action of cold water .

$$CaC_2 + 2H_2O = Ca(OH)_2 + C_2H_2$$

The product is usually contaminated with sulphuretted and phosphoretted hydrogen owing to the presence of calcium sulphide and phosphide in the carbide, but these gaseous impurities are largely removed by passing the crude gas through a solution of copper sulphate.

(*b*) *From ethylene dibromide*, by heating with alcoholic potash in a flask fitted with a water-cooled reflux condenser, when vinyl bromide and then acetylene are formed by the successive removal of hydrogen bromide :

$$\begin{array}{ccccc} CH_2Br & \xrightarrow{-HBr} & CHBr & \xrightarrow{-HBr} & CH \\ | & & \| & & \| \\ CH_2Br & & CH_2 & & CH \\ \text{Ethylene dibromide} & & \text{Vinyl bromide} & & \text{Acetylene} \end{array}$$

Pure acetylene can be prepared by this method, since the vinyl bromide is condensed and returned to the flask

(*c*) *By synthesis from its elements.*—Acetylene is a highly endothermic compound , in accordance with Le Chatelier's principle (p 558), therefore, it is formed from its elements at high temperatures, *e g* by passing hydrogen over an arc burning between carbon electrodes .

$$2C + H_2 \rightarrow C_2H_2 - 54{,}860 \text{ cal}$$

Although only traces of acetylene are produced in this way, this process provides the initial stage for many theoretically important syntheses Thus, when acetylene is passed through a red-hot tube, the aromatic hydrocarbon **benzene**, $C_6H_6$ (p. 771), is formed by direct polymerisation

$$3C_2H_2 \rightarrow C_6H_6.$$

**Properties of acetylene.**—Acetylene is a colourless gas, which condenses to a liquid at $-81°$ and freezes at $-84°$ It dissolves in its own volume of water at 0°. On account of its strongly endothermic character, compressed acetylene is liable to detonate , it is therefore not stored in

cylinders like oxygen, but it can be handled safely in solution (under pressure) in acetone (p 703)

Acetylene burns with a smoky but brilliantly luminous flame :

$$2C_2H_2 + 5O_2 = 4CO_2 + 2H_2O.$$

The flame of the oxy-acetylene blow-pipe is extremely hot (*circ* 2500°), it is therefore used for welding and also (with excess of oxygen) for " cutting " armour plate by burning right through it

EXPT 149 **Preparation and properties of acetylene.**

(*a*) Place about 15 grams of calcium carbide on a little sand in the bottom of a 500 c c flask Fit the flask with a cork, tap-funnel, etc , as depicted in Fig 170A, being careful to see that the tap-funnel has a long stem which is drawn into a jet—this ensures a sufficient head of water to drive acetylene out of the flask Add water slowly from the tap-funnel and (after the air has been displaced) collect by the displacement of water two gas-jars full of acetylene Ignite the gas in one jar and notice the appearance of the flame Add a little bromine water to the other jar and shake vigorously, note what happens

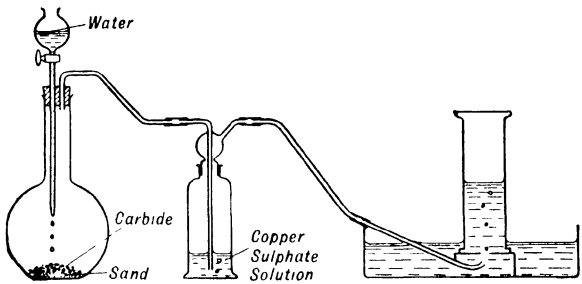



FIG 170A PREPARATION OF ACETYLENE

(*b*) In two boiling-tubes prepare ammoniacal solutions of cuprous chloride and silver nitrate Prepare the former by shaking about one gram of cuprous chloride with 20 c c of bench dilute ammonia, and the latter by adding ammonia to a dilute solution of silver nitrate until the initial precipitate dissolves Pass acetylene through each solution until no further change takes place, filter and examine the action of dilute acids on the precipitates What happens when small portions of each precipitate are dried and struck with a hammer ?

**Metallic derivatives of acetylene.**—Unlike the paraffins and olefines, the hydrogen of acetylene (and of those of its homologues which still contain the group $\equiv CH$) is readily displaced by metals Thus the gas can be detected by the precipitates of white **silver acetylide,** $C_2Ag_2$, and of red **cuprous acetylide,** $C_2Cu_2,H_2O$, which are formed when it is passed through ammoniacal solutions of a silver salt and of a cuprous salt

respectively Pure acetylene can then be made by the action of potassium cyanide on cuprous acetylide

$$C_2Cu_2 + 4KCN + 2H_2O = 2KCu(CN)_2 + 2KOH + C_2H_2$$

**Sodium acetylides,** $C_2HNa$ and $C_2Na_2$, are formed by passing acetylene over heated sodium, whilst **calcium carbide,** $CaC_2$, the most important of all the acetylides, is made by heating limestone with coke in the electric furnace (p 118)

**Addition reactions.**—(*a*) Acetylene is doubly unsaturated and will therefore combine with *four* univalent radicals, *e g*

$$C_2H_2 + H_2 = C_2H_4, \quad C_2H_4 + H_2 = C_2H_6,$$
$$C_2H_2 + 2Cl_2 = C_2H_2Cl_4 \quad \text{(Acetylene tetrachloride)} *$$

Addition of halogen acids takes place according to Markownikoff's rule (p 673), the addition of hydrogen bromide therefore gives rise to **ethylidene bromide,** $CH_3\,CHBr_2$, and not to the isomeric **ethylene dibromide,** $Br\,CH_2\,CH_2\,Br$, which is formed by the addition of bromine to ethylene

$$C_2H_2 + 2HBr \rightarrow CH_3\,CHBr_2 \quad \text{(Ethylidene bromide)}$$

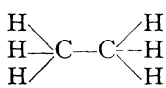
(*b*) The most important addition reaction is the combination of acetylene with water to form acetaldehyde

$$C_2H_2 + H_2O \rightarrow CH_3\,CHO \quad \text{(Acetaldehyde)}$$

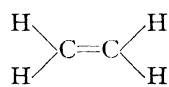
This takes place when the gas is passed into dilute sulphuric acid in which mercuric oxide is held in suspension by vigorous stirring, and is the basis of a long series of important syntheses The addition of water, like the addition of hydrogen bromide, takes place according to Markownikoff's rule, since it gives rise to a complete methyl group , but it is also possible that the aldehyde is formed by isomeric change from vinyl alcohol

$$HC \equiv CH + HOH \rightarrow H_2C{=}CH\,OH \rightarrow CH_3\,CHO$$

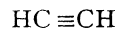
**Structure** —A highly characteristic feature (" alternating intensities ") of the absorption spectrum of acetylene provides conclusive evidence that the molecule is symmetrical, *i e* HCCH, and not $H_2CC$ Its relation to ethane and to ethylene is shown by writing the formula with a TRIPLE BOND, thus



Ethane



Ethylene



Acetylene

* In daylight chlorine and acetylene often react together with explosive violence giving mainly carbon and hydrogen chloride, but on a commercial scale the above addition is safely carried out in a solution of acetylene tetrachloride, using antimony pentachloride as a catalyst Acetylene tetrachloride is used to a limited extent as a non-inflammable solvent, but as it is highly toxic it is largely converted (by the action of steam and lime) into trichlorethylene, $C_2HCl_3$, which does not suffer from this defect, and is widely used in dry cleaning and as a solvent for fats, oils, rubber, etc

## CHAPTER LI

### THE ALCOHOLS

**General considerations.**—The alcohols are derived from the paraffins by the substitution of a HYDROXYL RADICAL for an atom of hydrogen They may therefore be represented by the general formula $(C_nH_{2n+1})OH$

The names, formulae and boiling-points of the simplest alcohols are set out below

| *Formula* | *Name* | *Structural formula* | *Boiling-point* |
|---|---|---|---|
| $CH_4O$ | Methyl alcohol | $CH_3OH$ | 65° |
| $C_2H_6O$ | Ethyl alcohol or methylcarbinol | $CH_3CH_2OH$ | 78° |
| $C_3H_8O$ | *n*-Propyl alcohol or ethylcarbinol | $CH_3CH_2CH_2OH$ | 97° |
| | *iso*-Propyl alcohol or dimethylcarbinol | $(CH_3)_2CHOH$ | 83° |
| $C_4H_{10}O$ | *n*-Butyl alcohol or *n*-propylcarbinol | $CH_3CH_2CH_2CH_2OH$ | 117° |
| | *iso*-Butyl alcohol or *iso*-propylcarbinol | $(CH_3)_2CHCH_2OH$ | 108° |
| | *sec*-Butyl alcohol or methylethylcarbinol | $CH_3CH_2CH(OH)CH_3$ | 99° |
| | *ter*-Butyl alcohol or trimethylcarbinol | $(CH_3)_3COH$ (m -pt 25°) | 83° |

There are *two* isomeric propyl alcohols, *four* butyl alcohols, and not less than *eight* amyl alcohols of the formula $C_5H_{11}OH$, not counting those which differ only in their configuration in space These isomeric alcohols are distinguished by describing them as derivatives of "carbinol," $CH_3OH$, in which the hydrogen atoms of the methyl radical have been replaced by alkyl radicals

**Methyl alcohol** or "methanol," $CH_3OH$, was discovered in 1834 by Dumas and Peligot as a constituent of "wood-spirit," prepared by the distillation of wood It is now made on a large scale by passing a mixture of carbon monoxide and hydrogen under a pressure of 200 atmospheres over a catalyst heated to 450°

$$CO + 2H_2 = CH_4O$$

When wood (*e g* in the form of sawdust) is distilled in iron retorts it yields (i) a gaseous mixture of CO, $CO_2$, $CH_4$, etc , (ii) a brown aqueous "pyroligneous acid" containing about 10% acetic acid, 3% methyl alcohol, and acetone , (iii) a heavy oily wood-tar , (iv) charcoal

After neutralising the pyroligneous acid with lime, the methyl alcohol (b -p 65°) and acetone (b -pt 56°) are distilled off as "wood-spirit" from the crude calcium acetate, and separated by fractional distillation Pure methyl alcohol can be prepared by combining it with anhydrous calcium chloride and then distilling it off from the **alcoholate**, $CaCl_2,4CH_4O$

EXPT 150 **Properties of methyl alcohol**

(*a*) Determine the boiling-point of methyl alcohol Notice the smell, inflammability and miscibility with water of the alcohol

(*b*) Pour about 1 c c of methyl alcohol into a hard glass test tube, which is clamped in a holder Ignite a small spiral of copper gauze in the blow-pipe flame, and while it is still red-hot, drop it carefully into the test tube Notice that the oxidised spiral is instantly reduced to bright metallic copper and a pungent gas—formaldehyde—is formed

Methyl alcohol has a smaller molecular weight and boils at a lower temperature (64 65°) than ordinary alcohol (78 37°), but resembles it very closely in many of its properties Thus it is miscible with water in all proportions and combines with calcium chloride to form a crystalline compound, $CaCl_2$, $4CH_4O$ It dissolves sodium, liberating hydrogen and giving a white deliquescent residue of **sodium methoxide,**

$$2CH_3OH + 2Na = H_2 + 2CH_3ONa \quad \text{(Sodium methoxide)}$$

When heated with salt and sulphuric acid it yields gaseous **methyl chloride,**

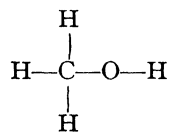
$$CH_3OH + HCl = H_2O + CH_3Cl \quad \text{(Methyl chloride)}$$

When oxidised, it yields **formaldehyde,** $CH_2O$, **formic acid,** $CH_2O_2$, and ultimately carbon dioxide,

$$\underset{\text{Methyl alcohol}}{CH_3OH} \rightarrow \underset{\text{Formaldehyde}}{CH_2{=}O} \rightarrow \underset{\text{Formic acid}}{HC{<}^{O}_{OH}} \rightarrow CO_2$$

Methyl alcohol is toxic, and crude wood-spirit is added to alcohol to make it undrinkable as "methylated spirit" It burns in air and is used as a liquid fuel It is also used in the synthesis of a vast range of organic compounds containing the methyl radical

**Structure of methyl alcohol.**—If we assume that hydrogen is univalent, oxygen bivalent and carbon quadrivalent, only one structural formula is possible for methyl alcohol, namely,



but the four radicals attached to the central carbon atom occupy the corners of a tetrahedron, instead of lying in the plane of the paper

This structure is confirmed by evidence which proves the presence of the methyl and hydroxyl radicals Thus, when methyl alcohol is converted into methyl chloride, the hydroxyl radical is removed and its place is taken by an atom of chlorine The *hydroxyl radical* is thus shown to be a component of the original molecule, whilst the presence of the *methyl radical* is obvious in the product, which is identical with that prepared by the action of chlorine on methane

$$CH_4 + Cl_2 = CH_3\,Cl + HCl.$$

The fact that one atom of hydrogen differs from the other three is also indicated by the action of sodium, which displaces only one of the four atoms of hydrogen

**Preparation of alcohol.**—**Ethyl alcohol**, $C_2H_5OH$, is the principal product of the " alcoholic " or " vinous " fermentation of sugar and starch, but it can also be prepared from ethylene

(*a*) Alcohol is manufactured industrially by fermenting " molasses " *i e* the mother-liquor left after crystallising out as much sugar as possible from beet or cane-sugar syrups The liquors are diluted and made slightly acid and are then fermented, at a temperature of 27°, by the action of yeast The production of alcohol is effected by ENZYMES or " ferments " (of unknown composition and structure) produced by the living yeast cells. Thus the enzyme INVERTASE hydrolyses sucrose (so-called cane-sugar) to a mixture of glucose and fructose (p 738),

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O = \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6},$$

which, under the influence of other enzymes in yeast, undergo very complex changes to give ultimately alcohol and carbon dioxide

$$C_6H_{12}O_6 = 2C_2H_6O + 2CO_2$$

(*b*) Starch, $(C_6H_{10}O_5)_n$, is slowly hydrolysed to glucose by the action of warm dilute sulphuric acid

$$(C_6H_{10}O_5)_n + nH_2O = nC_6H_{12}O_6.$$

After neutralising with lime, the aqueous liquor can be fermented by the action of yeast The same hydrolysis can be brought about by the action of ferments as follows Sliced potatoes are heated with steam under pressure at 150°, when the tissues are broken down and a mash of starch is produced After adding malt (*i e* partially germinated barley) the starch is hydrolysed at 55° to **maltose**, $C_{12}H_{22}O_{11}$, by the enzyme DIASTASE in the malt

$$\underset{\text{Starch}}{(C_6H_{10}O_5)_{2n}} + nH_2O = \underset{\text{Maltose}}{nC_{12}H_{22}O_{11}}$$

After cooling to 17° and adding yeast, the maltose is hydrolysed to glucose by the enzyme MALTASE of the yeast and is then fermented to alcohol .

$$\underset{\text{Maltose}}{C_{12}H_{22}O_{11}} + H_2O = 2\underset{\text{Glucose}}{C_6H_{12}O_6}$$

(*c*) Alcohol can also be prepared by the addition of water to ethylene, $C_2H_4 + H_2O = C_2H_6O$ In this way ethylene in coke-oven gases, or formed as a by-product in the hydrogenation of coal, can be converted into alcohol The addition of water may be effected by absorption in sulphuric acid (p 670) or by the action of steam under pressure in presence of a solid catalyst

The dilute solutions of alcohol obtained by fermentation are concentrated to about 87% by distillation in specially constructed stills Further fractionation yields a mixture of constant boiling-point containing 96% of alcohol (p 501), ABSOLUTE ALCOHOL, containing only a trace of water, is therefore prepared by distillation with quicklime The last traces of water can then be removed by the action of metallic calcium or of aluminium amalgam

**Beer, wines and spirits.**—Beer is a "malt liquor," prepared by steeping malt in water at 55° (and so bringing about a partial diastatic fermentation), boiling the resulting WORT with hops, and then fermenting with yeast It usually contains 3 to 6% of alcohol, with dextrin from the partial hydrolysis of starch, unfermented sugars and colouring matters

Red and white wines are obtained by the fermentation of the glucose in grape juices It is not necessary to add yeast, since this is present in the "bloom" which covers the outside of the grape

Whisky is made by a similar process to that used in the brewing of beer, but the diastatic fermentation of the malt is carried out for a longer period, so that a larger proportion of maltose is produced Fermentation with yeast then yields a larger quantity of alcohol, which is concentrated to about 40% by distillation "Proof-spirit," which formerly meant a spirit which would just ignite gunpowder when poured upon it and burnt, is now defined by Act of Parliament as "such a spirit as shall at a temperature of 51° F weigh exactly $\frac{12}{13}$ of an equal measure of distilled water" This corresponds with a mixture of alcohol and water containing only 49 3% (by weight) of alcohol

**Properties of alcohol**—Alcohol is a liquid of density 0 789 at 20°, which mixes in all proportions with water It burns in air with a blue flame and is used in "spirit lamps," usually in the form of "methylated spirits," *e g* mixed with 10% of crude wood-spirit and with naphtha to make it undrinkable It is added to petrol for use as a liquid fuel in countries which do not produce petroleum In addition to its use in fermented liquors, and in a more concentrated form in "spirits" of various descriptions, it is one of the most important raw materials of organic chemistry, and is used in a wide range of organic preparations, and as a solvent for many compounds which will not dissolve in water

EXPT 151 **Preparation and properties of alcohol**

(*a*) Dissolve 200 grams of sugar in about six times its weight of water Add to the solution a little brewers' yeast, previously made into a paste with water Place the solution in a flask, fitted with a delivery tube bent twice at right angles Place the end of the tube just below the surface of lime water in a beaker Leave the whole for several days in a fairly warm place. Observe the change in the liquid What gas is formed ?

(*b*) Filter the liquid in the flask Distil the solution in a distillation apparatus, fitted with a thermometer Collect the condensed liquid until the temperature rises to about 88° In the liquid thus obtained place some lumps of quicklime, set it aside for at least a day Now decant off the liquid and distil it again When the temperature rises to 80° stop the distillation

(*c*) Examine the liquid thus obtained Note its smell Place a little on a crucible lid and apply a light to it

(*d*) Examine by the following methods the products formed when alcohol burns in air Place the flame of a spirit lamp below a retort, cooled by means of a stream of water Collect a little of the liquid formed and identify it Then allow the lamp to burn in a wide jar Pour a little lime water into the jar and shake, decide what gas is formed when alcohol burns What knowledge have you gained as to the elements present in alcohol ?

(*e*) Dissolve a small piece of sodium in alcohol and compare the action with that between sodium and water Identify the gas which is liberated

(*f*) When the sodium has completely dissolved, evaporate a small portion of the solution to dryness by heating it in a basin on a water-bath Examine the residue Find whether it dissolves in water, and if so, whether the solution affects the colour of litmus

The principal chemical reactions of alcohol are summarised below, except the formation of esters which is described in Chapter LIV

(*a*) *Replacement of hydrogen*—As in the case of methyl alcohol, one atom of hydrogen can be replaced by sodium

$$2C_2H_5OH + 2Na = H_2 + 2C_2H_5ONa \quad \text{(Sodium ethoxide)}$$

The action is much less violent than with water, and the **sodium ethoxide** readily crystallises out, it is hydrolysed by water and thus provides a convenient method for preparing standard solutions of sodium hydroxide from weighed quantities of metallic sodium (p 415)

$$C_2H_5ONa + H_2O = C_2H_5OH + NaOH$$

(*b*) *Replacement of hydroxyl*—Gaseous hydrogen chloride passed into an alcoholic solution of zinc chloride gives **ethyl chloride**, $C_2H_5Cl$, just as methyl alcohol is converted into methyl chloride by the action of salt and sulphuric acid

$$C_2H_5OH + HCl \rightleftharpoons C_2H_5Cl + H_2O$$

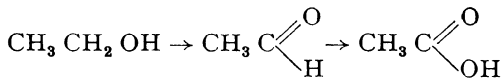
Ethyl chloride is a volatile liquid, boiling at 12 5°, which is used as a local anaesthetic to produce numbness by rapid evaporation The replacement of the hydroxyl group by a halogen can also be effected by the more drastic action of phosphorus pentachloride, by the action of a mixture of red phosphorus with bromine or iodine, as well as by the direct action of hydrogen bromide or iodide, *e g*

$$C_2H_5OH + PCl_5 = C_2H_5Cl + HCl + POCl_3.$$

$$3C_2H_5OH + P + 3I = 3C_2H_5I + H_3PO_3$$

The products are described in the following chapter.

(*c*) *Oxidation and reduction*.—Alcohol is oxidised successively to acetaldehyde (p 689) and to acetic acid (p 709) by air in presence of a suitable catalyst, or by oxidising agents such as chromic acid



Alcohol Acetaldehyde. Acetic acid

Nitric acid oxidises the methyl group also and finally yields oxalic acid

$$CH_3\,CH_2\,OH \rightarrow HO\,CO\,CO\,OH$$

In presence of mercury, however, **mercury fulminate**, $HgC_2N_2O_2$, $\frac{1}{2}H_2O$, is produced by the action of nitric acid on alcohol

Reduction to ethane is effected most readily after replacing the hydroxyl group by a halogen

(*d*) *Action of sulphuric acid*.—(i) When mixed with an equal volume of sulphuric acid and heated on a water-bath, alcohol is converted reversibly into **ethyl hydrogen sulphate** $(C_2H_5)HSO_4$ (p. 728)

$$(C_2H_5)OH + H_2SO_4 \rightleftharpoons (C_2H_5)HSO_4 + H_2O$$

(ii) When heated with sulphuric acid at 140°, alcohol is converted by loss of water into **ether** (p 721)

$$2(C_2H_5)OH = (C_2H_5)_2O + H_2O$$

This is not a direct dehydration, but a secondary action, in which ethyl hydrogen sulphate is decomposed by a second molecule of alcohol

$$(C_2H_5)HSO_4 + (C_2H_5)OH = (C_2H_5)_2O + H_2SO_4$$

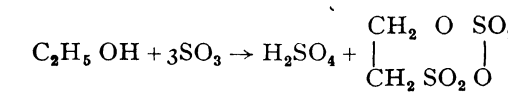
(iii) At a higher temperature (180°) and in presence of a larger proportion of sulphuric acid, alcohol is converted into **ethylene** (p 668), probably by the thermal decomposition of ethyl hydrogen sulphate

$$(C_2H_5)HSO_4 = C_2H_4 + H_2SO_4$$

Syrupy phosphoric acid at 230°, and alumina at 450°, can also be used to convert alcohol into ethylene and water

$$C_2H_5\,OH = C_2H_4 + H_2O$$

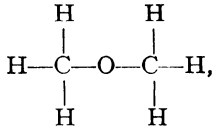
(iv) Finally, by the still more drastic action of sulphuric anhydride, alcohol is converted into **carbyl sulphate**, $C_2H_4S_2O_8$, which can also be prepared as an addition compound of ethylene with sulphur trioxide



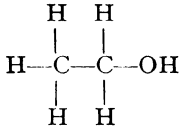
Carbyl sulphate

**Structure of alcohol.**—If we assume that hydrogen is univalent, oxygen bivalent and carbon quadrivalent, there are only two structures

possible for a molecule of the formula $C_2H_6O$. These are assigned as follows

I. 

Methyl ether
(b -pt -21°)

II. 

Ethyl alcohol
(b -pt 78°)

(*a*) The symmetrical formula I contains two methyl groups linked by an atom of oxygen A compound of this composition, and presumably having the structure I, can be prepared by heating methyl alcohol with sulphuric acid, or methyl iodide with silver oxide

$$2CH_3\,OH = (CH_3)_2O + H_2O \text{ or } 2CH_3I + Ag_2O = (CH_3)_2O + 2AgI$$

It is found to be a gas and not a liquid There is therefore strong *negative* evidence that alcohol cannot be I and must therefore be II.

(*b*) *Positive* evidence in support of this structure is based on the proof that a molecule of alcohol contains three radicals, namely

| | | |
|---|---|---|
| —OH | or | hydroxyl, |
| $—CH_2—$ | or | methylene, |
| $—CH_3$ | or | methyl |

The six atoms of hydrogen are therefore distributed as $1 + 2 + 3 = 6$, instead of $3 + 3 = 6$ as in formula I

(i) The fact that only *one* out of six atoms of hydrogen can be replaced by sodium confirms the presence of the unique hydrogen of the *hydroxyl* group ; and the replacement of hydroxyl by chlorine to produce ethyl chloride enables us to formulate the alcohol with certainty as ethyl hydroxide, $C_2H_5\,OH$

(ii) If, on the other hand, we oxidise alcohol to acetic acid, *two* atoms of hydrogen, and two only, are replaced by oxygen, thus enabling us to recognise the two hydrogen atoms of the *methylene* group

(iii) The presence of a *methyl* group in acetic acid can be established by synthesising it from methyl alcohol, as described below (p 709), we can then infer its presence in ethyl alcohol, since it is most unlikely that a group so rich in hydrogen could have been created during the oxidation of alcohol to acetic acid

(*c*) These arguments are united in the following transformations

$$\underset{\text{Alcohol}}{CH_3\,CH_2\,OH} \xrightarrow{O} \underset{\text{Acetic acid}}{CH_3\,CO\,OH} \xrightarrow{Cl_2} \underset{\substack{\text{Trichlor-}\\\text{acetic acid}}}{CCl_3\,CO\,OH} \xrightarrow{NaOH} \underset{\substack{\text{Sodium trichloro-}\\\text{acetate}}}{CCl_3\,CO\,ONa.}$$

Thus, *two* atoms of hydrogen are replaced by oxygen when alcohol is oxidised to acetic acid, *three* atoms of hydrogen (and three only) can then be replaced by *chlorine* to form trichloracetic acid, and finally the *one*

remaining atom of hydrogen is replaced by sodium when this acid is neutralised by soda In this way the grouping of the hydrogens as $1+2+3=6$, can be established conclusively, since the members of each group are displaced by a different element

**Higher homologues.**—Several of the higher homologues of alcohol occur amongst natural products, or can be prepared easily from them

(*a*) Starch can be fermented in such a way that the main products are (i) acetone, $CH_3\,CO\,CH_3$ (p 703), which can be reduced to ***iso*-propyl alcohol** $(CH_3)_2CH\,OH$, and (ii) ***n*-butyl alcohol** $CH_3\,CH_2\,CH_2\,CH_2\,OH$, thus providing two additional members of the homologous series of alcohols

(*b*) The " fusel oil," which is separated as a high-boiling impurity from alcohols made by fermentation with yeast, contains two isomeric **amyl alcohols,** $C_5H_{11}\,OH$

*iso*-Amyl alcohol, $\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!CH\,CH_2\,CH_2\,OH,$

*act*-Amyl alcohol, $\begin{matrix}CH_3\,CH_2\\CH_3\end{matrix}\!\!>\!CH\,CH_2\,OH$

The latter contains an " asymmetric carbon atom " (shown in heavy type), *i e* a carbon atom linked to four different univalent radicals (p 744), and is " optically active " (p 743)

(*c*) Beeswax contains ***n*-cetyl alcohol,** $C_{16}H_{33}OH$, as **cetyl palmitate,** $C_{16}H_{33}\,O\,CO\,C_{15}H_{31}$, it is used as a sulphate, *e g* $C_{16}H_{33}\,O\,SO_2\,ONa$, in modern detergents (pp 76 and 718)

(*d*) Other alcohols can be prepared, when required, by reduction from the acids (Chap LIII), which occur in greater variety than the alcohols

**Unsaturated alcohols.**—**Allyl alcohol,** $CH_2{=}CH\,CH_2\,OH$, is prepared by heating glycerol with oxalic acid (p 737)

$$\underset{\text{Glycerol}}{C_3H_8O_3} + \underset{\text{Oxalic acid}}{H_2C_2O_4} \longrightarrow \underset{\substack{\text{Allyl}\\\text{alcohol}}}{C_3H_6O} + 2H_2O + 2CO_2$$

It is a colourless liquid, which boils at 97° and mixes with water in all proportions It is of interest as an UNSATURATED ALCOHOL, which exhibits the properties both of an olefine and of an alcohol Thus it can be reduced to propyl alcohol and oxidised by alkaline permanganate to glycerol, and by silver oxide to acrolein and acrylic acid (p 747)

$$\underset{\text{Propyl alcohol}}{CH_3{\cdot}CH_2\,CH_2\,OH} \xleftarrow{+2H} \underset{\text{Allyl alcohol}}{CH_2{=}CH{\cdot}CH_2{\cdot}OH} \xrightarrow[KMnO_4]{+2OH} \underset{\text{Glycerol}}{HO{\cdot}CH_2\,CH(OH){\cdot}CH_2\,OH}$$

$$\underset{\text{Allyl alcohol}}{CH_2{=}CH{\cdot}CH_2\,OH} \xrightarrow{Ag_2O} \underset{\text{Acrolein}}{CH_2{=}CH\,CHO} \xrightarrow{Ag_2O} \underset{\text{Acrylic acid}}{CH_2{=}CH{\cdot}CO\,OH}$$

**Primary, secondary and tertiary alcohols.**—(*a*) *Classification* —The alcohols are generally classified as follows

(i) *Primary alcohols* or monoalkylcarbinols, $R\,CH_2\,OH$,

(ii) *Secondary alcohols* or dialkylcarbinols, $\begin{matrix}R\\R\end{matrix}\!\!>\!CH\cdot OH$,

(iii) *Tertiary alcohols* or trialkylcarbinols, $\begin{matrix}R\\R\\R\end{matrix}\!\!>\!C\,OH$.

The alkyl radicals may be similar to one another, or different The three types of alcohol can be distinguished (see also pp 769-770) by their different behaviour on oxidation as follows

(i) A *primary alcohol* can be oxidised to an aldehyde and acid *with the same number of atoms of carbon* and therefore without breaking down the carbon chain

$$R\,CH_2\,OH \longrightarrow R\,C\begin{matrix}=O\\H\end{matrix} \longrightarrow R\,C\begin{matrix}=O\\OH\end{matrix}$$

Primary alcohol Aldehyde (p 689) Acid (p 717)

(ii) A *secondary alcohol* can be oxidised to a ketone without loss of carbon , but only one of the two alkyl radicals survives the further oxidation to an acid, the other being partially or wholly destroyed

$$\begin{matrix}R\\R\end{matrix}\!\!>\!CH\,OH \rightarrow \begin{matrix}R\\R\end{matrix}\!\!>\!C{=}O \rightarrow \left[R\,C\begin{matrix}=O\\OH\end{matrix}\right]$$

Secondary alcohol Ketone (p 689) Acid

(iii) *Tertiary alcohols* are less easily oxidised, but finally yield acids in which only one of the three radicals survives

$$\begin{matrix}R\\R\\R\end{matrix}\!\!>\!C\,OH \rightarrow R\,C\begin{matrix}=O\\OH\end{matrix}$$

(*b*) *Preparation and interconversion of alcohols* —Primary, secondary and tertiary alcohols can be prepared as follows

(i) By hydrolysing the corresponding mono-halogen derivatives with hot water, dilute alkalis, or freshly precipitated silver hydroxide, *e g*

$$C_2H_5Br + KOH = KBr + C_2H_5\,OH,$$
$$C_3H_7I + AgOH = AgI + C_3H_7\,OH$$

(ii) By heating the corresponding halogen derivatives with an alcoholic solution of silver acetate or potassium acetate

$$C_2H_5I + Ag\,O{\cdot}CO{\cdot}CH_3 = C_2H_5O\,CO\,CH_3 + AgI$$

The alkyl acetate is then hydrolysed by dilute alkali, etc. This method is

particularly useful when applied to halogen-derivatives of the higher paraffins, which usually give olefines when heated with alkalis

(iii) By the action of nitrous acid on a primary amine (p 762), *e g*

$$C_2H_5 \cdot N H_2 + O N \dot{:} OH = C_2H_5 OH + N_2 + H_2O$$

(iv) By reducing aldehydes and ketones, when aldehydes give primary alcohols and ketones give secondary alcohols, *e g*

$$CH_3 CHO + H_2 = CH_3 CH_2 OH,$$
$$CH_3 CO CH_3 + H_2 = CH_3 CH(OH) CH_3$$

On the other hand, by the action of the Grignard reagent, aldehydes can be converted into secondary alcohols and ketones into tertiary alcohols (p 727)

(v) Olefines can be converted into alcohols by absorption in strong sulphuric acid, *e g*

$$CH_3 CH{=}CH_2 + H_2SO_4 \rightarrow \begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!CH\ O\ SO_2\ OH.$$

Propylene — *iso*-Propyl hydrogen sulphate

The alkyl sulphate thus produced is then hydrolysed to the alcohol by boiling water

$$\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!CH\ O\ SO_2\ OH + H_2O = \begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!CH\ OH + H_2SO_4$$

Since propylene can be prepared from propyl alcohol, this method can be used to convert a *primary* alcohol into a *secondary* alcohol (p 685) When applied to *iso*-butyl alcohol, the same process leads to the conversion of a *primary* into a *tertiary* alcohol, as indicated by the upper arrows in the scheme

$$\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!CH\ CH_2{\cdot}OH \rightleftharpoons \begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!C{=}CH_2 \rightleftharpoons \begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!C\!<\!\begin{matrix} CH_3 \\ OH \end{matrix}$$

*iso*-Butyl alcohol — *iso*-Butylene — *ter*-Butyl alcohol

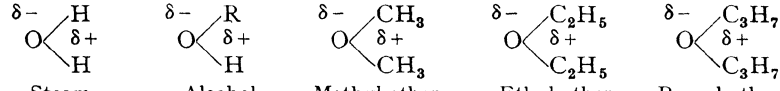
The product is a solid (m -p 25°) which can be purified rigidly Evidence of the converse change from a *tertiary* to a *primary* alcohol (as indicated by the lower arrows in the preceding scheme) is then provided by the fact that pure *ter*-butyl alcohol, when oxidised by chromic acid in presence of sulphuric acid, yields *iso*-butyric acid (p 719) amongst the products of oxidation

$$\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!CH\ CH_2\ OH \rightarrow \begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!CH{\cdot}CO{\cdot}OH.$$

It therefore appears that, in presence of sulphuric acid, the two alcohols (or their sulphates) exist in a condition of dynamic equilibrium with one another, whereas in the absence of the acid they are both completely

stable This condition of equilibrium between isomers is known as DYNAMIC ISOMERISM

**Reactivity of the alcohols.**—(*a*) The alcohols differ from the paraffins mainly in being miscible with water and far more reactive It can now be asserted with some confidence that these far-reaching differences are related to the fact that the two bonds of bivalent oxygen are not arranged in a straight line, but are inclined at an angle, which does not differ greatly from the angle ($109\frac{1}{2}°$) between the four bonds of methane The alcohols are therefore characterised by a dipole moment, which does not cancel out as it does in the case of carbon tetrachloride




| Steam | Alcohol | Methyl ether | Ethyl ether | Propyl ether |
|---|---|---|---|---|
| $\mu = 1\ 84 \times 10^{-18}$ | $\mu = 1\ 7 \times 10^{-18}$ | $\mu = 1\ 32 \times 10^{-18}$ | $\mu = 1\ 14 \times 10^{-18}$ | $\mu = 0\ 86 \times 10^{-18}$ |

The molecular dipole moment of the alcohols is rather less than that of steam , but it is practically constant throughout the homologous series In the ethers, on the other hand, the dipole moment decreases as the alkyl radicals get bigger, perhaps because the valency angle is increased by the bulkiness of the heavier radicals

The existence of this dipole moment brings the alcohols into the class of " polar liquids " (p 498) and accounts fully for the miscibility of the lower homologues with water , but, when the hydrocarbon chain is elongated, the molecules as a whole become less polar, and from amyl alcohol, $C_5H_{11}$ OH, the alcohols only dissolve in water to a limited extent

(*b*) The reactivity of the alcohols can be accounted for in part by the presence of a dipole moment, since this promotes their association with polar reagents Even more important, however, is the electronegative character (p 52) of the oxygen atoms, which is manifested by its tendency to acquire electrons and form negatively-charged ions, *e g* $OH^-$ and $O^{--}$ This " electron-affinity " restricts the readiness of the oxygen to share electrons with other atoms, and causes it to relax its hold on the atoms to which it is bound by these shared electrons Thus, in presence of metallic sodium, the alcohols *liberate an atom of hydrogen*, and are converted into (ethoxyl, etc ) ions

$$C_2H_5\ OH + Na \rightarrow C_2H_5\ \overset{-}{O}\overset{+}{N}a + H$$

The link which binds the oxygen to carbon can also be broken quite readily, *e g* in the conversion of alcohol into ethyl chloride The principal reactions of the alcohols can thus be accounted for by the electron affinity of the oxygen atom and the consequent weakness of the bonds by which it is linked to *hydrogen* and to *carbon*

(*c*) Alcohol, however, is also oxidised with a readiness that has no parallel among the inert paraffins, *e.g*

$$CH_3{\cdot}CH_2{\cdot}OH \rightarrow CH_3{\cdot}CO\ OH$$

Unlike the atom of hydrogen which is displaced by the action of sodium, the two atoms of hydrogen which are displaced in this oxidation are not

linked to *oxygen* at all, but only to *carbon* Their loose attachment is however, obviously associated with the introduction of an oxygen atom into the molecule and is attributed to an " electron-drift," whereby all the electrons in the neighbourhood of the oxygen are drawn towards it, and lose some of their binding-power for other atoms In this way the two hydrogen atoms of the methylene group acquire a mobility which they did not possess before, and are selectively removed by the oxidising agent, whilst the more remote hydrogens of the methyl group are retained at this stage, although they are eliminated in the further oxidation of the acid.

# CHAPTER LII

## ALDEHYDES AND KETONES

**General considerations**—When alcohol is oxidised, *e g* with chromic acid, a pleasant but pungent smell is observed The product, a volatile liquid boiling at 21°, has long been known as **aldehyde** (*al*cohol *dehyd*rogenatum) because it is formed from alcohol by removal of hydrogen and not by addition of oxygen, but it is distinguished as **acetaldehyde,** because it is converted by further oxidation into **acetic acid**

$$\underset{\text{Alcohol}}{CH_3\,CH_2\,OH} \rightarrow \underset{\text{Aldehyde}}{CH_3\,CO\,H} \rightarrow \underset{\text{Acetic acid}}{CH_3\,CO\,OH}$$

The term ALDEHYDE is applied to describe all the members of the series R CO H in which a carbonyl group $>C{=}O$ is linked to *one alkyl radical and one hydrogen atom* (or to two hydrogen atoms in formaldehyde), whilst those compounds in which a carbonyl group is linked to two alkyl radicals, R CO R′, are described as KETONES The aldehydes are formed by oxidation of *primary* alcohols, and yield primary alcohols on reduction, they are also easily oxidised to carboxylic acids, and are named after the acids produced in this way as formaldehyde, acetaldehyde, etc The ketones are not so easily oxidised, but yield *secondary* alcohols on reduction, they are named after the two alkyl radicals attached to the carbonyl group, which need not be the same, but **dimethyl ketone,** $CH_3\,CO\,CH_3$, is always known as **acetone**

### A ACETALDEHYDE

**Preparation.**—Acetaldehyde may be prepared by the following methods

(i) By oxidising ethyl alcohol with a hot solution of potassium dichromate and sulphuric acid

$$3C_2H_5\,OH + K_2Cr_2O_7 + 4H_2SO_4 = 3CH_3\,CHO + K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O$$

(ii) By passing alcohol vapour over copper heated to 300°

$$C_2H_5\,OH \rightarrow CH_3\,CHO + H_2$$

(iii) By passing acetylene into dilute sulphuric acid in which mercuric oxide is held in suspension by vigorous stirring (p 676)

$$C_2H_2 + H_2O \rightarrow CH_3\,CHO$$

(iv) By the action of superheated water on ethylidene dichloride ·

$$CH_3\,CHCl_2 + H_2O \rightarrow CH_3\,CHO + 2HCl$$

(v) By the distillation of a dry mixture of calcium acetate and formate :

$$\begin{matrix} CH_3\,CO\,\overset{-}{O} \\ H\,CO\,\underset{-}{O} \end{matrix}\overset{++}{Ca} \rightarrow CH_3\,CO\,H + CaCO_3$$

(vi) Aldehyde is also produced by the hydrolysis of **vinyl bromide** or **monobromoethylene,** $CH_2{=}CH\,Br$ This compound has already been shown (p 674) as an intermediate product in the conversion of ethylene dibromide into acetylene On hydrolysis, it would be expected to give **vinyl alcohol,** $CH_2{=}CH\,OH$ , but this alcohol is not known in the free state, since it changes at once to acetaldehyde, by a well-known type of isomeric change, known as PROTOTROPY, in which the migration of a proton, as shown by a dotted arrow, is accompanied by the wandering of a double bond, as shown by a curved arrow in the following equation

$$H_2C{=}CH{-}OH \rightarrow H_3C{-}CH{=}O$$

Vinyl alcohol contains a double bond like ethyl*ene* and a hydroxyl group like alcoh*ol*, it is therefore described as an ENOLIC FORM or ENOLIC ISOMERIDE of acetaldehyde (compare pp 732 and 751)

EXPT 152 **Preparation and properties of acetaldehyde**

(*a*) Into a 1-litre distilling flask pour 120 c c of water and add 30 grams of coarsely powdered potassium dichromate The flask is fitted with a dropping funnel containing a mixture of 30 grams of rectified spirit and 40 grams of concentrated sulphuric acid It is attached to a condenser and receiver cooled in ice and is warmed very gently on a sand-bath, while the mixture of spirit and sulphuric acid is run in slowly When the whole of the latter has been added, collect about 30 to 40 c c of distillate

(*b*) The distillate from (*a*) contains aldehyde, alcohol and water The flask containing it is fitted with a small reflux condenser (Fig 171), through which is circulated water at 35° The flask is heated by immersion in warm water or over a very small flame Under these conditions the alcohol and water condense and flow back into the flask, whilst the aldehyde, which boils at 21°, passes through the condenser and can be collected in a receiver cooled in ice and salt (not shown in Fig 171)

(*c*) By means of a bent delivery tube attached to the top of the condenser the aldehyde vapour can be made to bubble through a quantity of ether in two cooled test tubes (Fig 171) Prepare some crystals of aldehyde ammonia (p 694) by passing ammonia gas into the ethereal solution The crystals can be drained on a filter and kept in a specimen bottle They are soluble in water and give the reactions of aldehydes

(*d*) Test the action of aldehyde and of aldehyde-ammonia on silver nitrate and on SCHIFF'S REAGENT, *i e* a solution of the dye *magenta,* which has been just bleached by bubbling sulphur dioxide through it.

(*e*) Notice the peculiar smell of paraldehyde (p 698) Find its boiling-point and test whether it acts on silver nitrate and on Schiff's reagent

(*f*) Boil a few c c of acetaldehyde with a solution of caustic potash Observe the gradual formation of a yellow resin

**Physical properties of acetaldehyde.**—Acetaldehyde is a colourless liquid which boils at 21°, and has a pungent but not unpleasant smell It is completely miscible with water

**Structure and reactions of acetaldehyde.**—(*a*) *Reduction and oxidation* —(1) Aldehyde is formed from alcohol by the elimination of two atoms of

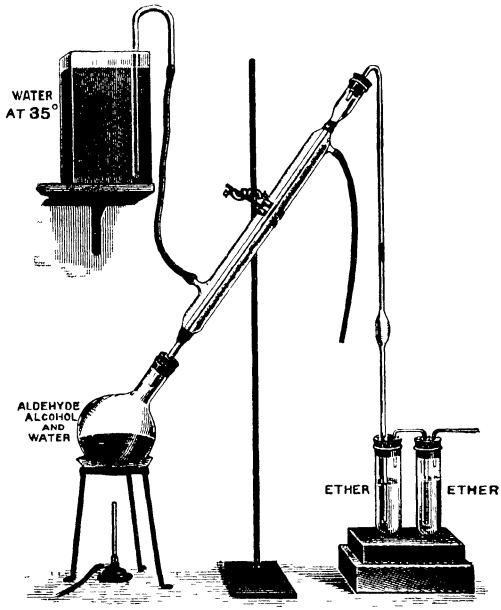



FIG 171 DISTILLATION OF ACETALDEHYDE

hydrogen, and can be reduced again to alcohol, *e g* by hydrogen in presence of finely divided platinum On the other hand, it is very easily oxidised to acetic acid and therefore often behaves as a reducing agent Thus it will reduce Fehling's solution (p 315) and will deposit a silver mirror from ammoniacal silver nitrate

$$2CuO + C_2H_4O = Cu_2O + C_2H_4O_2,$$
$$Ag_2O + C_2H_4O = 2Ag + C_2H_4O_2$$

The presence of a METHYL GROUP in acetic acid can be established by preparing it from methyl iodide through the cyanide (p 709)

$$CH_3I \rightarrow CH_3\,CN \rightarrow CH_3\,CO\,OH$$

Since aldehyde is made by oxidising alcohol, which contains a methyl

group, and is oxidised to acetic acid, which also contains a methyl group, the presence of this group in aldehyde may be accepted without further argument, and we can therefore write the formula as follows

$$\underset{\text{Alcohol}}{CH_3\,CH_2\,OH} \rightarrow \underset{\text{Aldehyde}}{CH_3\,CHO} \rightarrow \underset{\text{Acetic acid}}{CH_3\,CO\,OH}$$

(ii) Acetic acid can be reconverted into aldehyde by converting it into acetyl chloride (p 711) and then reducing it with nascent hydrogen

$$\underset{\substack{\text{Acetic acid}\\(\text{Acetyl hydroxide})}}{CH_3\,CO\,OH} \overset{\substack{PCl_5\\ \rightleftharpoons\\ H_2O}}{} \underset{\text{Acetyl chloride}}{CH_3\,CO\,Cl} \overset{2H}{\rightarrow} \underset{\substack{\text{Aldehyde}\\(\text{Acetyl hydride})}}{CH_3\,CO\,H}$$

These reactions show that the ACETYL GROUP, $CH_3\,CO$—, which is present as a chloride in acetyl chloride, and as a hydroxide in acetic acid, exists as a hydride in acetaldehyde We are therefore able to formulate this compound, not merely as $CH_3\,CHO$, but more precisely as $CH_3\,CO\,H$, since it contains not only a methyl radical, $CH_3$, but the bivalent CARBONYL RADICAL, —CO—, which is required to convert methyl into acetyl

(*b*) *Chlorination products* —The presence of a doubly-bound atom of oxygen in the form of a CARBONYL GROUP, $>C{=}O$, and of 1 + 3 atoms of hydrogen in acetaldehyde, can also be established from a study of the products of chlorination, thus

(i) Phosphorus pentachloride dissolves in pure acetaldehyde at 0° *without liberation of hydrogen chloride*, and converts it into **ethylidene chloride** .

$$CH_3\,CHO + PCl_5 = CH_3\,CHCl_2 + POCl_3$$

The replacement of one atom of oxygen by *two* atoms of chlorine is characteristic of the carbonyl group, whereas under similar conditions a hydroxyl group is replaced by *one* atom of chlorine and a molecule of hydrogen chloride is set free

$$PCl_5 + R\,OH \rightarrow RCl + POCl_3 + HCl$$

This reaction can also be used to demonstrate the presence of a methyl radical in ethylidene chloride, and thus provides important evidence in favour of a symmetrical formula, $Cl\,CH_2\,CH_2\,Cl$, for ethylene dichloride, and therefore also for ethylene (p 671)

(ii) **Chloral,** $CCl_3\,CO\,H$, in which the three hydrogens of the methyl group are replaced by chlorine, is the final product of the action of chlorine on aldehyde (Dumas, 1835), but is prepared most readily by chlorinating alcohol (Liebig, 1832), and is described on p 701 The last atom of hydrogen cannot be displaced directly by chlorine, and in this respect differs fundamentally from the other three

(iii) **Acetyl chloride,** $CH_3\,CO\,Cl$, in which the aldehydic hydrogen of acetaldehyde is replaced by chlorine, cannot be prepared by direct chlorination (contrast benzaldehyde and benzoyl chloride, p 786) Its preparation from acetic acid and reduction to aldehyde have, however,

already been cited as evidence of the presence of an acetyl group in all three compounds

The chlorination of acetaldehyde therefore provides independent evidence of the presence of (i) a carbonyl radical, which yields a *di*-chloro-derivative, (ii) a methyl radical, which yields a *tri*-chloro-derivative and (iii) an unique hydrogen atom These deductions are in harmony, not only with its behaviour on oxidation and reduction, but also with the coupling reactions which are set out below

**Structure of the carbonyl radical.**—In the preceding paragraphs the structure of acetaldehyde has been established as (i), on the assumption that all the atoms have their usual valencies It is of interest, however, to enquire whether the removal of two atoms of hydrogen from alcohol (leaving the methyl radical intact) might not yield products such as (ii) or (iii)

(i) $CH_3—C(=O)—H$ (ii) $CH_3—C(—)(—)—OH$, (iii) $CH_3—C(H)(—)—O—$

Formula (ii) is incompatible with the action of phosphorus pentachloride (p 692), which yields a product in which the hydrogen of the CHO group is attached directly to carbon , but formula (iii) would explain all the reactions cited above If it were correct, however, aldehyde would be expected to show the intense activity of a " free radical " (p 659), which is by no means the case There is therefore ample justification for assuming that the two atoms of hydrogen are removed from *contiguous atoms* and that the intense activity of the unsaturated " biradical " is mitigated, as in the case of ethylene (p 671), by the formation of a " double bond " between two contiguous unsaturated atoms, thus .

$$H—C(H)(H)—C(H)(H)—OH \xrightarrow{-2H} H—C(H)—C(H)—O— \rightarrow H—C(H)—C(=O)—H$$

**Addition compounds of aldehydes.**—In virtue of the double bond which it contains, aldehyde is classified as an *unsaturated compound* (p 668) The double bond, however, is no longer symmetrical, as it is in the olefines,

$$>C=C<,$$

but is strongly polar, with a constant dipole moment throughout the homologous series

$$>\overset{+}{C}=\overset{-}{O} \qquad \mu = 2\ 7 \times 10^{-18} \text{ e s u}$$

The aldehydes therefore tend to form addition compounds with reagents which are themselves unsymmetrical, and in particular with reactive

hydrides of the type HX The rule then is that *hydrogen is added to the oxygen and the rest of the molecule to the carbon*

$$>C{=}O + HX \rightarrow >C\begin{matrix}OH\\X\end{matrix}$$

(*a*) When aldehyde is distilled into ether, ammonia gas precipitates from the solution a crystalline addition compound which is described as **aldehyde-ammonia** (p 690)

$$CH_3\,CH{=}O + NH_3 \rightleftharpoons CH_3\,CH\begin{matrix}OH\\NH_2\end{matrix}$$

The aldehyde can then be recovered by distilling the crystalline addition product with sulphuric acid, when ammonia is removed and the aldehyde is set free again , but this method of separation involves considerable loss, owing to incomplete precipitation of aldehyde ammonia from ether into which alcohol and water have also been distilled Under these conditions the aldehyde may be separated more effectively by a simple fractional distillation

(*b*) Aldehyde combines with sodium hydrogen sulphite to form a **bisulphite-compound**

$$CH_3\,CH{=}O + NaHSO_3 \rightleftharpoons CH_3\,CH\begin{matrix}OH\\SO_2\,ONa\end{matrix}$$

Thus, aldehydes are commonly purified by shaking with a concentrated aqueous solution of sodium bisulphite, collecting the crystalline product and decomposing it with sodium hydroxide or sodium carbonate

The ability of aldehydes to compete with " fuchsin " (magenta) for the possession of sulphurous acid forms the basis of SCHIFF'S TEST, in which a solution of fuchsin or " magenta " (p 690), decolorised by sulphurous acid, becomes pink again in presence of an aldehyde

(*c*) Aldehyde unites with hydrogen cyanide to form an addition compound which is known as a **cyanhydrin**

$$CH_3{\cdot}CH{=}O \xrightarrow{HCN} CH_3\,CH\begin{matrix}OH\\CN\end{matrix} \xrightarrow{H_2O} CH_3\,CH\begin{matrix}OH\\CO\,OH\end{matrix}$$

Acetaldehyde — Acetaldehyde cyanhydrin — Lactic acid

This addition does not take place when pure hydrocyanic acid is used, but only in presence of a trace of an alkali The real reagent is therefore not the molecule, HCN, but the CYANIDE ION, $CN^-$, and the action is represented by the following scheme

$$CH_3\,CH{=}O \rightarrow CH_3\,\overset{+}{C}H{-}\overset{-}{O} \rightarrow CH_3{\cdot}CH{-}O^{-} \xrightarrow{+2H_2O} CH_3\,CH{\cdot}OH$$

$$\overset{-}{C}N + \overset{+}{K} \qquad \overset{-}{C}N + \overset{+}{K} \qquad CN\ \ \overset{+}{K} \qquad CO\ \overset{-}{O}\overset{+}{K} + NH_3$$

In this scheme, one link of the double bond is ionised under the influence of the cyanide ion, which then attaches itself to the $C^+$ atom and

neutralises its charge, leaving a negative charge on the oxygen atom of the ionised cyanhydrin salt The carbon-to-carbon bond, which is thus formed, is, however, extremely stable Thus hydrolysis converts the cyanhydrin into an acid of the $C_3$ series The CYANHYDRIN REACTION is therefore of great value in ascending homologous series, *e g* from $C_2$ to $C_3$

Reactions of this type, in which the carbon skeleton of an organic compound is extended, are described as CONDENSATIONS In the cyanhydrin reaction, the condensation depends on (i) an addition reaction, but in the conversion of acetylene to benzene, and in the " aldol condensation " (p 697), it depends on a process of (ii) polymerisation Finally there is a large range of cases, *e g* the conversion of methyl iodide into ethane (p 663), or of aldehyde into crotonaldehyde (p 697), in which it is accompanied by the elimination of a molecule of some simple inorganic substance, such as iodine or water, and therefore comes under the general heading of (iii) COUPLING (Gerhardt, 1839)

**Addition reactions of olefines and aldehydes contrasted.**—It is of interest to note that, whilst ethylene combines readily with *strong* acids, such as $H_2SO_4$ and HCl, aldehydes combine only with *weak* acids, such as HCN This difference arises from the fact that the olefines form addition compounds with reagents which yield a *reactive kation*, whilst aldehydes form addition compounds with reagents which yield a *reactive anion*

(i) *Olefines* unite with concentrated sulphuric acid, and with anhydrous hydrogen chloride and bromide, because these yield a highly reactive proton, $H^+$, but they do not combine with dilute acids which contain the less reactive oxonium ion $H_3O^+$ They also combine with hypochlorous acid, HClO, which reacts as $HO^- + Cl^+$, and with chlorine, $Cl_2$, which reacts as $Cl^- + Cl^+$, compare the action of potash on chlorine

$$\overset{+}{K} + Cl—Cl + \overset{-}{O}H \rightarrow \overset{+}{K} + [\overset{-}{Cl} + \overset{+}{Cl}] + \overset{-}{O}H \rightarrow \overset{+-}{KCl} + ClOH$$

(ii) *Aldehydes*, on the other hand, unite with hydrides which yield reactive anions, *e g*

$$\overset{-}{C}N, \quad \overset{-}{N}H_2, \quad \overset{-}{O}\cdot SO\,\overset{-+}{O}Na$$

These ions are reactive because they are very ready to share their lone-pairs of electrons and thus to form covalent compounds The fact that their hydrides are all weak acids is clear proof of the readiness of these anions to share a lone-pair of electrons with a *proton*, and their readiness to form a similar link with *carbon* may be inferred by analogy On the other hand, strong acids, by definition, yield stable anions, *e g* $Cl^-$ and $SO_4^{-\,-}$; these have much less tendency to form covalent compounds and do not therefore form addition compounds with aldehydes

**Coupling with alcohol and with acetic acid.**—Although acetaldehyde does not combine with water (like chloral, p 701) to form a hydrate of the type $CH_3\,CH(OH)_2$, it combines with alcohol, with elimination of water in presence of solid calcium chloride, to form **acetal**,

$$CH_3\,CH(OC_2H_5)_2,$$

a liquid (boiling at 104°) in which the function of an ether appears twice in the same molecule, as it does in dioxan (p 735)

$$CH_3CH{=}O + \begin{matrix} H & O\,CH_2\,CH_3 \\ H & O\,CH_2\,CH_3 \end{matrix} \rightarrow CH_3CH\!\begin{matrix} O\,CH_2\,CH_3 \\ O\,CH_2\,CH_3 \end{matrix} + H_2O$$

Acetal has the formula of an addition compound of aldehyde and ether, but the latter is much too inert to combine in this way An interesting example of the activating influence of oxygen is provided by the direct combination of aldehyde with acetic anhydride to form **ethylideneglycol diacetate**

$$CH_3CHO + O(CO\,CH_3)_2 \rightarrow CH_3CH\!\begin{matrix} O\,CO\,CH_3 \\ O\,CO\,CH_3 \end{matrix}$$

In this compound (b -pt 179°) the functions of an ester (p 720) appear twice in the same molecule

**Coupling with bases** —An important group of derivatives is formed by coupling aldehydes with amino-compounds, with elimination of a molecule of water, according to the general equation,

$$>C{=}O + H_2N\,X \rightarrow >C{=}NX + H_2O,$$

where X represents a radical such as OH, $NH_2$, etc

(i) $CH_3CHO + H_2N\,OH \rightarrow CH_3CH{=}NOH + H_2O$
Hydroxylamine — Acetaldoxime

(ii) $CH_3CHO + H_2N\,NH_2 \rightarrow CH_3CH{=}N\,NH_2 + H_2O$
Hydrazine — Hydrazone of acetaldehyde

(iii) $CH_3CHO + H_2N\,NH\,C_6H_5 \rightarrow CH_3CH{=}N\,NH\,C_6H_5 + H_2O$
Phenylhydrazine — Phenylhydrazone of acetaldehyde

(iv) $CH_3CHO + H_2N\,NH\,CO\,NH_2 \rightarrow CH_3CH{=}N\,NH\,CO\,NH_2 + H_2O$
Semicarbazide — Semicarbazone of acetaldehyde

These products are formed by substitution of the bivalent radical=NX for oxygen, but it is probable that addition products are first formed (compare aldehyde-ammonia), with subsequent elimination of water, *e g*

$$CH_3CH{=}O \xrightarrow{+NH_2X} CH_3CH\!\begin{matrix} OH \\ NHX \end{matrix} \xrightarrow{-H_2O} CH_3CH{=}NX$$

These reactions are of importance because they give almost quantitative yields of derivatives of higher molecular weight, which usually crystallise readily from organic solvents and can be easily purified They are therefore generally used for the isolation and identification of aldehydes (including complex hydroxyaldehydes such as glucose), and have the further merit that the pure aldehyde can often be regenerated from them by hydrolysis, *i e.* by a reversal of the preceding equations.

**Polymerisation and condensation of acetaldehyde.**—On account of their unsaturated character, aldehydes share with olefines the property of undergoing polymerisation (i) When acetaldehyde is left in contact with a dilute solution of potassium carbonate it is converted into **aldol,** a compound of identical composition, but with twice as many atoms in the molecule

$$2C_2H_4O \rightarrow C_4H_8O_2$$

The product is a colourless, odourless liquid, which is miscible with water in all proportions and can be distilled unchanged under a pressure of 12 mm It is formed by adding one molecule of acetaldehyde to another, in accordance with the usual rule, whereby an atom of hydrogen is added to oxygen and the rest of the molecule (—$CH_2$ CHO) to carbon

$$2CH_3\,CHO \rightarrow CH_3\,CH\begin{matrix}\diagup OH\\ \diagdown CH_2\,CHO\end{matrix}$$

Since, however, the addition results in the formation of a carbon-to-carbon bond, the action cannot be reversed and we have definitely passed from the $C_2$ to the $C_4$ series, just as in preparing the cyanhydrin we pass from the $C_2$ to the $C_3$ series The preceding type of polymerisation is therefore described as the ALDOL CONDENSATION

(ii) The product of the aldol condensation is an alcohol-aldehyde which is capable of further condensation under the influence of alkalis to " aldehyde resin " Aldol itself, however, exhibits all the usual properties of an aldehyde , thus it reduces ammoniacal silver nitrate and is easily oxidised to $\beta$-hydroxybutyric acid and thence to acetoacetic acid (p 730), a condensation product of acetic acid

$$\underset{\text{Aldol}}{CH_3\,CH(OH)\,CH_2\,CHO} \rightarrow \underset{\beta\text{-Hydroxybutyric acid}}{\overset{\gamma}{C}H_3\,\overset{\beta}{C}H(OH)\,\overset{\alpha}{C}H_2\,COOH} \rightarrow \underset{\text{Acetoacetic acid}}{CH_3\,CO\,CH_2\,COOH}$$

When distilled under atmospheric pressure, aldol decomposes into water and an unsaturated aldehyde known as **crotonaldehyde .**

$$CH_3\,CH(OH)\,CH_2{\cdot}CHO \rightarrow CH_3{\cdot}CH{=}CH{\cdot}CHO + H_2O$$

This is a pungent liquid, which can be prepared directly from aldehyde, by heating it with dilute HCl, or with aqueous sodium acetate at 100° This condensation can be represented by the equation,

$$CH_3{\cdot}CH{=}O + H_2\,CH\,CH{=}O \rightarrow CH_3\,CH{=}CH{\cdot}CH{=}O\,,$$

but it is practically certain that an addition compound is first formed, just as with the bases described under (*e*) above

Crotonaldehyde is reduced by hydrogen in presence of a solid catalyst to ***n*-butyl alcohol**

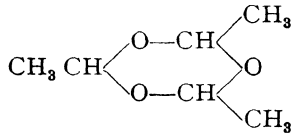
$$CH_3{\cdot}CH{=}CH{\cdot}CHO \xrightarrow{+4H} CH_3\,CH_2\,CH_2\,CH_2\,OH$$

By this process ethyl alcohol can be converted on a large scale into butyl alcohol, with acetaldehyde, aldol and crotonaldehyde as intermediate products

(iii) If a drop of sulphuric acid is added to aldehyde, it gets hot, contracts and yields a polymer (b -pt 124°) known as **paraldehyde**

$$3C_2H_4O \rightarrow C_6H_{12}O_3$$

If the same process is carried out below 0°, a solid product is obtained, which sublimes without melting at 112°, it has the same composition and molecular weight as paraldehyde and is known as **metaldehyde**, $C_6H_{12}O_3$ Both polymers can be reconverted into ordinary aldehyde by distilling with dilute sulphuric acid Since no new carbon-to-carbon bonds are formed, they are not regarded as condensation products but as cyclic anhydrides or ethers of the hydrate $CH_3\,CH(OH)_2$, and are formulated as follows



Since the aldehydic group is no longer present, it is not surprising that neither compound reduces ammoniacal silver nitrate

The two compounds appear to be stereoisomers (p 757), with the same structure, but with a different arrangement or configuration of the radicals in space Thus, since the methyl and hydrogen radicals do not lie in the plane of the ring, it is possible that one compound may have *three methyls* on one side of the ring and *three hydrogens* on the other side, whilst in the other compound there are *two methyls and one hydrogen* on one side, and *two hydrogens and one methyl* on the other side of the ring

## B Formaldehyde

**Preparation, properties and uses of formaldehyde.**—When methyl alcohol at a temperature of about 40° is vaporised in a current of air, and the mixture is passed over platinised asbestos, the alcohol is oxidised to **formaldehyde**, $CH_2O$, as shown in the equation

$$CH_4O + O \rightarrow CH_2O + H_2O$$

The product is a gas (b -pt −21°), but a 40% solution in water is sold as a disinfectant under the name of "formalin" This solution does not behave like an aqueous solution, but shows some similarity to propyl alcohol (b -pt 97°) and therefore probably consists to a large extent of the hydrate, **methylene glycol** $CH_2(OH)_2$ It distils below 100°, leaving behind a white solid residue of **paraformaldehyde**, $(CH_2O)_n$ Formaldehyde is a very active reagent, and is condensed with phenol, $C_6H_5\,OH$ (p 791), on a very large scale to form synthetic resins, which contain long-chain radicals such as .

$$—CH_2—O—C_6H_4—O—CH_2—O—C_6H_4—O—, \text{ etc.}$$

It also makes gelatine and glue insoluble in water, and is used in many organic syntheses

EXPT 153 **Preparation and properties of formaldehyde**

(*a*) Heat a spiral of platinum wire in the Bunsen flame, and plunge it quickly into a test tube containing a little methyl alcohol, so that the wire nearly touches the surface of the liquid Notice that it continues to glow and that formaldehyde can be detected by its strong smell

(*b*) Draw a current of air through an apparatus fitted up as shown in Fig 172 The flask *a* contains methyl alcohol and dips into a basin of warm water The vapour of the alcohol passes through a piece of combustion tubing containing platinised asbestos This is made by soaking asbestos fibre in a solution of platinum chloride and heating it until all the moisture and chlorine have been driven off The tube is heated at first with a Bunsen burner until the action starts, when enough heat will be developed to keep the asbestos glowing The vapours pass into a flask *b*, which is cooled with ice The liquid which condenses is a solution of formaldehyde in methyl alcohol

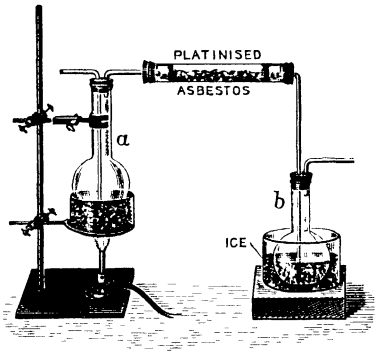



FIG 172
PREPARATION OF FORMALDEHYDE

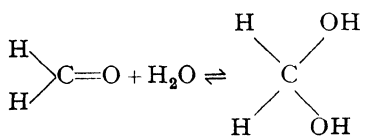
(*c*) A solution of the dye *magenta* is just bleached by bubbling sulphur dioxide through it The product is called Schiff's reagent (p 690) Try the effect on this solution of adding a few drops of formalin

(*d*) Add a few drops of formalin to a solution of silver nitrate in water and notice the colour of the precipitate

(*e*) Distil a small quantity of commercial formalin When about two-thirds of the quantity has distilled over, cool the remainder Notice that on standing it becomes white and solid

(*f*) Heat a little paraformaldehyde with water until it dissolves Notice the smell Test it with silver nitrate and with Schiff's reagent

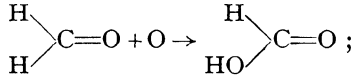
**Derivatives of formaldehyde.**—(*a*) *Hydration* —Formaldehyde shows many points of resemblance to acetaldehyde and must be represented by a similar structural formula , but it differs from acetaldehyde in the readiness with which it unites with water




Formaldehyde Methylene glycol

No alternative formulae are possible for formaldehyde, if we assume that hydrogen is univalent, oxygen is bivalent and carbon is quadrivalent

(*b*) *Oxidation* —Formaldehyde is oxidised readily to formic acid, just as acetaldehyde is oxidised to acetic acid,



Formaldehyde Formic acid

but since formic acid is itself a reducing agent (p 716) care is needed to prevent its further oxidation to carbon dioxide

(*c*) *Condensation* —In addition to its spontaneous and reversible polymerisation to paraformaldehyde, formaldehyde can be *condensed* in presence of lime water or magnesia to a sweet syrup, which contains a sugar, known as **formose**, $C_6H_{12}O_6$ This includes a chain of six carbon atoms and is perhaps a mixture of stereoisomers of glucose,

$$6CH_2O \rightarrow HO\,CH_2\,CH(OH)\,CH(OH)\,CH(OH)\,CH(OH)\,CH\quad O$$

It has therefore been suggested that formaldehyde (or an active isomer of formaldehyde, *e g* —CH(OH)—), is an intermediate product in the conversion of carbon dioxide (in presence of the green chlorophyll of leaves and under the influence of sunlight) into sugars of the formula $C_6H_{12}O_6$ or $C_{12}H_{22}O_{11}$, and starch, $(C_6H_{10}O_5)_n$ (p 741)

$$CO_2 + H_2O \rightarrow O_2 + CH_2O \quad \text{(Formaldehyde)},$$
$$6CH_2O \rightarrow C_6H_{12}O_6 \quad \text{(Glucose, etc )},$$
$$nC_6H_{12}O_6 \rightarrow nH_2O + (C_6H_{10}O_5)_n \quad \text{(Starch, etc )}$$

(*d*) *Action of ammonia* —Instead of combining like acetaldehyde with a single molecule of ammonia to form an addition compound, six molecules of formaldehyde couple up with four molecules of ammonia and lose six molecules of water to form a solid known as **hexamethylene tetramine**, $(CH_2)_6N_4$

$$6CH_2O + 4NH_3 \rightarrow C_6H_{12}N_4 + 6H_2O$$

This is used as a renal disinfectant under the name of **urotropine**

(*e*) *Action of caustic alkalis* —When formaldehyde is warmed with caustic soda or potash it undergoes self-oxidation and reduction to a formate and methyl alcohol as indicated in the equation

$$2CH_2O + KOH = CH_3OH + HCOOK$$

This behaviour, which is analogous to that of the aromatic aldehydes (p 787), is in marked contrast to that of acetaldehyde, which yields a resin of complex constitution.

## C. Chloral, Chloroform and Iodoform.

**Preparation and properties of chloral.**—**Trichloroacetaldehyde** or **chloral**, $CCl_3CHO$, was prepared in 1832 by the action of chlorine on alcohol, and is still made by a similar method. Chlorine is passed into cold alcohol, and then into the heated liquid, until no more is absorbed, on cooling, **chloral alcoholate** crystallises out, and is converted into chloral by distilling with concentrated sulphuric acid

$$\underset{\text{Alcohol}}{CH_3CH_2OH} \xrightarrow{Cl_2} \underset{\text{Aldehyde}}{CH_3CHO} \xrightarrow{3Cl_2} \underset{\text{Chloral}}{CCl_3CHO},$$

$$\underset{\text{Chloral}}{CCl_3CH{=}O} + \underset{\text{Alcohol}}{C_2H_5OH} \rightleftharpoons \underset{\text{Chloral alcoholate}}{CCl_3CH\begin{matrix}OH\\ O\,C_2H_5\end{matrix}}$$

Chloral is an oily liquid, boiling at 98°. It resembles the unsubstituted aldehydes in many of its properties. Thus it forms addition compounds with ammonia and with sodium bisulphite and has reducing properties, *e g* it is oxidised by hot fuming nitric acid to **trichloracetic acid** (p 713)

$$CCl_3CHO \rightarrow CCl_3CO\,OH$$

With a warm solution of sodium cyanide it undergoes a curious internal oxidation and reduction, whereby **dichloracetic acid** (p 713) is formed

$$CCl_3CHO + H_2O + NaCN \rightarrow CHCl_2CO\,OH + NaCl + HCN$$

When shaken with one-fifth of its volume of water, it becomes hot, and **chloral hydrate** crystallises out

$$CCl_3CH{=}O + H_2O \rightleftharpoons CCl_3CH(OH)_2$$

This violent combination with water is in complete contrast to the behaviour of acetaldehyde, since spectroscopic evidence shows that the double bond of acetaldehyde persists even in dilute aqueous solutions. The origin of this difference is discussed in Chapter LIII (p 714).

Expt 154 **Properties of choral hydrate**

(*a*) To a dilute solution of chloral hydrate in water add a little ammoniacal solution of silver nitrate and warm gently. A silver mirror is produced.

(*b*) Place a few grams of chloral hydrate crystals in a very small dry separating funnel. Cover the crystals with concentrated sulphuric acid and shake the mixture well. Observe the formation of an oily layer of chloral floating on the acid. Carefully remove the sulphuric acid, add a few drops of water to the oil and shake again. The mixture becomes hot and crystals of chloral hydrate are formed again.

(*c*) Add a little caustic soda solution to a solution of chloral hydrate in a test tube. Notice the smell of chloroform.

Chloral hydrate melts at 57°, boils at 97·5° and is freely soluble in water, it can be reconverted into chloral by distilling with sulphuric acid. It is used in medicine to induce sleep.

**Chloroform** or **trichloromethane**, $CHCl_3$ —When chloral is heated with an alkali, it breaks up into chloroform and a formate

$$\underset{\text{Chloral}}{CCl_3CHO} + NaOH = \underset{\text{Chloroform}}{CHCl_3} + \underset{\text{Sodium formate}}{HCOONa}$$

Chloroform is generally prepared, however, by the action of bleaching powder (p 286) on alcohol or acetone The reactions which occur are rather complex but may be represented as follows

(*a*) Alcohol and bleaching powder

$2CH_3CH_2OH + Ca(OCl)_2 = CaCl_2 + 2H_2O + 2CH_3CHO$ (Acetaldehyde),

$2CH_3CHO + 3Ca(OCl)_2 = 3Ca(OH)_2 + 2CCl_3CHO$ (Chloral),

$2CCl_3CHO + Ca(OH)_2 = Ca(OOCH)_2 + 2CHCl_3$ (Chloroform)

(*b*) Acetone and bleaching powder

$2CH_3COCH_3 + 3Ca(OCl)_2 = 3Ca(OH)_2 + 2CCl_3COCH_3$ (Trichloroacetone),

$2CCl_3COCH_3 + Ca(OH)_2 = Ca(OOCCH_3)_2 + 2CHCl_3$ (Chloroform)

Chloroform is also one of the products of the chlorination of methane, but is not made by this method

$$CH_4 + 3Cl_2 \rightarrow CHCl_3 + 3HCl$$

Chloroform is a heavy liquid, density 1 5, boiling at 61° It does not burn in air, but is readily oxidised to **phosgene** or **carbonyl chloride** (p 149), especially in sunlight or in presence of acids

$$CHCl_3 + O \rightarrow COCl_2 + HCl$$

Since chloroform is used as an anaesthetic, it is essential that this poisonous oxidation product should not be present , chloroform should therefore be stored in small full bottles (preferably brown rather than blue in colour) and is often mixed with 1% of alcohol in order to eliminate hydrogen chloride and carbonyl chloride as fast as they are formed

Chloroform can be recognised by the fact that it gives an intolerable odour of **phenyl carbylamine** or *isocyanide*, $C_6H_5NC$, when warmed with aniline and an alcoholic solution of caustic soda

$$C_6H_5NH_2 + CHCl_3 + 3KOH \rightarrow C_6H_5\overset{+}{N}\equiv\overset{-}{C} + 3KCl + 3H_2O$$

Chloroform is not attacked by water, but is hydrolysed to a formate by heating with caustic soda or caustic potash, especially in alcoholic solution $CHCl_3 + 4KOH = HCOOK + 3KCl + 2H_2O$

EXPT 155 **Preparation and properties of chloroform.**

(*a*) Grind 100 grams of bleaching powder into a smooth cream with 100 c c of water in a mortar, and transfer the product to a 1-litre round-bottomed flask with the aid of 250 c c of water Fit the flask with a cork and water-cooled reflux condenser, then pour 35 c c of acetone down the condenser and swirl the flask round to mix the ingredients thoroughly Heat the flask on a water-bath until the reaction starts (shown by bubbling), when the latter subsides, reheat the flask for about five minutes Now cool the flask in a bath of cold water, so that as little chloroform as

possible is lost whilst the condenser is rearranged for distillation, as in Fig 176, p 726 Then heat the flask again on a water-bath until no more oily drops of chloroform distil over Shake the distillate in a separating funnel with a very dilute solution of caustic soda to remove acid impurities, then run off the lower layer of chloroform and dehydrate it with calcium chloride for about twenty minutes Distil the chloroform from a small distillation flask, fitted with a water-cooled condenser, and collect the fraction which boils between 60° and 63°

(*b*) Wash a little chloroform by shaking it with water and remove the aqueous layer Then add more water and a little silver nitrate solution and shake again Is any precipitate formed?

(*c*) Boil a few drops of chloroform with an alcoholic solution of caustic soda, then add dilute nitric acid until the liquid is acid Test for *chloride* by adding silver nitrate solution

(*d*) Boil 1 c c of chloroform with 3 c c of Fehling's solution for about five minutes What deduction can you draw?

**Iodoform,** $CHI_3$, may be prepared in a similar manner to chloroform, by the action of sodium hypoiodite ($NaOH + I_2$) on ethyl alcohol or acetone :

$$CH_3\,CH_2{\cdot}OH \rightarrow CH_3{\cdot}CHO \rightarrow CI_3{\cdot}CHO \rightarrow CHI_3 + H\,CO\,ONa,$$

$$CH_3{\cdot}CO\,CH_3 \rightarrow CH_3\,CO\,CI_3 \rightarrow CHI_3 + CH_3\,CO\,ONa$$

Since methyl alcohol does not give iodoform under these conditions, this reaction can be used as a qualitative test to distinguish it from ethyl alcohol Iodoform is a yellow crystalline solid (m -pt 119°), which is almost insoluble in water but moderately soluble in alcohol It has a characteristic penetrating smell, and is used extensively as an antiseptic.

EXPT 156 **Preparation of iodoform.**

(*a*) Add 4 c c of industrial alcohol to 1 gram of iodine in a test-tube Then add 4 c c of a 10% solution of caustic soda, and shake vigorously until the brown colour of the iodine has been completely replaced by a yellow precipitate of iodoform

(*b*) Repeat (*a*), using 1 c c of acetone in place of ethyl alcohol

## D ACETONE

**Preparation and purification of acetone.**—(*a*) **Acetone,** $CH_3\,CO\,CH_3$, is a minor product of the distillation of wood and therefore occurs with methyl alcohol in "wood spirit" (p 678) It can also be manufactured directly from starch by the action of a bacterium which converts the starch into acetone and *n*-butyl alcohol instead of into ethyl alcohol and carbon dioxide

(*b*) Acetone can be prepared by distilling calcium acetate (p 710)

$$CH_3{\cdot}CO{\cdot}\dot{\underset{\cdot}{\overset{\cdot}{O}}}\,\overset{-}{\underset{}{}}\,\overset{++}{Ca}\,\overset{-}{\underset{}{}}\,\dot{\underset{\cdot}{\overset{\cdot}{O}}}\,CO\;\;CH_3 \rightarrow CH_3\,CO\,CH_3 + CaCO_3$$

MIXED KETONES, containing two different alkyl radicals, can be prepared by using a mixture of fatty acids in this preparation Thus **methylethyl ketone,** $CH_3 CO C_2H_5$, is formed (together with acetone and diethyl ketone) by distilling a mixture of calcium acetate and calcium propionate

$$CH_3{\cdot}CO\ \overset{-}{O}\ \overset{++}{Ca}\ \overset{-}{O}\ CO\ C_2H_5 \rightarrow CH_3 CO C_2H_5 + CaCO_3$$

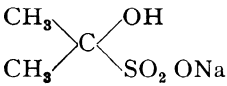
Aldehydes can also be prepared by this method (p 690) by using calcium formate as one of the two salts, but, as in the case of ketones, the yields are poor Acetone, however, is made from acetic acid by a continuous process, in which the vapour of acetic acid is passed over quicklime (or thorium dioxide), heated to a temperature at which the calcium (or thorium) salt is decomposed as fast as it is formed

$$2CH_3{\cdot}CO{\cdot}OH \rightarrow CH_3{\cdot}CO\ CH_3 + H_2O + CO_2$$

(*c*) Acetone is now manufactured on a large scale directly from ethyl alcohol by a process in which a mixture of alcohol and steam is passed over a solid catalyst (ferric oxide and chalk ?) which promotes the liberation of hydrogen and carbon dioxide from this mixture

$$2C_2H_6O + H_2O = C_3H_6O + CO_2 + 4H_2$$

Crude acetone can be separated from methyl alcohol and other organic compounds of similar boiling-point by conversion into the solid **bisulphite compound** This is drained and washed, and is then decomposed by distillation with a solution of sodium carbonate




$$+ Na_2CO_3 \rightarrow CH_3 CO CH_3 + Na_2SO_3 + NaHCO_3$$

An even more specific method of purification is to saturate nearly pure acetone with sodium iodide and then to cool with ice and salt, in order to secure a maximum yield of the crystalline product, NaI, $3C_3H_6O$ The acetone is recovered in a very pure state by warming the dry crystals

Acetone is a volatile liquid (b -pt 56°) with a pleasant odour It mixes in all proportions with water, alcohol and ether, and is used industrially as a solvent for acetylene (p 675), nitrocellulose (p 741), etc When it has been used as a solvent, the vapour can be recovered by absorbing it in a strong solution of bisulphite and liberating it by distillation with sodium carbonate as described above

EXPT 157 **Properties of acetone**

(*a*) Notice the characteristic smell of acetone Determine its boiling-point, and notice the appearance of the flame when acetone burns Test its miscibility with water, alcohol and ether

(*b*) Carry out or recall Expts 155 (*a*) (p 702) and 156 (*b*) (p 703)

(*c*) Prepare a concentrated aqueous solution of sodium bisulphite and mix with it an equal volume of acetone Shake well until a crystalline precipitate is obtained Remove the crystals on a filter Mix them with a little sodium carbonate solution and distil Acetone distils over

(*d*) To a small amount of acetone in a dry flask add three times its weight of phosphorus pentachloride The latter dissolves, and the liquid turns yellow Pour it into a mixture of ice and water and allow it to stand for some time Separate the heavy layer from the aqueous solution, wash it by shaking with a small quantity of fresh water. Separate the lower layer again Dry it by means of anhydrous sodium sulphate, and purify it by distillation Notice the boiling-point of the product

**Structure and reactions of acetone.**—(*a*) *Chlorination* —The presence of a carbonyl group in acetone can be shown by the action of phosphorus pentachloride, which converts it into **dichloropropane,**

$$C_3H_6O + PCl_5 = C_3H_6Cl_2, + POCl_3$$

*without liberation of hydrogen chloride* (compare acetaldehyde, p 692)

(*b*) *Reduction and oxidation* —The carbonyl group is also indicated by reducing acetone to *iso*-**propyl alcohol** by sodium amalgam

$$CH_3\ CO\ CH_3 + 2H = CH_3\ CH(OH)\ CH_3$$

This alcohol can be identified as a secondary alcohol (p 685) by its re-oxidation to acetone, and by the fact that it cannot be oxidised (like a primary alcohol) to an acid with an equal number of carbon atoms, since it yields only acetic acid and carbon dioxide

$$CH_3\ CO\ CH_3 + 4O \rightarrow CH_3\ CO\ OH + CO_2 + H_2O.$$

(*c*) *Addition compounds* —Acetone does not combine with ammonia, but it resembles the aldehydes in forming addition compounds with prussic acid, and with sodium bisulphite

$$CH_3{\cdot}CO\ CH_3 + HCN \rightarrow \begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!C\!<\!\!\begin{matrix} OH \\ CN \end{matrix}$$ (Acetone cyanhydrin),

$$CH_3\ CO\ CH_3 + NaHSO_3 \rightarrow \begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!C\!<\!\!\begin{matrix} OH \\ SO_2\ ONa \end{matrix}$$ (Bisulphite compound)

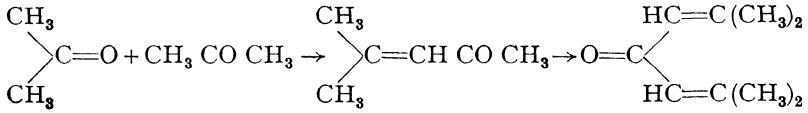
(*d*) *Coupling with bases* —Acetone combines with all the usual reagents of the type $NH_2X$ (p 696) except ammonia itself .

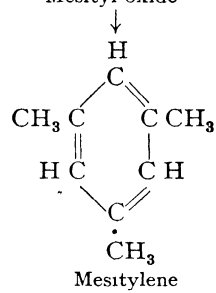
$$CH_3\ CO\ CH_3 + H_2N{\cdot}OH \rightarrow \begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!C{=}N{\cdot}OH + H_2O$$ (Acetoxime),

$$CH_3{\cdot}CO\ CH_3 + H_2N{\cdot}NH{\cdot}C_6H_5 \rightarrow \begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!C{=}N\ NH\ C_6H_5 + H_2O$$ (Phenylhydrazone),

$$CH_3{\cdot}CO\ CH_3 + H_2N\ NH{\cdot}CO\ NH_2 \rightarrow \begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!C{=}N\ NH\ CO{\cdot}NH_2 + H_2O$$ (Semicarbazone).

(*e*) *Condensation* —In presence of sulphuric acid, water is eliminated from the carbonyl group of one molecule and a methyl group of another



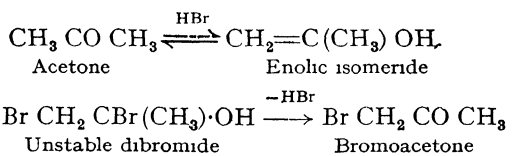




Mesitylene

**Mesityl oxide** is of interest as an UNSATURATED KETONE, which combines the properties of a ketone with those of an olefine It is also remarkable in that, like acetaldehyde, it forms an addition compound with ammonia (p 694) , but the radicals, $NH_2$ and H, are added to the olefinic double bond, and not to the carbonyl group (p 784)

The final product is an aromatic hydrocarbon, **mesitylene,** or *sym*-**trimethylbenzene,** $C_9H_{12}$, in which a ring of six carbon atoms has been formed by the elimination of three molecules of water from three molecules of acetone It might be expected that, under similar conditions, three molecules of acetaldehyde might condense to form a molecule of benzene, by eliminating three molecules of water This does not occur , but a precisely analogous condensation takes place when acetylene (from which acetaldehyde can be prepared by hydration, p 689), polymerises directly to benzene without change of composition

**Action of bromine on acetone.**—It has been found that the velocity with which bromine acts upon acetone is *independent of the concentration of bromine*, but is *proportional to the concentration of hydrogen bromide* This surprising observation can be explained by supposing that acetone does not react directly with bromine, but that the bromine acts only upon the enolic isomeride of the ketone (p 690)




The hydrogen bromide is assumed to act as a catalyst, which increases the velocity of transformation of acetone into the enol and *vice versa*, but

without altering the proportions in which the two isomerides are in equilibrium with one another Since only a trace of the enol is formed in this equilibrium, the velocity of bromination depends on the *rate* of enolisation , it is therefore proportional to the catalytic activity of the acid, and can be used to compare the catalytic activities of different acids and bases

**General properties of ketones.**—Acetone and its homologues resemble the aldehydes in many of their properties, *e g* in forming addition compounds with hydrogen cyanide and with sodium bisulphite, and in coupling with bases, such as phenylhydrazine , but the following points of contrast should also be noted

(i) Ketones are not easily oxidised and are therefore without action on Fehling's solution, ammoniacal silver nitrate, etc

(ii) When oxidised, they are converted into carboxylic acids with a *smaller* number of carbon atoms

(iii) On reduction, they yield *secondary* instead of primary alcohols, *e g* acetone gives *iso*-propyl alcohol, $CH_3 CH(OH) CH_3$

(iv) They are a little less ready to form addition compounds, and in particular they do not combine directly with ammonia

(v) They are not polymerised by the action of acids and alkalis, although (like the aldehydes) they readily undergo condensation *with elimination of water*

**Methyl ethyl ketone**, $CH_3 CH_2 CO CH_3$, a by-product of the preparation of acetone from wood-spirit, is the simplest example of a MIXED KETONE It can be prepared by distilling a mixture of calcium acetate and calcium propionate,

$$\begin{matrix} C_2H_5\ CO\ O^- \\ \\ CH_3\ CO\ O^- \end{matrix} \quad Ca^{++} \rightarrow \quad \begin{matrix} C_2H_5 \\ \diagdown \\ \\ \diagup \\ CH_3 \end{matrix} \!\!> CO + CaCO_3 ,$$

but it is obtained more readily from the normal butylene of cracked petroleum gases, as follows

$$\underset{n\text{-Butylene}}{CH_3 CH_2 CH{=}CH_2} \xrightarrow{+H_2O} \underset{sec\text{-Butylalcohol}}{CH_3 CH_2 CH(OH) CH_3} \xrightarrow{-2H} \underset{\text{“ M E K ”}}{CH_3 CH_2 CO{\cdot}CH_3}.$$

Methyl ethyl ketone resembles acetone, but boils 25° higher at 81° instead of 56° It was used under the abbreviated title “ M E K ” instead of acetone as a solvent in the preparation of cordite from gun-cotton and nitroglycerine , but it also has important chemical applications Thus, it can be reduced to *sec*-butyl alcohol, and is readily oxidised to propionic, acetic and carbonic acids , but it can also be oxidised by selenium dioxide to **diacetyl**, $CH_3{\cdot}CO{\cdot}CO\ CH_3$, the simplest example of an α-diketone This is a yellow liquid, with a characteristic odour It can be reduced to **acetoin**, $CH_3{\cdot}CH(OH)\ CO{\cdot}CH_3$, the aliphatic analogue of benzoin (p 787), and an isomer of ethyl acetate and of butyric acid (p 719) Acetoin is present in butter, to which it imparts a characteristic flavour and odour, apparently by oxidation to diacetyl. An optically

active form of acetoin, prepared by fermentation of sugar with a special organism, is therefore sold as a " butter-flavour "

The reactivity of the methylene group in M E K is obviously due to its contiguity to the >CO group, but may perhaps be associated (like the bromination of acetone) with the possibility of enolisation

$$—CH_2·CO— \rightleftharpoons —CH=C(OH)—$$

This reactivity is further illustrated by the fact that M E K interacts with nitrous acid to form the **monoxime** of diacetyl, from which the parent diketone can then be prepared by hydrolysis

$$\underset{\text{Methylethyl ketone}}{CH_3CH_2CO} + \underset{\text{Nitrous acid}}{ONOH} \xrightarrow{-H_2O} \underset{\text{Diacetyl monoxime}}{CH_3C(=NOH)CO} \xrightarrow[+HCl]{+H_2O} \underset{\text{Diacetyl}}{CH_3C(=O)CO} + \underset{\text{Hydroxylamine hydrochloride}}{H_2NOH, HCl}$$

The **dioxime** is used as a test for nickel (p 404) under the name of **dimethyl glyoxime**

$$HON=C(CH_3)\,C(CH_3)=NOH.$$

# CHAPTER LIII

## CARBOXYLIC ACIDS

### A. Acetic Acid.

**Preparation of acetic acid.**—(i) When fermented liquors are exposed to the air they become sour, owing to the oxidation to **acetic acid** of the alcohol which they contain.

$$CH_3{\cdot}CH_2\,OH + O_2 = CH_3\,CO\,OH + H_2O.$$

This oxidation is brought about under the influence of an organism known as *Mycoderma aceti*, and cultures of this organism on birch twigs are used to convert malt liquors into vinegar. It is also effected on a large industrial scale by oxidation in presence of a solid catalyst in much the same way as aldehyde is oxidised to acetic acid under (iii) below

(ii) Acetic acid is also produced by the distillation of wood, which yields an aqueous distillate known as " pyroligneous acid " (p 678). This liquid contains about 10% of acetic acid, which is isolated by neutralising with chalk or lime, evaporating down to separate solid **calcium acetate,** heating to get rid of tar and resinous matter and then distilling with hydrochloric acid

$$Ca(C_2H_3O_2)_2 + 2HCl \rightarrow CaCl_2 + 2C_2H_4O_2$$

(iii) Acetic acid is now manufactured from calcium carbide Acetylene, liberated by the action of water on the carbide, is passed into dilute sulphuric acid in which mercuric oxide is held in suspension by vigorous stirring, the acetaldehyde thus produced is oxidised by air in presence of manganous acetate at 25° to 40°·

$$C_2H_2 + H_2O = CH_3{\cdot}CHO\,,\quad 2CH_3{\cdot}CHO + O_2 = 2CH_3\,CO{\cdot}OH.$$

(iv) Acetic acid can be synthesised from methyl alcohol and carbon monoxide at 320° under a pressure of 200 atmospheres in presence of phosphoric acid and copper phosphate

$$CH_3\,OH + CO = CH_3\,CO{\cdot}OH$$

(v) In the laboratory, acetic acid can be synthesised from methyl alcohol, through the iodide and cyanide (p 767).

$$CH_3\,OH \xrightarrow{HI} CH_3{\cdot}I \xrightarrow{KCN} CH_3\,CN \xrightarrow{2H_2O} CH_3{\cdot}CO{\cdot}ONH_4\,(\text{Ammonium acetate}).$$

The cyanide radical forms a carbon-to-carbon bond with the methyl radical, and this bond persists when the nitrogen is eliminated in the form of ammonia by hydrolysis.

Acetic acid can be purified by converting it into **sodium acetate**, $NaC_2H_3O_2$, $3H_2O$, and distilling the fused anhydrous salt with concentrated sulphuric acid to produce **glacial acetic acid** This name is given because the anhydrous acid (b -pt 119°, m -pt 16 7°) freezes very readily in cold weather Distillation from potassium dichromate can be used to remove impurities from the glacial acid, since acetic acid is resistant to oxidation by chromic acid ; but the final purification is effected by freezing, and then pouring off the residues until the freezing-point of the liquid is constant

EXPT 158 **Properties of glacial acetic acid.**

Cool a quantity of glacial acetic acid in a boiling-tube by plunging it into a mixture of ice and water Observe the appearance of the crystals Ascertain the temperature at which the crystals form Boil a small quantity in a test tube and find out whether the vapour is inflammable

**Structure and reactions of acetic acid** —The presence of an unique *hydrogen* atom in acetic acid is shown by the fact that it is a monobasic acid , the presence of a *hydroxyl group* is shown by displacing this group with chlorine by the action of phosphorus trichloride , the presence of a *methyl group* is shown by its synthesis from methyl alcohol , the presence of a bivalent *carbonyl group* can then be inferred by subtraction, since this is the residue by which the univalent methyl and hydroxyl radicals are held together in the molecule $CH_3\,CO\,OH$ Alternatively, in view of its synthesis from methyl cyanide, we can regard acetic acid as derived by the union of a univalent methyl group with a univalent CARBOXYL GROUP, $—CO_2H$ This summary proof of the structure of acetic acid is amplified in the following paragraphs, in which some of the principal derivatives of acetic acid are described

(*a*) **Acetates** —Acetic acid is a weak monobasic acid, in which one only of the four hydrogen atoms can be replaced by metals, yielding a series of soluble ACETATES Thus **sodium acetate**, $CH_3\,CO\,ONa$, $3H_2O$, crystallises from aqueous solutions with three molecules of water of crystallisation When distilled with caustic soda (or soda-lime) the anhydrous salt liberates **methane** and leaves a residue of sodium carbonate

$$CH_3{\cdot}CO\,ONa + NaO{\cdot}H \rightarrow CH_4 + NaO\,CO\,ONa$$

**Calcium acetate**, $(CH_3\,CO\,O)_2Ca$, also splits off carbon dioxide (in the form of chalk) when heated, but gives a distillate of acetone

$$CH_3\,CO{\cdot}O\,Ca\,O\,CO{\cdot}CH_3 \rightarrow CH_3\,CO\,CH_3 + CaCO_3$$

**Ammonium acetate**, $CH_3\,CO\,ONH_4$, on the other hand, splits off a molecule of *water* when distilled and gives a distillate of **acetamide**, $CH_3\,CO\,NH_2$ (p 712) , when heated with phosphoric oxide it loses two molecules of water and is converted into **acetonitrile**, $CH_3\,C{\equiv}N$, which is identical with **methyl cyanide** prepared by the action of potassium cyanide on methyl iodide **Lead acetate**, $(CH_3\,CO\,O)_2Pb$, $3H_2O$, prepared by dissolving lead carbonate in acetic acid, is known as " sugar of lead," since it has a sweet taste , but its use in mediaeval times to sweeten sour wine had fatal results and was therefore prohibited under penalty of death

(*b*) **Acetyl chloride,** $CH_3\,CO\,Cl$ If phosphorus trichloride is added gradually to glacial acetic acid, which is then warmed to expel hydrogen chloride and finally distilled, acetyl chloride is obtained as a liquid, boiling at 55°, which fumes in the air like phosphorus pentachloride:

$$3CH_3{\cdot}CO\,OH + PCl_3 \rightarrow 3CH_3\,CO\,Cl + H_3PO_3$$

Acetyl chloride is one of the most active liquids in organic chemistry Thus it is hydrolysed quickly to **acetic acid** by water, gives **ethyl acetate** with alcohol, and **acetamide** with ammonia or ammonium carbonate

$$CH_3\,CO\,Cl + H_2O \rightarrow HCl + CH_3\,CO\,OH \quad \text{(Acetic acid)},$$

$$CH_3\,CO\,Cl + C_2H_5\,OH \rightarrow HCl + CH_3\,CO\,OC_2H_5 \quad \text{(Ethyl acetate)},$$

$$CH_3\,CO\,Cl + 2NH_3 \rightarrow NH_4Cl + CH_3\,CO\,NH_2 \quad \text{(Acetamide)}$$

In general, acetyl chloride can be used to introduce the ACETYL RADICAL, $CH_3\,CO$—, in place of hydrogen in any alcohol and in any derivative of ammonia which still carries a hydrogen atom on the nitrogen, *e g*

$$\underset{\text{Aniline}}{C_6H_5\,NH_2} + CH_3\,CO\,Cl \rightarrow \underset{\text{Acetanilide}}{C_6H_5\,NH\,CO\,CH_3} + HCl.$$

The chlorine atom in acetyl chloride is much more reactive than that in ethyl chloride, $C_2H_5Cl$, just as the hydroxyl group in acetic acid is more reactive than that in ethyl alcohol in each case the superior activity is obviously due to the presence of the carbonyl group

| | |
|---|---|
| $CH_3\,CH_2\,OH$ (neutral), | $CH_3\,CH_2\,Cl$ (reactive), |
| $CH_3\,CO\,OH$ (acidic), | $CH_3\,CO\,Cl$ (intensely reactive). |

EXPT 159 **Preparation and properties of acetyl chloride**

(*a*) About 20 grams of glacial acetic acid are placed in a small distilling flask, fitted with a dropping funnel and a Liebig's condenser (Fig 173).

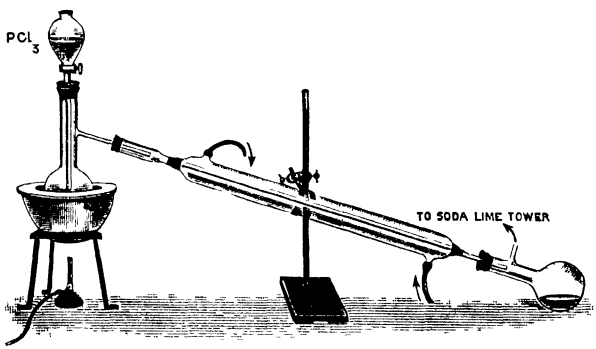



FIG 173 PREPARATION OF ACETYL CHLORIDE

About 16 grams of phosphorus trichloride are added slowly from the dropping-funnel to the acetic acid, which is warmed on the water bath

to 50° The hydrogen chloride, which is formed first on account of the presence of water in the glacial acetic acid, is absorbed by passing it through a soda-lime tower (not shown in the diagram) The mixture is then heated to the boiling-point of water, when acetyl chloride distils over

(*b*) Note the effect of adding a little water to an equal quantity of acetyl chloride in a test tube

(*c*) Add a little alcohol to acetyl chloride in a test tube Cool the mixture and add a strong solution of common salt Notice the separation of a layer of ethyl acetate, which is recognised by its smell

(*c*) **Acetic anhydride,** $(CH_3\,CO)_2O$, cannot be prepared by the direct dehydration of acetic acid, but is readily produced by the action of acetyl chloride on sodium acetate

$$CH_3\,CO\,\overset{-}{O}\;\overset{+}{Na} + Cl{\cdot}CO\,CH_3 \rightarrow NaCl + CH_3\,CO\,O\,CO\,CH_3$$

It is a pungent liquid, boiling at 137°, which is hydrolysed only slowly to acetic acid and is used like acetyl chloride as an ACETYLATING AGENT

$$(CH_3\,CO)_2O + H_2O \rightarrow 2CH_3\,CO\,OH,$$

$$(CH_3\,CO)_2O + C_2H_5\,OH \rightarrow \underset{\text{Ethyl acetate}}{CH_3\,CO\,OC_2H_5} + \underset{\text{Acetic acid}}{CH_3\,CO\,OH},$$

$$(CH_3\,CO)_2O + 2NH_3 \rightarrow \underset{\text{Ammonium acetate}}{CH_3\,CO\,ONH_4} + \underset{\text{Acetamide}}{CH_3\,CO\,NH_2}$$

EXPT 160 **Preparation and properties of acetic anhydride.**

(*a*) Introduce 25 grams of powdered anhydrous sodium acetate into a dry distilling flask Add slowly 20 grams of acetyl chloride, cooling the flask in cold water and shaking to mix the ingredients thoroughly Then attach a condenser and thermometer and heat very cautiously Acetic anhydride distils over between 130° and 140° Note its smell

(*b*) Gently boil a mixture of equal volumes (5 c c ) of glacial acetic acid, acetic anhydride and aniline ($C_6H_5NH_2$), in a small round-bottomed flask fitted with a reflux water-cooled condenser After half an hour, pour the hot liquid gradually and with constant stirring into 100 c c of cold water Recrystallise the precipitate of crude acetanilide, $C_6H_5NH\,CO\,CH_3$, from about 30 c c of 50% aqueous acetic acid Wash the purified crystals with cold water, dry them, and determine their melting point (113°) The *acetylation* effected in this experiment may be represented thus

$$C_6H_5NH_2 + (CH_3CO)_2O = CH_3COOH + C_6H_5NH\,CO\,CH_3.$$

(*d*) **Acetamide,** $CH_3{\cdot}CO\,NH_2$, is prepared by distilling ammonium acetate, and collecting the portion which distils above 213° :

$$CH_3{\cdot}CO\,ONH_4 \rightarrow CH_3{\cdot}CO{\cdot}NH_2 + H_2O.$$

It is a solid, which melts at 82°, boils at 220° and usually smells of mice. It is an example of an ACID AMIDE, and is discussed on p. 762.

**Expt. 161 Preparation and properties of acetamide.**

(*a*) Heat about 100 grams of ammonium acetate in a 500 c c flask, fitted with a cork and upright tube of about 1 cm diameter and 40 cms in height supported by a clamp At the top of the open tube place a thermometer, with its bulb as high up as possible, fitted into a cork which has been cut at the side to leave part of the end open to the air Continue to heat the flask and contents for about five hours so that the thermometer registers 100° In this way most of the water is driven off and a crude specimen of acetamide is left in the flask Distil the acetamide into an air condenser and collect that fraction which comes over above 180°, then redistil, collecting the fraction which comes over above 200° Note the smell of the product

(*b*) Heat a small portion of acetamide with caustic soda in a test tube, identify the gas evolved

(*c*) Warm acetamide with acidified sodium nitrite What gas is evolved?

(*d*) Mix 10 grams of acetamide with 15 grams of phosphoric oxide in a small dry distilling flask and heat over a small flame The flask should be attached to a condenser The acetonitrile which distils over is purified by redistillation It boils at 82°

(*e*) **Chloracetic acids** When gaseous chlorine is passed into glacial acetic acid, particularly in presence of a halogen carrier such as iodine, it displaces the three hydrogen atoms of the methyl radical, without attacking the hydroxylic hydrogen

$$CH_3\,CO\,OH + Cl_2 = HCl + CH_2Cl\,CO\,OH \text{ (Monochloracetic acid)},$$
$$CH_2Cl\,CO\,OH + Cl_2 = HCl + CHCl_2\,CO\,OH \text{ (Dichloracetic acid)},$$
$$CHCl_2\,CO\,OH + Cl_2 = HCl + CCl_3\,CO\,OH \text{ (Trichloracetic acid)}$$

**Monochloracetic acid** (m -pt 62°) is used in the preparation of glycine (p 763), ethyl malonate (p 751) and indigo **Dichloracetic acid**, already described as a transmutation product of chloral (p 701), is a liquid The final product, **trichloracetic acid**, $CCl_3\,CO\,OH$ (m -pt 55°), is identical with the acid obtained by oxidising chloral with nitric acid

$$CCl_3\,CHO \rightarrow CCl_3\,CO\,OH$$

(*f*) **Ethyl acetate**, $CH_3\,CO\,OC_2H_5$, distils as a volatile liquid (b -pt 77°) with a fragrant odour of apples, when a mixture of acetic acid and alcohol is heated to 140° with concentrated sulphuric acid (Expt 167)

$$CH_3\,CO\,OH + C_2H_5\,OH = CH_3\,CO\,OC_2H_5 + H_2O$$

Compounds of this type, in which the acidic hydrogen of an acid is displaced by an alkyl group, are described as ESTERS, and are discussed in greater detail in the next chapter

**Reactivity of acetic acid.**—(*a*) *Acidity of the carboxyl-group* We have already seen (p 687) that the hydroxylic hydrogen of alcohol is more reactive than that of the hydrocarbons, because the electronegative oxygen is reluctant to share its electrons with another atom and is therefore ready

to relinquish its hold upon the proton and to pass into an ethoxyl ion, *e.g* in the presence of metallic sodium

$$CH_3\,CH_2\,OH \rightarrow CH_3\,CH_2\,\bar{O}$$

We have also seen that the influence of the oxygen extends to the contiguous methylene group, since the hydrogen atoms of this group are more reactive than those of the methyl group This effect is attributed to an " electron-drift " of the electrons in the direction of the electronegative oxygen atom In acetic acid, the two hydrogens of the methylene group have both been replaced by an atom of oxygen, so that the carboxyl group contains *two* electronegative atoms In these circumstances it is not surprising that this group will hand over its proton to any substance which will *accept* it, *i e* to any base, instead of merely to a metal like sodium as in the alcohols We are therefore dealing, by definition, with an acid which will form a salt with any base, and thus has all the usual attributes of a weak acid

(*b*) *Acylous and basylous radicals* —Trichloracetic acid is much stronger than acetic acid, in virtue of the introduction of three halogens into the methyl radical To account for this, we must notice that chlorine is even more strongly electronegative than oxygen, since the chloride ion is extremely stable, and hydrogen chloride is a much more active proton-donor than water In trichloracetic acid, the chlorine and hydrogen are separated by two atoms of carbon and one atom of oxygen, but the facts compel us to recognise that the electron-drift, $\overleftarrow{Cl—C—C—O—H}$, must extend along the chain of five atoms, since the presence of the chlorine obviously weakens the attachment of the hydrogen to oxygen, as is shown by the fact that it gives rise to a much stronger acid

| $CH_3\,CH_3$ | $CH_3\,CH_2\,OH$ | $CH_3\,CO\,OH$ | $CCl_3\,CO\,OH$ |
|---|---|---|---|
| Inert | Reactive | Acidic | Strongly acidic |

Substituents such as —Cl, —O—, OH, $NO_2$, etc , which thus increase the strength of an acid are described as ACYLOUS RADICALS , but the effects which they produce decrease very rapidly as they are displaced away from the carboxyl group, *e g* along a chain of carbon atoms Acylous radicals are all characterised by a great affinity for electrons and invariably contain electronegative atoms Substituents which have the opposite effect are described as BASYLOUS RADICALS

(*c*) *Formation of hydrates* —The greediness which makes an atom of oxygen or chlorine reluctant to act as a " donor " by sharing a lone pair of electrons with a proton, has also the converse effect of making it eager, as an " acceptor," to share a lone pair of electrons belonging to a hydroxyl ion Acylous radicals, which weaken the hold of contiguous atoms on a proton therefore strengthen their hold on the hydroxyl radical or ion The readiness with which chloral yields a hydrate, as compared with the inability of acetaldehyde to combine with water (p 701), can therefore be attributed to the same causes which make trichloracetic acid so much stronger than acetic acid , and, in the same way, the greater readiness of formaldehyde to become hydrated may be correlated with the greater strength of formic acid (p 715).

## B Formic Acid

**Preparation and purification.**—Formic acid, $H_2CO_2$, the lower homologue of acetic acid, derives its name from its presence in stinging ants (Latin *formica*, an ant) Sodium formate is synthesised industrially by passing carbon monoxide under pressure into a 10% solution of sodium hydroxide heated to 160°

$$CO + NaOH \rightarrow H\,CO\,ONa$$

Formic acid (97-98%) can then be prepared by distilling sodium formate with twice its weight of sodium hydrogen sulphate In the laboratory formic acid is generally made by heating oxalic acid with glycerol at 110° (p 737), when the oxalic acid loses carbon dioxide as shown in the equation

$$H\,O\,CO{\cdot}CO\,OH \rightarrow H\,CO\,OH + CO_2$$

The mechanism of this decomposition is discussed on p 737

Since formic acid is decomposed by strong sulphuric acid, it cannot be purified in the same way as acetic acid It is therefore converted into the lead salt by boiling the crude aqueous acid with lead carbonate, and extracting repeatedly with boiling water, from which crystals of **lead formate**, $Pb(CO_2H)_2$, separate Pure formic acid is then made by passing sulphuretted hydrogen over the dry lead salt at 110° and condensing the acid A final purification may be effected (as in the case of acetic acid) by freezing, and then pouring off the unfrozen residue The product thus obtained melts at 8° and boils at 101° (compare water) It has a pungent odour, raises blisters on the skin, and is four times stronger than acetic acid, although not so strong as monochloracetic acid

Expt 162 **Preparation of formic acid**

Equal weights of glycerol and oxalic acid are heated together in a retort or distilling flask to which a condenser is fixed A thermometer is placed in the flask in such a way that its bulb dips just below the surface of the mixture, which is heated to about 110°, until the evolution of carbon dioxide has nearly ceased The temperature is then raised to 120°, when a mixture of water and formic acid distils over, and can be collected in a small flask

The crude distillate is purified by conversion into lead formate For this purpose it is neutralised at the boiling-point with lead carbonate, and filtered On cooling, the filtrate deposits crystals of lead formate, these are dried on a water-bath and, except for about one-tenth, are packed into a wide tube, which is clamped in a sloping position Hydrogen sulphide, which has been washed with water and dried with calcium chloride, is then passed into the upper end of the tube On heating gently, formic acid is liberated and can be collected in a receiver at the lower end The lead sulphide is prevented from falling into the receiver by a plug of glass wool The formic acid is then freed from hydrogen sulphide by distilling it with the remainder of the lead formate

EXPT 163 **Properties of formic acid.**

(*a*) Warm a dilute solution of formic acid with

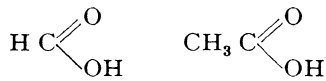
(i) an ammoniacal solution of silver nitrate,

(ii) an acidified solution of potassium permanganate

Interpret the observed effects

(*b*) Add formic acid to concentrated sulphuric acid in a test tube and warm What gas is evolved ?

**Structure and reactions of formic acid.**—As in the case of methyl alcohol, there is little or no choice as regards the structural formula of formic acid Thus, the mere fact that it is an acid, of molecular formula $CO_2H_2$, suggests that it is a lower homologue of acetic acid, formed by the elimination of $CH_2$ from the methyl radical, thus



Formic acid Acetic acid

This structure is confirmed by the fact that ammonium formate is produced by the slow hydrolysis of aqueous prussic acid

$$H\,CN + 2H_2O \rightarrow H\,CO\,ONH_4 \quad \text{(Ammonium formate)}$$

The formula for formic acid is, however, unique in that the central carbonyl radical is linked on one side to *hydroxyl*, as in the carboxylic *acids*, and on the other side to *hydrogen* as in the *aldehydes* This fact is responsible for the unique behaviour of formic acid as the lowest member of the homologous series of carboxylic acids, and for many of the most interesting reactions of the acid and of its derivatives Thus, the acid-function is made evident in the usual way by the formation of salts, as well as of an amide, esters, etc, whilst the aldehydic function is made evident by the fact that formic acid and the formates are *reducing agents*, in marked contrast to acetic acid, which is resistant to oxidation even by chromic acid Thus, sodium formate reduces mercuric to mercurous chloride, gives a silver mirror with silver nitrate and is readily oxidised by potassium permanganate, etc

$$H\,CO\,ONa + 2HgCl_2 \rightarrow NaCl + HCl + CO_2 + Hg_2Cl_2,$$
$$H\,CO\,ONa + 2AgNO_3 \rightarrow NaNO_3 + HNO_3 + CO_2 + 2Ag.$$

When warmed with concentrated sulphuric acid, formic acid loses water, and liberates **carbon monoxide**

$$H\,CO\,OH \rightarrow H_2O + CO.$$

Formates behave similarly with sulphuric acid, but, when sodium formate is heated alone, it loses hydrogen, and yields **sodium oxalate :**

$$2H{\cdot}CO{\cdot}ONa \rightarrow H_2 + NaO\,CO\,CO\,ONa \quad \text{(Sodium oxalate)}$$

**Formamide**, $H{\cdot}CO{\cdot}NH_2$, prepared by heating ammonium formate to 180° and then fractionating under very low pressures, is a liquid, freezing

at $-1°$, which resembles water in its solvent properties It distils below 100° under 0 5 mm pressure but decomposes above 100° into ammonia and carbon monoxide or into water and prussic acid

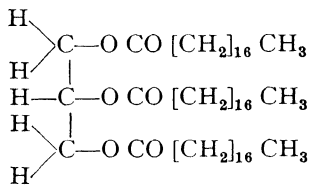
$$NH_3 + CO \leftarrow H\,CO\,NH_2 \rightarrow H_2O + HCN$$

It also yields prussic acid when distilled with phosphoric oxide

**Methyl formate**, H CO $OCH_3$, cannot be prepared by the same method as ethyl acetate (p 713), since formic acid is decomposed by sulphuric acid , it is therefore made by the action on calcium formate of a saturated solution of hydrogen chloride in methyl alcohol It is of interest because on chlorination it yields **methyl chloroformate,** Cl CO $OCH_3$, a compound which combines the active functions of an acid chloride with those of an ester

## C The Fatty Acids

**Higher fatty acids** —The acids of the series $C_nH_{2n+1}$ CO OH are described as the FATTY ACIDS, because the higher homologues are present in oils and fats, mainly in combination with the trihydric alcohol **glycerol,** $C_3H_8O_3$ (p 735). Thus the principal constituent of hard fats such as mutton fat is **stearin** or **glyceryl tristearate,** $C_3H_5(O\,CO\,C_{17}H_{35})_3$



When boiled with caustic soda this yields glycerin and **sodium stearate,** $C_{17}H_{35}$ CO ONa, a typical constituent of HARD SOAP

$$C_3H_5(O\,CO\,C_{17}H_{35})_3 + 3NaOH \rightarrow C_3H_5(OH)_3 + 3C_{17}H_{35}\,CO\,ONa$$

In the manufacture of SOAP, melted fats are boiled with 10% caustic soda in large pans by blowing in steam, more alkali being added from time to time The soap is separated as a curd by adding strong brine * , glycerin remains in solution and is run off from under the curd. Unchanged fats are removed by boiling the curd with further quantities of soda, without dissolving the soap SOFT SOAP is a mixture of potassium salts, obtained by using caustic potash instead of caustic soda

The conversion of these glyceryl esters into soaps is described as SAPONIFICATION, and this term is also used generally to describe the " hydrolysis " of any ester by an alkali Hydrolysis with water under pressure (usually in presence of an emulsifying agent) gives free **stearic acid,** $C_{17}H_{35}$ CO OH, which is used to make candles since

* This process, which is known as " salting-out ", must not be confused with the precipitation of a sparingly soluble electrolyte by the addition of a common ion. The soap is present in solution as a lyophilic colloid (p 642), and its precipitation is due, in part at any rate, to the dehydration of the colloid particles by the salt

its melting-point (69°) is higher than that of the fats from which it is prepared

$$C_3H_5(O\ CO\ C_{17}H_{35})_3 + 3H_2O \rightarrow C_3H_5(OH)_3 + 3C_{17}H_{35}\ CO\ OH$$

The curd formed by the action of soap on hard water consists of insoluble calcium and magnesium salts of the fatty acids, *e g*

$$(C_{17}H_{35}\ CO\ O)_2Ca \quad \text{and} \quad (C_{17}H_{35}\ CO\ O)_2Mg$$

Calcium stearate — Magnesium stearate

Palm oil consists largely of the glyceryl ester of **palmitic acid**, $C_{15}H_{31}\ CO\ OH$, so that the vegetable soaps derived from it consist largely of **sodium palmitate**, $C_{15}H_{31}\ CO\ ONa$ The chief constituent of lard is the glyceryl ester of **oleic acid**, an unsaturated acid which has a carbon-chain of the same length as stearic acid, but with a double bond in the middle.

$$CH_3\ [CH_2]_7\ CH{=}CH[CH_2]_7\ CO\ OH$$

The double bond of oleic acid can be eliminated by combination with hydrogen in presence of finely-divided nickel, in this way soft (unsaturated) fats and oils are converted on a large scale into hard fats, *e g* for use in margarine

$$C_3H_5(O\ CO\ C_{17}H_{33})_3 + 6H \rightarrow C_3H_5(O\ CO\ C_{17}H_{35})_3$$

Olein (triolein) or glyceryl trioleate — Stearin (tristearin) or glyceryl tristearate

Soaps which do not yield a curd with hard water may be prepared by selecting a long-chain acid of which the calcium and magnesium salts are soluble in water This can be done by introducing a sulphate radical instead of a carboxyl group at the end of the hydrocarbon chain, *e g* **cetyl sodium sulphate,**

$$C_{16}H_{33}\ O\ SO_2\ ONa \quad \text{compare} \quad C_2H_5\ O\ SO_2\ OK,$$

is an excellent detergent of this class

Butter contains **butyric acid** as the glyceride **tributyrin**.

$$C_3H_5(O\ CO\ C_3H_7)_3$$

It can therefore be distinguished from margarine by estimating the proportion (about 7%) of "volatile fatty acids" which it yields on saponification, *i e* of acids which can be vaporised in a current of steam

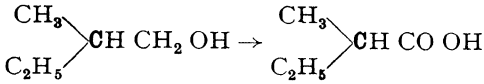
$$C_3H_5(O\ CO\ C_3H_7)_3 + 3KOH \rightarrow C_3H_8O_3 + 3C_3H_7\ CO\ OK,$$
$$2C_3H_7\ CO\ OK + H_2SO_4 \rightarrow 2C_3H_7\ CO\ OH + K_2SO_4$$

The characteristic smell of rancid butter is due to butyric acid, formed by bacterial action from tributyrin, bacteria are also used to prepare butyric acid on a large scale from sugar or starch by BUTYRIC FERMENTATION

$$C_6H_{12}O_6 = C_4H_8O_2 + 2CO_2 + 2H_2$$

Glucose — Butyric acid

*act*-**Valeric acid** or **methylethylacetic acid** is of interest because it contains an asymmetric carbon atom and is " optically active " like amyl alcohol (p. 684), from which it can be prepared by oxidation



*act*-Amyl alcohol *act*-Valeric acid

**General methods for the preparation of fatty acids.**—Fatty acids may be prepared by the following methods

(i) By the oxidation of alcohols and aldehydes

$$R\,CH_2\,OH + O_2 = R\,CO\,OH + H_2O$$

(ii) By the hydrolysis of esters, amides and cyanides

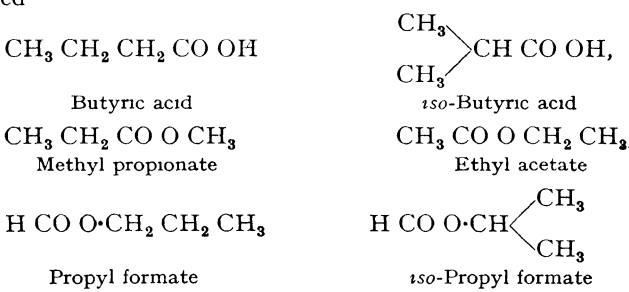
$$R\,CO\,OC_2H_5 + H_2O \xrightarrow{HCl} R\,CO\,OH + C_2H_5\,OH$$
$$R\,CO\,NH_2 + H_2O + HCl = R\,CO\,OH + NH_4Cl$$
$$R\,CN + 2H_2O + HCl = R\,CO\,OH + NH_4Cl$$

(iii) By the action of carbon monoxide on alcohols, under pressure and in presence of a catalyst

$$R\,OH + CO \rightarrow R\,CO\,OH$$

(iv) By synthesis from ethyl acetoacetate (p 731), ethyl malonate (p 752) and Grignard reagents (p 726)

**Isomerism of the fatty acids** —Isomerism in the fatty acids begins at the $C_4$ member, where the following isomeric acids and esters have been prepared

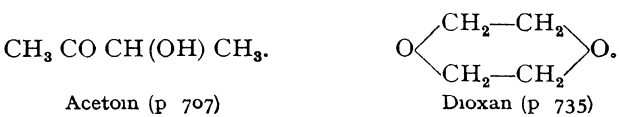


Butyric acid *iso*-Butyric acid

Methyl propionate Ethyl acetate

Propyl formate *iso*-Propyl formate

Two other isomers of the same series are



Acetoin (p 707) Dioxan (p 735)

# CHAPTER LIV

## ETHERS AND ESTERS

**General considerations.**—(*a*) **Ethers**—Ether has been known during a period of more than 600 years as a volatile product of the action of oil of vitriol on alcohol

$$2C_2H_5OH = (C_2H_5)_2O + H_2O$$

Alcohol and ether were two of the first organic compounds to be analysed (1807, 1814), and their vapour densities were determined by Gay Lussac in 1815, but, although it was obvious that ether was derived from alcohol by removal of water, it was thought that alcohol was a hydrate of ether and therefore more complex (in spite of its lower vapour density) This point was finally settled by Williamson's synthesis (1852) of ether from ethyl iodide and potassium ethoxide

$$C_2H_5\,O\,|\,K + I\cdot C_2H_5 \rightarrow C_2H_5\,O\,C_2H_5 + KI$$

The diethyl oxide thus produced is distinguished as **ethyl ether,** but is typical of a series of alkyl oxides of the general formula R O R′ Symmetrical ethers are prepared from the alcohols, but MIXED ETHERS, in which the radicals RR′ are different, can be prepared by Williamson's method as described above

(*b*) **Esters.**—The dehydration by sulphuric acid of a mixture of alcohol and acetic acid gives rise to **ethyl acetate** by removal of a molecule of water

$$CH_3\,CO\,O\,H + HO\cdot C_2H_5 \rightleftharpoons CH_3\,CO\,O\,C_2H_5 + H_2O$$

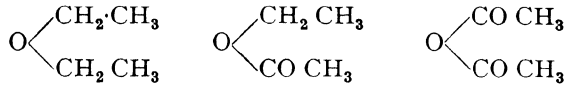
The process bears a superficial resemblance to neutralisation by an alkali,

$$CH_3\,CO\,OH + H\overset{-}{O}\,\overset{+}{Na} = CH_3\,CO\,\overset{-}{O}\,\overset{+}{Na} + H_2O,$$

but differs fundamentally in that it is not an ionic reaction, since neither the alcohols nor the esters are ionised, moreover, the action is slow, even in presence of a catalyst, and proceeds to completion only in presence of a dehydrating agent The product was formerly described as an "ethereal salt," since it unites the composition of an alkyl acetate with the properties of an ether; but it is now described as an ESTER, and the process is known as ESTERIFICATION These terms are also used when the acidic hydrogens of a mineral acid are displaced by alkyl radicals. More

difficult esterifications can be effected by the action of an alkyl iodide on the silver salt of an acid

(*c*) It is instructive to compare the three following oxides :



I Ether II Ethyl acetate III Acetic anhydride

(i) All three compounds can be prepared by a generalisation of Williamson's method, *e g* ethyl acetate from ethyl iodide and silver acetate (p 729) and acetic anhydride from acetyl chloride and sodium acetate (p 712)

(ii) They are all volatile liquids (b -pts , 35°, 77°, 140°) , but, whereas ether is almost as inert as a hydrocarbon, acetic anhydride is active enough to be used as an organic reagent Ethyl acetate is intermediate, since it responds to many of the reagents of organic chemistry, but is itself used as a solvent rather than as a reagent Again, acetic anhydride is hydrolysed completely by water, although not violently like acetyl chloride Ethyl acetate is hydrolysed slowly and reversibly by water, more rapidly in presence of acids, and fairly rapidly and non-reversibly by alkalis Ether, on the other hand, is completely inert to water and to alkalis, and is only attacked by concentrated mineral acids, which do not hydrolyse it, but convert it into esters (p 724).

## A Ethers

**Methyl ether**, $CH_3\,O\,CH_3$, can be prepared (i) from *methyl alcohol* by the action of sulphuric acid on the liquid, or of alumina at 250° on a current of the vapour, (ii) from *methyl iodide* by the action of silver oxide or of sodium methoxide

(i) $$2CH_3\,OH = CH_3\,O\,CH_3 + H_2O,$$

(ii) $$2CH_3I + Ag_2O = CH_3\,O\,CH_3 + 2AgI$$

$$CH_3I + NaOCH_3 = CH_3\,O\,CH_3 + NaI$$

It is a gas (b -pt $-25°$), and has already been referred to as an isomer of ethyl alcohol (p 683)

**Ethyl ether**, $C_2H_5\,O{\cdot}C_2H_5$, can be prepared by the action of sodium ethoxide, $NaOC_2H_5$, or silver oxide on ethyl iodide (compare $(CH_3)_2O$), but it is always manufactured by dehydrating alcohol, either with sulphuric acid or by passing the vapour over alumina at 250°

$$2C_2H_5OH = (C_2H_5)_2O + H_2O$$

In the CONTINUOUS PROCESS (Expt 164) alcohol is run into a mixture of equal volumes of sulphuric acid and alcohol, heated to 140°, when ether and water distil in approximately molecular proportions, together with some unchanged alcohol The ether is separated, washed with alkali to remove sulphur dioxide and other acid impurities, and distilled from calcium chloride to hold back water and alcohol, as described in Expt 164.

The last traces of water and alcohol can be removed by keeping the distilled ether over sodium wire and pouring it off when required for use

In the continuous process the acid appears to act as a mere catalyst, to promote the conversion of alcohol into ether and water, *e g* by raising the boiling-point of the liquid to a temperature at which this decomposition can proceed continuously Since, however, the liquid obviously contains

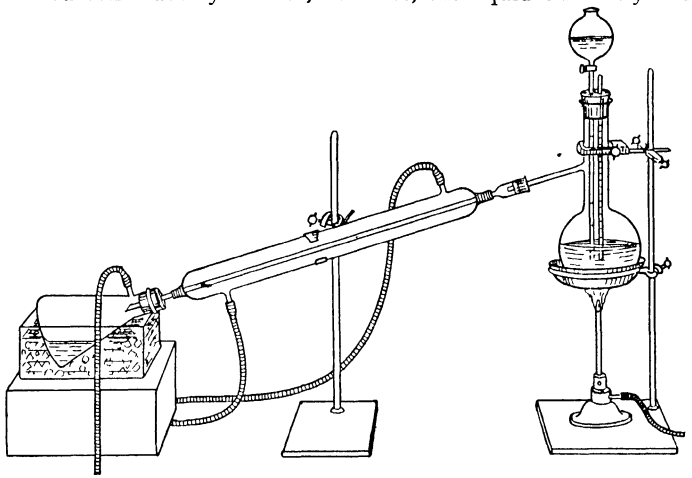


FIG 174 PREPARATION OF ETHER

ethyl hydrogen sulphate, it is believed that the formation of ether depends on the interaction of this compound with alcohol, regenerating sulphuric acid according to the equation

$$(C_2H_5)HSO_4 + C_2H_5OH = (C_2H_5)_2O + H_2SO_4$$

In theory the dehydration of alcohol to ether could proceed indefinitely when a continuous supply of alcohol is provided, but in practice oxidation and charring of the alcohol take place, as a result of which sulphuric acid is reduced to sulphur dioxide and lost, so that the action is only continuous over a limited period of operation

EXPT 164 **Preparation of ethyl ether**

*N B* —**Great care must be taken in this experiment as ether vapour forms a very explosive mixture with air**

Place about five grams of clean sand (to assist the subsequent distillation) in the bottom of a ½-litre distilling flask, and fit the flask with a cork, dropping funnel and thermometer, in such a way that the ends of the funnel tube and thermometer are almost touching the sand Run 100 c c of rectified spirit into the flask, and then add slowly 75 c c of concentrated sulphuric acid, the flask being shaken at intervals, and kept cool by immersion in cold water Now place the flask on a sand-bath and fit it to a condenser and ice-cooled receiver, as in the diagram, Fig 174 Be careful to see that the exit tube from the receiver is fitted with a long piece of rubber tubing which leads to the floor , in this way the heavy ether vapour that escapes condensation has no chance of coming in contact with the burner

on the bench Heat the mixture to about 140-145°, and add about 70 c c of rectified spirit from the funnel at about the same rate as the crude ether distils over It is essential to add the spirit slowly, otherwise the distillate will contain a large amount of unchanged alcohol , the temperature must also be controlled at 140-145°

Extinguish all flames before transferring the distillate to a separating funnel (Fig 175) containing 30 c c of a 10 per cent solution of caustic soda Shake vigorously, and after settling, run off the lower layer of alkali and reshake the ether with 30 c c of distilled water, which is run off as before In this way the ether is purified from sulphurous acid and most of the alcohol The remainder of the alcohol and most of the water are removed by transferring the ether to a flask containing about 30 grams of calcium chloride After an interval of at least half an hour, pour the ether into a 250 c c distillation flask, which is fitted up as in the first part of the experiment, except that the tap funnel is dispensed with and the bulb of the thermometer is placed on a level with the exit tube of the flask, and not in the liquid Distil off the ether by immersing the flask to a suitable depth in a bath of water at 60°, and see that all burners are extinguished whilst the distillation is proceeding Collect the fraction which distils between 34-38°



FIG 175 SEPARATING FUNNEL

Ether is a liquid of density 0 736, which boils at 35° It is a good solvent for many covalent compounds, *e g* mercuric chloride, and mixes in all proportions with alcohol It floats on the surface of water, the upper ethereal layer being saturated with 1% of water and the lower aqueous layer with 5% of ether It is therefore often used to separate organic compounds from aqueous solutions by ETHER EXTRACTION, when the organic material passes preferentially into the ethereal layer and can be removed to any desired extent by repeated extraction (see p 798)

Ether has a pleasant smell, but the vapour produces unconsciousness and is used as an anaesthetic , the rapid evaporation of the liquid also produces marked cooling

Ether is very inflammable, but otherwise is not very reactive, since it is not attacked by alkalis or dilute acids, nor by the ordinary oxidising or reducing agents Ozone, however, converts it into an explosive peroxide, and similar products appear to be formed by exposure to air When heated with phosphorus pentachloride, ether is converted into ethyl chloride *without liberation of hydrogen chloride* (compare acetone, p 705), thus proving the absence of a hydroxyl radical and confirming the oxide structure of the compound

$$(C_2H_5)_2O + PCl_5 = 2C_2H_5Cl + POCl_3$$

The whole of the hydrogen can be replaced step by step by the action of chlorine, and the final product is **perchloroether**, $C_4Cl_{10}O$ (m -pt 68°)

Concentrated mineral acids also act upon ether and convert it into an

ester Thus fuming sulphuric acid converts it into ethyl hydrogen sulphate and water

$$(C_2H_5)_2O + 2H_2SO_4 = 2(C_2H_5)HSO_4 + H_2O$$

Nitric acid or nitric anhydride at $-15°$ converts it into ethyl nitrate and alcohol,

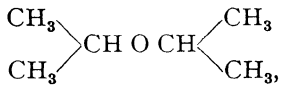
$$(C_2H_5)_2O + HNO_3 = C_2H_5\,O\,NO_2 + C_2H_5OH,$$

and hydrogen iodide converts it into ethyl iodide

$$(C_2H_5)_2O + HI = C_2H_5I + C_2H_5\,OH$$

Hydrogen bromide has a similar action, but hydrogen chloride does not act upon it

**General properties of the ethers.**—In general, ethers can be prepared by the four methods described for making ethyl ether, *e g* ***iso*-propyl ether** (b.-pt 69°),



is prepared by dehydrating *iso*propyl alcohol and is used as a solvent, but the higher alcohols cannot be converted into ethers by direct dehydration, since they form olefines much more readily than the lower homologues The higher homologues are less volatile than ethyl ether, but resemble it in their behaviour towards chemical reagents, such as acids, alkalis and phosphorus pentachloride

## B. Esters of Inorganic Acids

**Alkyl halides.**—(*a*) *Preparation* —Alkyl halides are produced (i) by the action of chlorine or bromine on the paraffins (p 666), (ii) by the action of hydrogen chloride, bromide or iodide on the olefines (p 670), but they are usually prepared from the alcohols, (iii) by the action of hydrogen chloride, bromide or iodide, added if necessary by a dehydrating agent and catalyst such as zinc chloride or sulphuric acid, or (iv) by the action of a halide of phosphorus

(iii) $C_2H_5\,OH + HCl \rightarrow C_2H_5Cl + H_2O,$

$C_2H_5\,OH + HBr \rightarrow C_2H_5Br + H_2O$

(iv) $3C_2H_5\,OH + PI_3 \rightarrow 3C_2H_5I + H_3PO_3$

(*b*) *Properties* —Methyl chloride (b -pt $-24°$), methyl bromide (b -pt $+4\,5°$), ethyl chloride (b -pt $+12\,5°$), and some of the fluorides, are gases, but most of the others are colourless liquids, which are sparingly soluble in water and burn with a green-edged flame Their chemical properties are summarised below

(i) Reduction with a zinc-copper couple yields the corresponding paraffin (p 663)

$$2C_2H_5I + 2Zn + H_2O = 2C_2H_6 + ZnI_2 + ZnO.$$

(ii) Condensation to a more complex hydrocarbon is effected by reduction with sodium (p 663)

$$2CH_3I + 2Na = C_2H_6 + 2NaI$$

(iii) Hydrolysis with *aqueous* alkali gives the alcohol

$$C_2H_5Br + NaOH = C_2H_5\,OH + NaBr.$$

(iv) Hydrolysis with *alcoholic* alkali gives an olefine

$$C_2H_5Br + NaOH = C_2H_4 + NaBr + H_2O$$

(v) Heating with alcoholic potassium cyanide at 100° gives a cyanide, which can be hydrolysed to a carboxylic acid (p 709)

$$C_2H_5I + KCN = C_2H_5\,CN + KI$$

(vi) Alkyl halides interact with silver salts, and can thus be used to prepare esters, such as **diethyl sulphate**, $(C_2H_5)_2SO_4$, which cannot be prepared directly from the acid

$$2C_2H_5I + Ag_2SO_4 = (C_2H_5)_2SO_4 + 2AgI$$

(vii) Alcoholic ammonia gives amines (p 760) in the form of substituted ammonium salts

$$C_2H_5I + NH_3 = [C_2H_5\,NH_3]^+I^-$$

(viii) Alkyl iodides interact with zinc to give spontaneously inflammable liquids known as **zinc alkyls**, and with magnesium to form the GRIGNARD REAGENT (see below)

$$2CH_3I + 2Zn = ZnI_2 + Zn(CH_3)_2 \quad \text{(Zinc methyl)},$$
$$CH_3I + Mg = CH_3MgI \quad \text{(Grignard reagent)}$$

The preceding reactions (i) to (viii) are also characteristic of dihalides such as **ethylene chloride** or **iodide**, which contain two halogens on different carbon atoms **Ethylidene chloride**, with two halogens on the same carbon atom, has been referred to on p 692, and the special properties of chloroform, iodoform and carbon tetrachloride are described on pp 702, 703 and 149

EXPT 165 **Properties of ethyl chloride**

Procure a tube of ethyl chloride Allow the jet of liquid to impinge for a moment on the skin and notice the cold that is produced Allow a little of the liquid to evaporate in a gas-jar, set fire to the vapour and notice the green colour of the flame

EXPT 166 **Preparation of ethyl bromide**

(*a*) Add concentrated sulphuric acid (50 c c ) to water (30 c c ) contained in a half-litre round-bottomed flask, then add ethyl alcohol (50 c c ), taking care, by cooling under the tap, that the temperature does not rise unduly on mixing Add potassium bromide (40 grams) and connect the flask to a Liebig's condenser, to the other end of which is fitted an adapter which dips into 50 c c of ice-cold water in a small receiver (Fig 176) Heat the mixture

cautiously until no more oil condenses in the receiver, then transfer the distillate to a separating funnel and run off the lower layer of ethyl bromide Shake this with 30 c c of dilute sodium carbonate to remove acids, followed by 30 c c of water to remove traces of surplus alkali Then dry it over calcium chloride (in a corked flask to avoid evaporation) until the liquid has lost its turbidity Finally, distil the ethyl bromide via a water-cooled condenser into an ice-cooled boiling-tube, collecting the fraction which boils between 35-40°

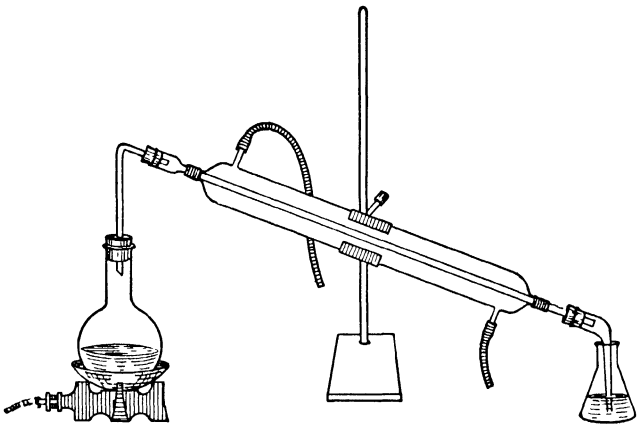


FIG 176 PREPARATION OF ETHYL BROMIDE

**The Grignard reagent.**—When magnesium turnings are added to a solution of an alkyl iodide in ether, they give rise to an addition compound known as the GRIGNARD REAGENT, *e g*

$$CH_3I + Mg + 2(C_2H_5)_2O = CH_3MgI,\ 2(C_2H_5)_2O$$

In general, the reagent must be prepared in specially purified ether This cannot be replaced by any other solvent, and is known in certain cases to form an integral part of the product of interaction Grignard reagents can be prepared from a wide range of organic halides and have the merit that they need not be isolated They are very important agents in condensation, since they are particularly efficient in producing carbon-to-carbon bonds and are therefore used extensively in organic syntheses, but the ether does not play any obvious part in these reactions and is generally ignored in discussing them

The following products can be prepared with the help of Grignard reagents

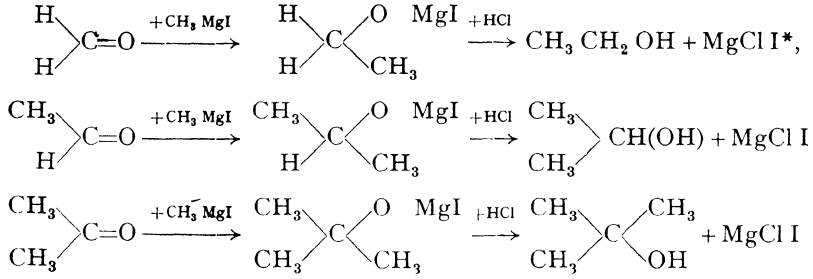
(*a*) *Paraffins* by the action of (i) water, (ii) alcohols, (iii) alkyl iodides

$$CH_3MgI + H_2O = CH_4 + Mg(OH)I,$$
$$CH_3MgI + CH_3OH = CH_4 + Mg(OCH_3)I,$$
$$CH_3MgI + CH_3I = C_2H_6 + MgI_2$$

(*b*) *Primary alcohols* by the action of dry oxygen, followed by treatment with a dilute acid

$$2CH_3\,Mg\,I \xrightarrow{+O_2} 2\,CH_3O\,Mg\,I \xrightarrow{+2HCl} 2CH_3\,OH + MgCl_2 + MgI_2$$

(*c*) *Primary, secondary and tertiary alcohols* by interaction with formaldehyde, other aldehydes, and ketones, the resulting addition products being decomposed with dilute acid




(*d*) *Acids* by the action of carbon dioxide and subsequent decomposition by acid

$$CH_3\,Mg\,I + CO_2 \rightarrow CH_3\,CO\,O\,MgI \xrightarrow{HCl} CH_3\,CO\,OH + MgCl\,I$$

**Alkyl sulphates.**—(*a*) **Methyl hydrogen sulphate** is formed when methyl alcohol is warmed with concentrated sulphuric acid

$$CH_3\,OH + H_2SO_4 \rightleftharpoons CH_3\,O\,SO_2\,OH + H_2O$$

It can be separated in the form of a potassium salt in the same way as the ethyl ester (p 728), and hydrolysed to produce pure methyl alcohol, free from acetone When the crude product is heated under reduced pressure **dimethyl sulphate** distils over, leaving a residue of sulphuric acid

$$2(CH_3)HSO_4 = (CH_3)_2SO_4 + H_2SO_4$$

Dimethyl sulphate is a valuable methylating agent, but of a different class from the Grignard reagent, since it serves to replace the hydrogen of hydroxyl groups by methyl Thus it can be used to methylate compounds such as glucose, fructose, sucrose, starch and cellulose, and thus to determine the number of hydroxyl groups in the molecules of these complex carbohydrates

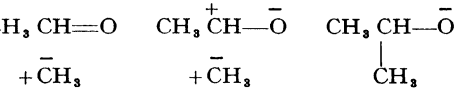
The contrast between the two types of methylating agents may be interpreted by noticing that (i) zinc methyl and the Grignard reagent give a metallic cation and must therefore liberate the methyl radical as an *anion*, whilst (ii) methyl iodide and dimethyl sulphate give an acid anion and must therefore liberate the methyl radical as a *cation*

(i) $Zn(CH_3)_2 \rightarrow \overset{++}{Zn} + 2\overset{-}{CH_3}$, $CH_3\,Mg\,I \rightarrow \overset{++}{Mg} + \overset{-}{I} + \overset{-}{CH_3}$,

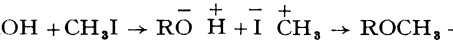
(ii) $CH_3I \rightarrow \overset{-}{I} + \overset{+}{CH_3}$, $(CH_3)_2SO_4 \rightarrow \overset{--}{SO_4} + 2\overset{+}{CH_3}$

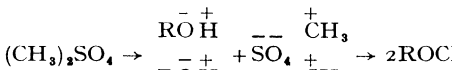
* The by-product is a mixture of magnesium chloride and iodide

The methylating agents in group (i) therefore interact with the positively charged carbon of (activated) aldehydes and ketones,



where the negative charge on the oxygen is balanced by the positive charge on the metal, just as in the cyanhydrin reaction (p 694) On the other hand, the methylating agents of group (ii) replace the proton of a hydroxyl group





(*b*) **Ethyl hydrogen sulphate,** $C_2H_5 \cdot O\,SO_2\,OH$, is formed, by a reversible reaction, when a mixture of equal volumes of sulphuric acid and alcohol is heated on a water-bath

$$(C_2H_5)OH + H_2SO_4 \rightleftharpoons (C_2H_5)HSO_4 + H_2O.$$

It can be separated from unchanged alcohol and sulphuric acid by neutralising with chalk, since the acid is not readily hydrolysed in neutral or alkaline solutions After filtering from chalk and gypsum, the calcium is precipitated with potassium carbonate and **potassium ethyl sulphate** is crystallised out

$$(C_2H_5O\,SO_2\,O)_2Ca + K_2CO_3 = CaCO_3 + 2C_2H_5O\,SO_2\,OK$$

Calcium ethyl sulphate — Potassium ethyl sulphate

Alternatively, the mixture can be neutralised with barium carbonate, the solution filtered from barium sulphate and excess of carbonate, and the **barium ethyl sulphate** precipitated with sulphuric acid to liberate **ethyl hydrogen sulphate** or " sulphovinic acid "

$$2C_2H_5\,O\,SO_2\,OH + BaCO_3 = (C_2H_5\,O\,SO_2\,O)_2Ba + CO_2 + H_2O,$$
$$(C_2H_5\,O\,SO_2\,O)_2Ba + H_2SO_4 = 2C_2H_5\,O{\cdot}SO_2\,OH + BaSO_4$$

The barium sulphate is again filtered off and the solution is evaporated under reduced pressure to drive off water and alcohol The product is a thick sour liquid, which is readily hydrolysed (by autocatalysis, since its solutions are always acid) but yields salts which can be evaporated to dryness without hydrolysis Its decomposition to ethylene and sulphuric acid at 180°, and its interaction with alcohol at 140° to produce ether have already been described, but it cannot be converted into diethyl sulphate by distillation This compound must therefore be prepared from ethyl iodide and silver sulphate (p 725) and is too costly to be used as a laboratory reagent.

**Ethyl nitrate** can be prepared by cautiously heating ethyl alcohol with rather less than its own weight of concentrated nitric acid (S G = 1 42)

$$C_2H_5\,OH + HNO_3 = C_2H_5\,O\,NO_2 + H_2O$$

It is essential to avoid the presence of oxides of nitrogen, since they cause a violent oxidation of the alcohol The nitric acid is therefore mixed with urea before it is added to the alcohol.

$$CON_2H_4 + N_2O_3 = CO_2 + 2N_2 + 2H_2O$$

Ethyl nitrate is a colourless pleasant-smelling liquid, which boils at 87°, and has the usual properties of an ester

### C Esters of Organic Acids.

**Ethyl acetate** is prepared by the action of sulphuric acid on a mixture of acetic acid and alcohol as described in Expt 167

$$C_2H_5\,OH + CH_3\,CO\,OH = CH_3\,CO\,OC_2H_5 + H_2O$$

It is a pleasant-smelling liquid, which boils at 77°, and is moderately soluble in water Like the esters of the mineral acids, it is hydrolysed by water, acids and alkalis, but differs from them in that it reacts with concentrated ammonia to form an ACID AMIDE

$$CH_3\,CO\,OC_2H_5 + NH_3 = CH_3\,CO\,NH_2 + C_2H_5\,OH$$

**Homologous series of esters.**—The simplest ester is **methyl formate**, H CO $OCH_3$, an isomer of acetic acid Since formic acid is decomposed by sulphuric acid, the esters of formic acid are made by the action of formic acid or a formate on the alcohol in presence of hydrogen chloride (p 717) In other cases the alcohol (*e g ter*-butyl alcohol) is unstable in presence of sulphuric acid A general method of preparation in such cases is by the interaction of an alkyl halide with the silver salt of the acid

$$RI + R'\,CO\,OAg \rightarrow R'\,CO\,OR + AgI$$

A vast range of isomerism is opened up by the fact that the homologous series can be ascended by using either a higher alcohol or a higher fatty acid Thus there are not less than nine * esters which are isomeric with the four * valeric acids $C_5H_{10}O_2$, in addition to compounds which are neither acids nor esters

The esters are generally liquids, often with a pleasant fruity odour, and many of them are used as flavourings (pear-drop, pineapple, etc ) **Methyl oxalate**, $CH_3O\,CO\,CO\,OCH_3$, prepared by heating methyl alcohol with anhydrous oxalic acid, is of interest because it is a solid (m -pt 54°) like the acid (p. 749), whilst the ethyl ester is a liquid

EXPT 167 **Preparation of ethyl acetate.**

Fit a ½-litre distilling flask with a cork and tap funnel, the end of which is well below the side tube of the flask Run 50 c c of rectified spirit into the flask, and follow this with a similar volume of concentrated sulphuric acid, being careful to add the acid slowly and with constant shaking Now

* Optical isomers are not included in these numbers.

place the flask in a bath of paraffin oil and attach it to a water-cooled condenser and receiving flask, as in Fig 173, p 711 Heat the paraffin bath to 140°, and add very slowly from the tap funnel a mixture of 100 c c of glacial acetic acid and 100 c c of alcohol After a few minutes, adjust the rate of addition of this mixture to equal that at which the liquid distils When all the mixture has been added, continue the distillation for another five minutes, then transfer the distillate to a separating funnel and shake it with 50 c c of a strong solution of sodium carbonate (about 30 per cent ) to remove acetic acid, etc It is better to leave the funnel unstoppered until the effervescence has become less vigorous , the funnel may then be inverted, shaken, and the tap opened to release carbon dioxide When no further action appears to be taking place, run off the lower alkaline layer and reshake the crude ethyl acetate with a solution of calcium chloride (50 grams in 50 c c of water) to remove free alcohol Separate the ester and dry it with calcium chloride for about half an hour before transferring it to a ½-litre distilling flask, which is fitted with a thermometer, water cooled condenser and receiver Heat the flask on a water-bath, raising the temperature of the latter gradually, so that the ether that is present as an impurity in the ester may distil over below 40° Collect the fraction which boils between 74-79°, since this is fairly pure ethyl acetate

EXPT 168 **Hydrolysis of ethyl acetate**

Fit up a round-bottomed flask with a reflux condenser Introduce a little ethyl acetate into the flask and a strong solution of caustic soda Boil the liquid for about 20 minutes Cool the flask and connect it by means of a piece of bent tube to the condenser, so that when the liquid is heated any volatile substance will distil over In this way the alcohol can be distilled over and the iodoform test applied (see p 703) The residue in the flask contains sodium acetate Warm it with sulphuric acid and note the smell of vinegar

**Ethyl acetoacetate,** $CH_3\,CO\,CH_2\,CO\,OC_2H_5$ (*a*) *Preparation* —An important condensation is effected by the action of metallic sodium on ethyl acetate

$$CH_3\,CO{\cdot}OC_2H_5 + H{\cdot}CH_2\,CO\,OC_2H_5$$

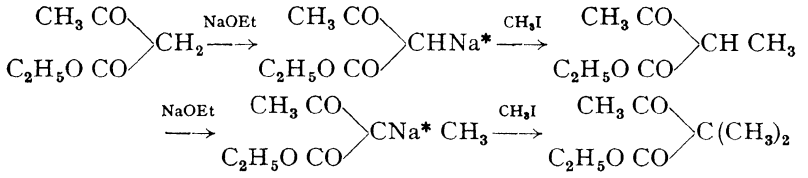
$$= CH_3\,CO\,CH_2\,CO\,OC_2H_5 + C_2H_5\,OH.$$

In this condensation, a molecule of alcohol is eliminated as sodium ethoxide, $C_2H_5\,ONa$, and the condensation-product is also produced in the form of a sodium-derivative (see below) It is set free by the action of hydrochloric acid as a colourless liquid (b -pt 181°), which is sparingly soluble in water but miscible in all proportions with alcohol and ether

(*b*) *Reactivity* —The central methylene group of ethyl acetoacetate lies between *two* carbonyl groups, —CO $CH_2$ CO— It is therefore even more reactive than the methylene group of methylethyl ketone (p 707), as is shown (1) by the readiness with which hydrolysis occurs on either side of this radical (p 731)

$$—CO\,\underset{|}{CH_2}\,CO—$$

(ii) by its ready enolisation (p 732), and (iii) by the fact that the two hydrogens can be replaced one at a time by sodium (using a solution of sodium ethoxide in alcohol) and then by alkyl radicals



This condensation can be effected with almost any organic radical which can be prepared in the form of a reactive halide, and is therefore of great value in organic syntheses

(*c*) *Hydrolysis* —By the action of strong alcoholic potash, the preceding condensation is reversed, and ethyl acetoacetate is converted into potassium acetate by ACID HYDROLYSIS

$$CH_3\,CO{\cdot}CH_2\,CO\,OC_2H_5 + 2KOH = 2CH_3\,CO\,OK + C_2H_5\,OH$$

Under less strongly alkaline conditions, *e g* in presence of dilute acid or alkali, KETONIC HYDROLYSIS takes place, with formation of acetone

$$CH_3\,CO\,CH_2{\cdot}CO\,OC_2H_5 + 2KOH = CH_3\,CO\,CH_3 + C_2H_5\,OH + K_2CO_3$$

These two hydrolyses can also be effected with derivatives of ethyl acetoacetate, in which one or both of the hydrogen atoms of the central methylene radical have been replaced by other radicals, thus

*Acid hydrolysis* $CH_3\,CO{\cdot}CR'R''\,CO\,OC_2H_5 + 2KOH$

$= CH_3\,CO\,OK + CHR'R''\,CO\,OK + C_2H_5OH,$

*Ketonic hydrolysis* $CH_3\,CO\,CR'R''{\cdot}CO\,OC_2H_5 + 2KOH$

$= CH_3\,CO\,CHR'R'' + C_2H_5\,OH + K_2CO_3$

In this way it is possible to synthesise

(i) any mono- or di-substituted acetic acid of the type $CH_2R\,CO{\cdot}OH$ or $CHR'R''\,CO\,OH$, *e g*

**valeric acid** $\begin{matrix} CH_3 \\ C_2H_5 \end{matrix}\!\!>\!CH\,CO\,OH$, where $R'R'' = CH_3,\ C_2H_5$,

(ii) any mono- or di-substituted acetone of the type $CH_3\,CO\,CH_2R$ or $CH_3\,CO\,CHR'R''$, *e g* ***iso*-propyl methyl ketone**

$$CH_3\,CO\,CH\!<\!\begin{matrix} CH_3 \\ CH_3 \end{matrix}, \text{ where } R'R'' = CH_3,\ CH_3.$$

* The sodium compounds are actually derived from the " enolic " form of the ester, but are here shown as occupying the same positions as the alkyl radicals by which they are finally replaced

Note that dicarboxylic acids and diketones can be synthesised by using a suitable di-iodide, *e g* elementary *iodine* can be used to synthesise succinic acid

$$2CH_3\,CO\,CHNa\,CO\,OC_2H_5 \xrightarrow{+I_2} \begin{matrix} CH_3\,CO\cdot CH\,CO\,OC_2H_5 \\ | \\ CH_3\cdot CO\cdot CH\,CO\,OC_2H_5 \end{matrix} + 2NaI$$

Ethyl sodioacetoacetate — Ethyl diacetylsuccinate

$$\begin{matrix} CH_2\,CO\,OK \\ | \\ CH_2\,CO\,OK \end{matrix} \xrightarrow{+4KOH} + 2CH_3\,CO\,OK + 2C_2H_5\,OH$$

Potassium succinate — Potassium acetate — Alcohol

(*d*) *Enolisation* —Liquid ethyl acetoacetate (in presence of a trace of alkali) is an equilibrium-mixture of two isomers

$$CH_3\,CO\,CH_2\,CO\,OC_2H_5 \rightleftharpoons CH_3\,C(OH){=}CH\,CO\,OC_2H_5$$

Ketonic form (92%) — Enolic form (8%)

It is therefore a good example of DYNAMIC ISOMERISM or equilibrium amongst isomers (p 687) The proportion of the enolic form is reduced to ½% by using water as a highly polar solvent and increased to nearly 50% by using hexane as a non-polar solvent The KETONIC FORM can be frozen out from the mixture as a solid (m -pt $-39°$) by cooling a solution of the ester to $-80°$ On the other hand, complete enolisation can be effected by preparing the sodium-derivative, and the ENOLIC FORM can be prepared by precipitating sodium chloride from a suspension of the sodium-derivative in light petroleum by the action of gaseous hydrogen chloride at $-80°$

$$CH_3\,C(OH){=}CH{\cdot}CO\,OC_2H_5 \overset{Na}{\underset{HCl}{\rightleftharpoons}} CH_3\,C(ONa){=}CH\,CO\,OC_2H_5$$

Enolic form — Sodium derivative

Since the interconversion of the isomers is very slow at low temperatures, the enolic form was isolated as a glass by evaporating the solution, it was then distilled under reduced pressure at 33°, since the interconversion of the isomers is suspended in the vapour For the same reason Kurt Meyer was able to separate the two isomers by ASEPTIC DISTILLATION, *i e* by fractional distillation in a silica flask in the absence of alkaline catalysts The equilibrium-mixture may be described conveniently as **acetoacetic ester.**

(*e*) *Tautomerism* —Acetoacetic ester gives the reactions of both isomers, and therefore appears to have two different structures at the same time This phenomenon is described as TAUTOMERISM

*Ketonic reactions*, in which the ester appears to have the structure $CH_3\,CO{\cdot}CH_2\,CO\,OC_2H_5$, include

(i) acid and ketonic hydrolysis (p 731),

(ii) coupling with bases to form an oxime, etc ;

(iii) condensation with alkyl iodides, etc. (p. 731).

*Enolic reactions*, in which the ester appears to have the structure $CH_3$ C(OH) CH CO $OC_2H_5$, include

(i) bromination (compare bromination of acetone, p 706),

(ii) action of sodium to form a sodium-derivative of the enolic form (compare sodium ethoxide),

(iii) blue coloration with ferric chloride (compare phenol, p 792)

It is noteworthy that when the ketonic form has been separated by freezing it does not react with bromine or give a coloration with ferric chloride until there has been time for the enolic isomer to be produced

## CHAPTER LV

### POLYHYDRIC ALCOHOLS

**Glycol.**—Organic molecules may contain more than one hydroxyl group, giving rise to POLYHYDRIC ALCOHOLS The simplest of these is the DIHYDRIC ALCOHOL, **ethylene glycol,** $HO\,CH_2\,CH_2\,OH$, which can be prepared by boiling ethylene chloride with aqueous potassium carbonate and separated by distillation

$$Cl\,CH_2\,CH_2\,Cl + K_2CO_3 + H_2O \rightarrow 2KCl + CO_2 + HO\,CH_2\,CH_2\,OH$$

Glycol is a viscous liquid, boiling at 195°, which has a sweet taste (Greek, γλυκύς, sweet) and dissolves freely in water

The polyhydric alcohols resemble the monohydric alcohols, but give more varied derivatives, since the hydroxyl groups can be attacked one at a time Thus glycol is reconverted into ethylene chloride by the action of phosphorus pentachloride, but hydrogen chloride displaces only one hydroxyl group and yields **ethylene chlorhydrin,** $HO\,CH_2\,CH_2\,Cl$

$$HO\,CH_2\,CH_2\,OH + HCl \rightarrow H_2O + HO\,CH_2\,CH_2\,Cl$$

This compound is prepared on a large scale directly from ethylene by the action of hypochlorous acid (*e g* from bleaching powder and carbon dioxide), and its hydrolysis provides an improved method of making glycol industrially

$$C_2H_4 + HO\,Cl \rightarrow HO\,CH_2\,CH_2\,Cl \underset{HCl}{\overset{H_2O}{\rightleftharpoons}} HO\,CH_2\,CH_2\,OH$$

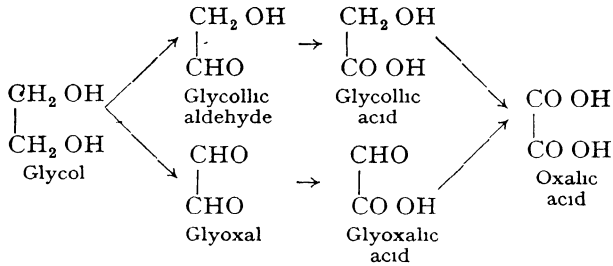
In addition to the chlorides described above, glycol yields mono- and di-sodium derivatives, and mono- and di-acetates with acetyl chloride

$$\begin{array}{l} CH_2\,OH \\ | \\ CH_2\,OH \end{array} \xrightarrow{Na} \begin{array}{l} CH_2\,ONa \\ | \\ CH_2\,OH \end{array} \xrightarrow{Na} \begin{array}{l} CH_2\,ONa \\ | \\ CH_2\,ONa \end{array}$$

$$\begin{array}{l} CH_2\,OH \\ | \\ CH_2\,OH \end{array} \xrightarrow{CH_3\,CO\,Cl} \begin{array}{l} CH_2\,O\,CO\,CH_3 \\ | \\ CH_2\,OH \end{array} \xrightarrow{CH_3\,CO\,Cl} \begin{array}{l} CH_2\,O\,CO\,CH_3 \\ | \\ CH_2\,O\,CO\,CH_3 \end{array}$$

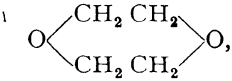
Esters of this type are used extensively as solvents for cellulose lacquers, etc

Since it is a primary alcohol twice over, glycol yields a complex series of oxidation products by simple oxidation of —$CH_2\,OH$ with nitric acid to —CHO and —CO OH, thus




The three acids have all been isolated as oxidation-products of glycol, but the two aldehydes (glycollic aldehyde and glyoxal) are too easily oxidised to survive and have only been prepared by other methods

When heated with 4% of its weight of sulphuric acid, glycol is converted by a continuous process into **dioxan,**



an isomer of ethyl acetate (p 719) This cyclic ether (m -pt 11 7°, b -pt 101 5°, density 1 035, compare water) is a valuable solvent, since it is miscible in all proportions with water, alcohol, ether and most other organic liquids

**Glycerol,** or glycerin, $C_3H_5(OH)_3$, is a trihydric alcohol, which is present as a **tristearate, trioleate** or **tripalmitate** in fats and oils, and in part as a **tributyrate** in butter The name "glycerol" has been introduced to express the fact that it is an alcohol, but its esters (p 717) are known as **tristearin, triolein, tripalmitin, tributyrin,** etc

It is prepared by hydrolysing the fats with water under pressure, or by saponifying them with a caustic alkali (p 718)

$$C_3H_5(O\ CO\ R)_3 + 3H_2O \rightarrow C_3H_5(OH)_3 + 3R\ CO\ OH,$$
$$C_3H_5(O\ CO\ R)_3 + 3NaOH \rightarrow C_3H_5(OH)_3 + 3R\ CO\ ONa,$$

where $R = C_{17}H_{35}$, $C_{17}H_{33}$ or $C_{15}H_{31}$ It remains behind in the aqueous liquor, from which it is removed (after concentration) by a current of superheated steam, the distillate is then concentrated by boiling off the water

Glycerol is a viscous liquid with a sweet taste, which mixes in all proportions with water It boils with slight decomposition at 290°, but can be distilled under reduced pressure or in a current of superheated steam The liquid does not readily crystallise, but when pure the crystals melt at 17°

**Structure and properties of glycerol.**—(*a*) Glycerol is readily shown to be a trihydric alcohol

(1) It is found as a trihydric ester, *e g* tristearin, triolein or tripalmitin, $C_3H_5(O\ CO\ R)_3$, where $R = C_{17}H_{35}$, $C_{17}H_{33}$ or $C_{15}H_{31}$, and it is readily converted into a mono-, di- or tri-**acetate** by the action of acetyl chloride

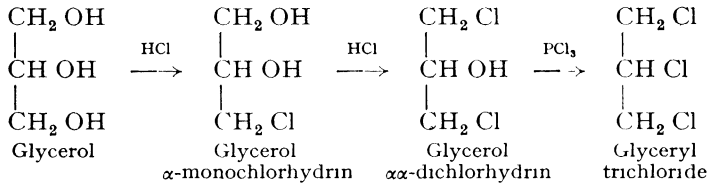
$$C_3H_8O_3 + 3CH_3\ CO\ Cl \rightarrow C_3H_5(O\ CO\ CH_3)_3 + 3HCl$$
Triacetin

(ii) When sprayed into a well-cooled mixture of nitric and sulphuric acids it yields **glyceryl trinitrate,** well known as an explosive under the name of **nitroglycerin**

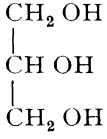
$$C_3H_8O_3 + 3HNO_3 \rightarrow C_3H_5(O\,NO_2)_3 + 3H_2O$$

The heavy oil, which separates when the nitration-product is poured into water, is freed from acid by washing with water and with dilute sodium carbonate and stabilised by absorption in kieselguhr as " dynamite," or by making it into a sort of dough with nitro-cellulose or " gun-cotton " (p 741) to form " blasting gelatin "

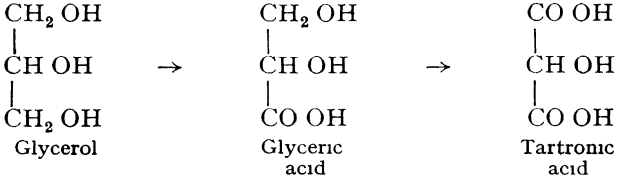
(iii) It yields a mono-, di- and tri-**chloride** by the action of hydrogen chloride on the liquid, of hydrogen chloride on a solution in acetic acid and finally of phosphorus trichloride on the liquid



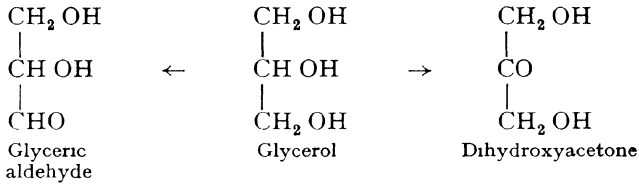

(*b*) If we write glycerol as $C_3H_5(OH)_3$, it is clear that the molecules must be held together by carbon-to-carbon bonds, since all the oxygen atoms are present as univalent hydroxyl groups Moreover, a chain of three carbon atoms cannot be branched Glycerol is therefore a trihydroxy derivative of **propane,** $CH_3\,CH_2\,CH_3$, and it only remains to show that the three hydroxyls are all attached to different carbon atoms This can easily be done because polyhydric alcohols with two or three hydroxy groups on the same carbon atom, *e g* $R\,CH(OH)_2 \rightleftharpoons R\,CHO + H_2O$, lose water so easily that only a few of them are known as hydrates (p 714) We are therefore able to write the structural formula of glycerol as



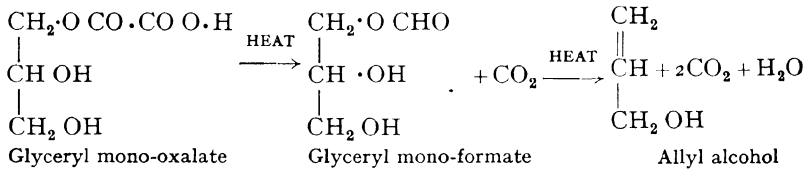

(*c*) On this basis, glycerol contains two primary alcohol groups and one secondary alcohol group The presence of the two primary alcohol groups can be established by oxidation with nitric acid to **glyceric acid** and **tartronic acid**



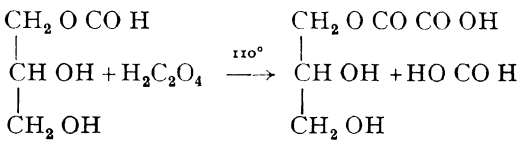
The presence of a primary and of a secondary alcohol group can be established by oxidation with bromine water, when **glyceric aldehyde** is formed by oxidation of a $-CH_2OH$ group and **dihydroxyacetone** by oxidation of a $-CH(OH)-$ group




(*d*) The preparation of formic acid by heating equal weights of crystalline, hydrated oxalic acid and glycerol at 100°-110°, and of allyl alcohol by heating glycerol with one-fifth of its weight of oxalic acid at 200°-260° (Expt 169), can both be explained by the formation of a glyceryl mono-oxalate and its decomposition into a glyceryl mono-formate




Thus, when the liquid is heated above 200°, the mono-formate decomposes into **allyl alcohol,** carbon dioxide and water as set out above On the other hand, addition of more crystalline oxalic acid at 110° results in the displacement of formic acid by the less volatile oxalic acid, the mono-formate being thus reconverted into mono-oxalate as set out below




EXPT 169 **Preparation and properties of allyl alcohol**

Ten grams of oxalic acid are mixed with 50 grams of glycerol in a distilling flask to which is attached a condenser A thermometer dips below the surface of the liquid in the flask When the thermometer registers 180° the distillate is collected, and at 260° distillation is stopped After dehydration with solid potassium carbonate, the allyl alcohol (b -pt 95°) is purified by redistillation What happens when allyl alcohol is (i) treated with bromine, (ii) boiled with acidified dichromate ?

(*e*) Finally we may note that, when glycerol is heated with potassium hydrogen sulphate (Expt 170), it loses the elements of water

and gives **acrolein**, a volatile liquid with the acrid odour of burnt fat

$$\begin{array}{l} CH_2\,OH \\ | \\ CH\,OH \\ | \\ CH_2\,OH \\ \text{Glycerol} \end{array} \quad -2H_2O \rightarrow \quad \begin{array}{l} CH_2 \\ \| \\ CH \\ | \\ CHO \\ \text{Acrolein} \end{array}$$

The product has the dual functions of an olefine and an aldehyde Thus it decolorises bromine, and is readily oxidised to **acrylic acid**

$$CH_2{=}CH\,CHO + Br_2 \rightarrow Br\,CH_2\,CHBr\,CHO \quad (\alpha\beta\text{-Dibromopropion-aldehyde})$$

$$CH_2{=}CH\,CHO + O \rightarrow CH_2{=}CH{\cdot}CO{\cdot}OH \quad (\text{Acrylic acid})$$

EXPT 170 **Preparation and properties of acrolein**

A small quantity of glycerol is mixed with excess of potassium bisulphate in a test tube and heated A pungent-smelling vapour is produced which, if distilled through a condenser, yields a colourless liquid possessing the properties of an olefine and an aldehyde

Test the acrolein with a little bromine water and with an ammoniacal solution of silver nitrate

**Mannitol**, $C_6H_{14}O_6$, the characteristic constituent of manna, may be referred to briefly at this stage as an example of a polyhydric alcohol of greater complexity, since it contains two primary alcohol groups and four secondary alcohol groups

$$HO\,CH_2\,CH(OH)\,CH(OH)\,CH(OH)\,CH(OH){\cdot}CH_2\,OH$$

**Dulcitol** and **sorbitol** have the same structural formula, but different configurations of the radicals in space

**The carbohydrates**, $C_m H_{2n} O_n$, which compete with the proteins for the primary place in the chemistry of animal and vegetable organisms, have the empirical composition of *carbon* plus *water* The oxygen is not present, however, in the form of water, as it is in salts which contain "water of crystallisation," but exists mainly in the form of hydroxyl groups, so that the carbohydrates always include amongst their functions that of a polyhydric alcohol Thus the isomeric carbohydrates, **glucose** or grape sugar, and **fructose** or fruit sugar, $C_6H_{12}O_6$, differ from the hexahydric alcohols, mannitol, dulcitol and sorbitol, $C_6H_{14}O_6$, by containing two atoms of hydrogen less in each molecule Since both sugars yield a cyanhydrin, it appears that one of the $>CHOH$ groups has been replaced by a $>C{=}O$ group This relationship is confirmed by the fact that glucose is reduced by sodium amalgam and water to sorbitol, whilst fructose yields a mixture of mannitol and sorbitol on reduction Glucose and fructose reduce Fehling's solution quantitatively and may be estimated by this method (p 315)

The presence of an unbranched chain of 6 carbon atoms in glucose and fructose is shown by reduction with hydriodic acid and phosphorus to *n*-hexyl iodide and thence to *n*-hexane. When, however, the cyanhydrins

of the two sugars are hydrolysed to carboxylic acids, and then reduced in such a way as to eliminate all the hydroxyl groups, it is found that glucose yields a *straight-chain acid*, *n*-**heptoic acid**, $C_6H_{13}CO\,OH$, whilst fructose yields an isomeric *branched-chain acid*, **methyl-*n*-butyl-acetic acid**, $C_4H_9\,CH(CH_3)\,CO\,OH$ From these observations it is clear that glucose is an *aldehyde*, with the carbonyl group at the end of the chain of six carbon atoms, whilst fructose is a *ketone*, with the carbonyl group as the second member of the chain, thus

*Glucose* $HO\,CH_2\,CH(OH)\,CH(OH)\,CH(OH)\,CH(OH)\,CHO$,

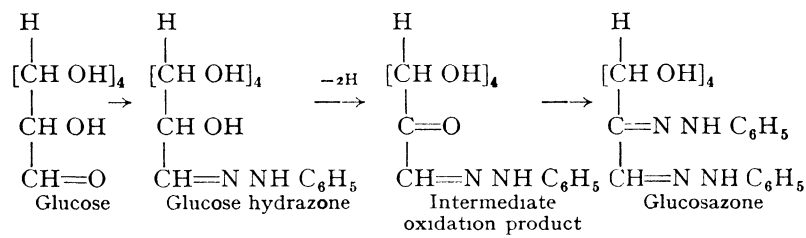
*Fructose* $HO\,CH_2\,CH(OH)\,CH(OH)\,CH(OH)\,CO\,CH_2\,OH$

Glucose and fructose do not form addition compounds with ammonia or with sodium bisulphite, but the presence of a carbonyl group is confirmed by the fact that each sugar yields an *oxime* with hydroxylamine (p 696)

The action of phenylhydrazine is complicated by the fact that, in addition to coupling with the carbonyl group, the phenylhydrazine oxidises the contiguous $>CHOH$ group to $>C{=}O$, and is itself reduced to a mixture of ammonia and aniline (p 796)

$$>CHOH + H_2N\,NH\,C_6H_5 \rightarrow >C{=}O + NH_3 + NH_2\,C_6H_5$$

The newly formed $>CO$ group then couples with another molecule of phenylhydrazine to form an OSAZONE, as set out below




Glucosazone and fructosazone are found to be identical and yield the same OSONE,

$$H\,[CH\,OH]_4\,CO\,CHO \text{ (Glucosone or fructosone)},$$

when the phenylhydrazine is eliminated by hydrolysis with acids The radical $H[CH\,OH]_4$ is therefore identical in these two sugars, *i e* it has the same configuration in space as well as the same structural formula

EXPT 171 **Properties of the sugars**

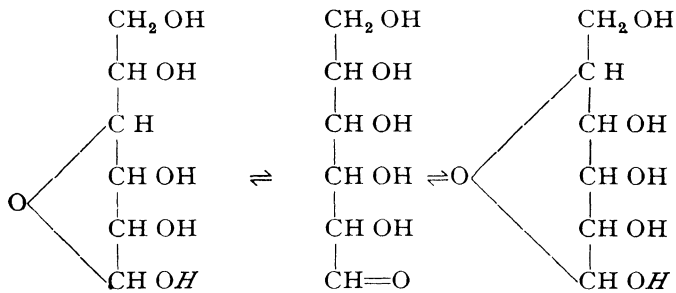
(*a*) *Reducing and non-reducing sugars* —Add a little caustic soda to a solution of copper sulphate in order to produce a precipitate of cupric hydroxide To small portions of this in separate test tubes add solutions of cane-sugar, grape-sugar and starch Boil the mixtures and explain any changes which you may observe

(*b*) *Inversion of cane-sugar* —Add a few drops of dilute sulphuric acid to a solution of cane-sugar in water Boil for 10 minutes under a small reflux condenser, and then test the solution with cupric hydroxide as in (*a*) Repeat the experiment, using starch instead of sugar, and continue the boiling for half an hour

**Ring-formation.**—In the preceding formulae the sugars and their derivatives have been represented as containing an open chain of six carbon atoms In practice, however, it has been found that the —CO— group tends to form an internal addition compound with one of the >CHOH groups, just as chloral combines with alcohol to form a SEMI-ACETAL in accordance with the equation

$$CCl_3\,CH{=}O + HO\,C_2H_5 \rightarrow CCl_3\,CH\begin{matrix}OH\\ OC_2H_5\end{matrix}$$

The sugars thus acquire a cyclic structure, with four or five atoms of carbon and one atom of oxygen in the ring, and the free >C=O group is replaced by an ether group



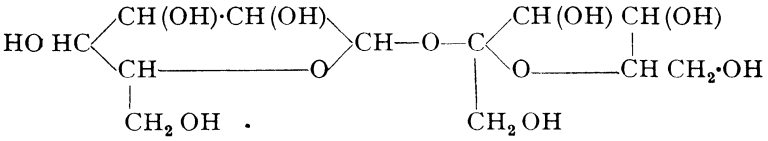

Five-atom ring Open chain Six-atom ring

The cyclic sugars then contain *five* hydroxyl groups from which penta-acetates, etc , can be prepared This ring-structure is easily destroyed in the sugars themselves, which very readily yield open-chain derivatives with reagents such as HCN and $NH_2OH$, but it becomes quite stable in derivatives in which the italicised hydrogen *H* of the preceding formulae has been displaced by carbon Thus cane-sugar or sucrose, $C_{12}H_{22}O_{11}$, which is hydrolysed by acids to a mixture of glucose and fructose,

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O \rightarrow \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6},$$

is derived from these sugars by linking together a six-atom ring form of

glucose and a (labile) five-atom ring form of fructose, with elimination of a molecule of water from two hydroxyl groups, thus




Glucose residue Fructose residue

Sucrose

It does not react with HCN and $NH_2$ OH, and does not reduce Fehling's solution like glucose and fructose, because the italicised hydrogens of both of these sugars have been eliminated **Cellulose** and **starch** are formed by a similar process of coupling, in which long chains of six-atom glucose rings are linked together through atoms of oxygen , but these chains are so long that the composition of these two complexes is almost indistinguishable from that of a simple anhydride of the formula $C_6H_{10}O_5$ Starch is readily hydrolysed to glucose (p 679), but cellulose is more stable and yields esters, in which each $C_6H_{10}O_5$-unit behaves as a trihydric alcohol like glycerol Thus **nitrocellulose,** prepared by action of nitric and sulphuric acids on cotton, is used as an explosive under the name of GUN-COTTON,

$$R(OH)_3 + 3HNO_3 = R(O\,NO_2)_3 + 3H_2O,$$

where $R = C_6H_7O_2$ , compare

$$C_3H_5(OH)_3 + 3HNO_3 = C_3H_5(O\,NO_2)_3 + 3H_2O$$

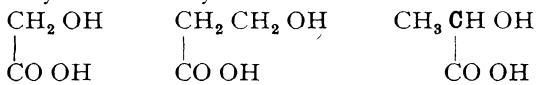
Similarly **cellulose acetate** is used in the form of " rayon " as a substitute for silk or cotton

## CHAPTER LVI

### HYDROXY ACIDS AND DICARBOXYLIC ACIDS

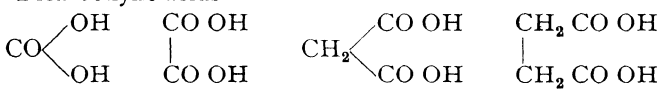
**General considerations.**—In the preceding chapter an account has been given of the polyhydric alcohols, in which the hydroxyl group with its characteristic functions occurs more than once in the same molecule The present chapter contains a similar account of those acids in which the carboxylic group, with its characteristic acid functions, occurs twice, or in which the acidity of the carboxyl group is reinforced by a (contiguous) hydroxyl group Several compounds of this composite type have already been cited as oxidation products of glycol and glycerol, together with some in which an aldehydic or ketonic carbonyl group is associated with a hydroxyl or carboxyl group The most interesting of these acids are formulated below

*A* Hydroxy-monocarboxylic acids



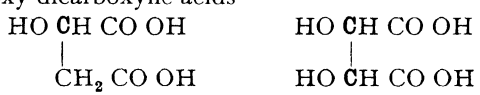
Glycollic acid — β-Hydroxy propionic acid — Lactic acid

*B* Dicarboxylic acids



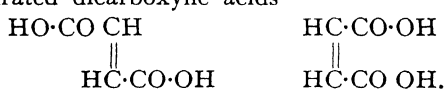
Carbonic acid — Oxalic acid — Malonic acid — Succinic acid

*C* Hydroxy-dicarboxylic acids



Malic acid — Tartaric acid

*D* Unsaturated dicarboxylic acids



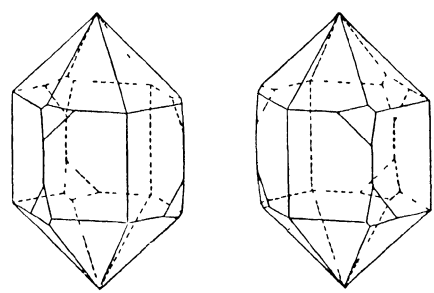
Fumaric acid — Maleic acid

**Chemistry in space.**—The structural formulae used in the preceding chapters have all been plotted in two dimensions This is a convenient way of writing or printing them and it suffices to show (i) the nature of the radicals in each molecule, and (ii) the sequence in which they are linked together, but it does not give any indication of (iii) the shape which the molecule assumes in space of three dimensions Thus, in the preceding chapter, the formula of glycol has been written in two ways as follows

$$\begin{matrix} CH_2\,OH \\ | \\ CH_2\,OH \end{matrix} \quad \text{and} \quad HO\,CH_2\,CH_2\,OH$$

Since these two schemes are both intended to represent the same molecule, it is clear that we have made a tacit assumption that the chain of radicals is flexible and that the shape which it assumes at any given moment is of no importance This assumption is justified by the remarkable way in which the behaviour and properties of organic compounds have been interpreted as functions of the radicals which they contain and of the sequence in which they are arranged It now remains to point out some of the phenomena which are beyond the scope of this system and which can only be interpreted by means of models in three dimensions

**Optical rotatory power.**—It was discovered by Biot in 1812 that plates of quartz, cut perpendicularly to the principal axis of the crystal, rotate the plane of polarisation of the incident light either to the right or to the left, through an angle which is proportional to the thickness of the plate Thus the plane of vibration of light which enters a DEXTROROTATORY plate from behind would be twisted in the same direction as the hands of a clock in passing through the plate, whilst in a LAEVOROTATORY plate, the direction of the twist would be reversed, although its magnitude would be the same as in a similar plate of opposite sign In 1815 Biot detected the same phenomenon in oil of turpentine and in certain other organic liquids



(*a*) Left-handed (*b*) Right-handed

FIG 177 HEXAGONAL CRYSTALS OF QUARTZ

Two enantiomorphous forms of the crystal are shown, which are "mirror-images" of one another

The OPTICAL ROTATORY POWER of quartz is associated with the degraded symmetry of the crystals These exist in two forms (Fig 177) which are not superposable on one another, but bear the same relationship as an object and its image in a mirror A right-handed rotation in one crystal would therefore correspond with a left-handed rotation in the other, as Herschel discovered in 1820 Pasteur in 1848 suggested that the rotatory power of liquids could be attributed in a similar way to MOLECULAR DISSYMMETRY, *i e* to the presence of molecules which are not superposable on their image in a mirror Thus, a *crystal* with a

structure like a spiral staircase or a *molecule* with the shape of an irregular tetrahedron could both give rise to optical rotatory power since neither figure could be superposed on its mirror-image, and each could therefore exist in dextrorotatory and laevorotatory forms

**The asymmetric carbon atom** —Pasteur's conception assumed a more precise form when le Bel and van 't Hoff in 1874 showed that optical activity in natural organic compounds was always associated with the presence of an ASYMMETRIC CARBON ATOM, *i e* a quadrivalent atom of carbon associated with *four different univalent radicals* This conclusion was based on the already familiar conception that the four valencies of a carbon atom are not arranged in a plane, but are directed to the four corners of a regular tetrahedron This figure only becomes dissymmetric when each apex is occupied by a different radical, and this

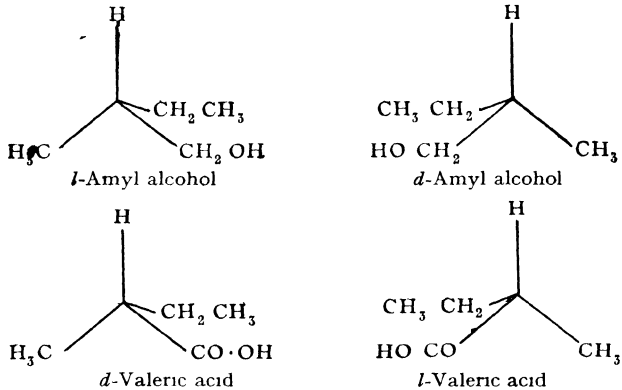
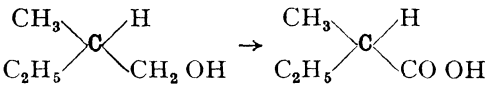



FIG. 178 ABSOLUTE CONFIGURATIONS OF AMYL ALCOHOL AND OF VALERIC ACID

is therefore the fundamental condition for the development of optical activity in carbon compounds

Two examples of optically active substances containing an asymmetric carbon atom have already been cited, namely *act*-**amyl alcohol** (p 684) from fusel oil, which is *laevorotatory*, and *act*-**valeric acid**, from *Valeriana officinalis*, which is *dextrorotatory*, but can be prepared also by oxidising *laevorotatory* amyl alcohol (p 719)




The asymmetric carbon atom is shown in heavy type in the two preceding formulae, but the tetrahedral configuration is not shown, although it is essential for the development of optical rotatory power, since dissymmetry is exclusively a property of three-dimensional figures, and cannot exist in any two-dimensional system. The presence of asymmetric

carbon atoms in lactic, malic and tartaric acids has also been indicated by the use of heavy type on p 742 In most cases it is not yet possible to say which of the two configurations of the asymmetric carbon atom corresponds to the dextrorotatory form of the compound and which corresponds to the laevorotatory form, but the assignments shown in Fig 178 have been made in the case of amyl alcohol and of valeric acid, where the sign of the rotation is reversed when —$CH_2$ OH is oxidised to —CO OH

## A Hydroxycarboxylic Acids

**Glycollic acid,** or **hydroxyacetic acid,** HO $CH_2$ CO OH, is the simplest of the hydroxycarboxylic acids, with the possible exception of carbonic acid, HO CO OH, which is not generally regarded as a member of this group of acids

*Preparation* —(i) It can be synthesised by hydrolysing the cyanhydrin of formaldehyde with hydrochloric acid

$$HO\ CH_2\ CN + 2H_2O + HCl = HO\ CH_2\ CO\ OH + NH_4Cl$$

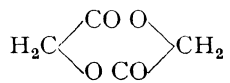
(ii) It is formed, together with other products (p 735), when glycol is oxidised with dilute nitric acid

$$HO\ CH_2\ CH_2\ OH + 2O = HO\ CH_2\ CO\ OH + H_2O$$

(iii) It is manufactured on a large scale by the hydrolysis of chloracetic acid, and may be prepared in the laboratory by boiling a concentrated aqueous solution of potassium chloroacetate, evaporating under reduced pressure, and extracting the free glycollic acid with acetone

$$Cl\ CH_2\ CO\ OK + H_2O = HO\ CH_2\ CO\ OH + KCl$$

*Properties* —Glycollic acid is a hygroscopic solid, which melts at 80°, and is freely soluble in water and alcohol It has the dual properties of a primary alcohol and a carboxylic acid Thus (i) the hydroxyl radical can be oxidised, acetylated, etc , just like ethyl alcohol, whilst (ii) the carboxyl radical can be neutralised by bases, esterified, etc Of special interest is the fact that, when heated to 100°, it yields a cyclic **anhydride,**



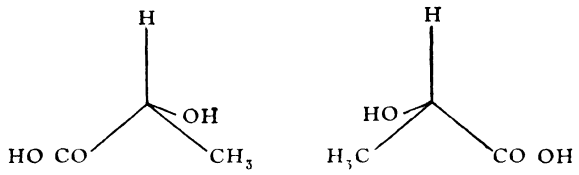
(compare lactide, p 747), in which the hydroxyl of one molecule has been esterified by the carboxyl of a second molecule, and conversely

**Lactic acid,** $CH_3$ **C**H(OH) CO OH, is present in an optically inactive form in sour milk, and in a dextrorotatory form (" sarcolactic acid ") in meat extract It can be prepared synthetically by hydrolysing the cyanhydrin of acetaldehyde with hydrochloric acid

$$\underset{\text{Aldehyde}}{CH_3\ CHO} \rightarrow \underset{\text{Aldehyde cyanhydrin}}{CH_3\ \mathbf{C}H(OH)\ CN} \rightarrow \underset{\text{Lactic acid}}{CH_3\ \mathbf{C}H(OH)\ COOH}$$

Since there is no factor in a synthetic preparation which would promote the preferential formation of a dextrorotatory or a laevorotatory form, the

product is a **RACEMIC MIXTURE** of equal quantities of both, and is optically inactive The two forms can be separated, however, by inoculating a supersaturated solution of **ammonium zinc lactate**, $AmZn(C_3H_5O_3)_3$, $2H_2O$, with a crystal of the salt of the natural dextro-acid, and thus leaving an excess of the salt of the laevo-acid in solution The two acids are represented in three-dimensions, as mirror-images of one another, in Fig 179,




*d*-Lactic acid *l*-Lactic acid

FIG 179 ABSOLUTE CONFIGURATIONS OF *d*- AND *l*-LACTIC ACID

where the four radicals lie at the apices of a tetrahedron, with the asymmetric carbon (not shown) in the centre

Lactic acid is a sour liquid, which exhibits the dual functions of an alcohol and of a carboxylic acid Thus **methyl lactate**,

$$CH_3\,CH(OH)\,CO\,OCH_3,$$

can be prepared by esterifying the carboxyl group by the usual methods, and **acetyl-lactic acid**,

$$CH_3\,CH\begin{cases} O\,CO\,CH_3 \\ CO\,OH \end{cases}$$

can be prepared by acetylating the hydroxyl group with acetic anhydride The presence of a *secondary* alcohol group is shown by its oxidation by permanganate to a ketonic acid, known as **pyruvic acid**

$$CH_3\,CH(OH)\,CO\,OH \rightarrow CH_3\,CO\,CO\,OH$$

It will be seen that the structure of lactic acid is thus established completely, since the residue left after subtracting —CH(OH)— and —CO OH from $C_3H_6O_3$ is the univalent methyl radical $CH_3$

A duplicate proof of the structure of lactic acid is provided by its synthesis from acetaldehyde, since this shows that the acid contains (i) a *methyl radical*, already present in acetaldehyde, (ii) a *hydroxyl radical*, as in the cyanhydrin, (iii) a *carboxyl radical*, produced by hydrolysis of the *cyanide radical* of the cyanhydrin This line of evidence is confirmed by the fact that, when lactic acid is heated, it decomposes into acetaldehyde, water and carbon monoxide, whilst when distilled with dilute sulphuric acid it breaks up again, by a reversal of the cyanhydrin synthesis, into acetaldehyde and formic acid

$$CH_3\,CH(OH)\,CO{\cdot}OH \rightarrow CH_3\,CHO + H{\cdot}CO\,OH.$$

Additional evidence of the structure of lactic acid is provided by (i) its isomerism with $\beta$-hydroxypropionic acid (see below), (ii) its optical

activity, which is accounted for by the presence of an asymmetric carbon atom in α-hydroxypropionic acid, but not in the β-acid

Finally dehydration of lactic acid by cautious heating converts it into an internal ester, known as **lactide**, in which the hydroxyl group of one molecule is esterified by the carboxyl group of another molecule and conversely

$$2CH_3\,CH(OH)\,CO\,OH \rightarrow 2H_2O + CH_3\,CH\begin{matrix}O\,CO\\ \diagup\quad\diagdown\\ CO\,O\end{matrix}CH\,CH_3$$

**Hydracrylic acid**, or β-hydroxypropionic acid, $HO\,CH_2\,CH_2\,CO\,OH$, an isomer of lactic acid, can be synthesised from ethylene through the cyanhydrin

$$C_2H_4 \xrightarrow{HOCl} HO\,CH_2\,CH_2\,Cl \xrightarrow{KCN} HO\,CH_2\,CH_2\,CN \xrightarrow{HCl} HO\,CH_2\,CH_2\,CO\,OH$$

Unlike lactic acid, it does not contain an asymmetric carbon atom, and is therefore optically inactive It also differs from lactic acid in that (i) it loses *water* when heated with dilute sulphuric acid and gives **acrylic acid**, $CH_2{=}CH\,CO\,OH$ (instead of aldehyde), (ii) when warmed with chromic acid, it is oxidised to **malonic acid** (see below)

$$HO\,CH_2\,CH_2\,CO\,OH \rightarrow HO\,CO\,CH_2\,CO\,OH$$

## B Dicarboxylic Acids

**Carbonic acid**, $HO\,CO\,OH$, does not contain two independent carboxylic groups, but may nevertheless be classified with the dicarboxylic acids, since both hydroxyl groups have acidic properties, in view of their contiguity to the central carbonyl group Since carbon dioxide and the metallic carbonates have already been described, it will suffice in the present chapter to describe the properties and derivatives which are related to those of the carboxylic acids Thus, we can now recognise that the reactivity of **phosgene**, $COCl_2$ (p 149), *e g* towards water and ammonia, is a normal characteristic of the chloride of a carboxylic acid It also interacts with alcohol to give successively **ethyl chloroformate**, $Cl\,CO\,OC_2H_5$, and **ethyl carbonate**, $C_2H_5O\,CO\,OC_2H_5$ Both of these esters interact with ammonia to give **urethane**, $NH_2\,CO\,OC_2H_5$, a volatile solid which combines the properties of an amide with those of an ester

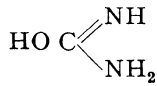
**Urea**, $CON_2H_4$, is a compound of great physiological importance, since it is a constituent of the urine of all mammals It is of unique historical interest on account of its synthesis from ammonium cyanate by a process of isomeric change (p 651) It can also be prepared synthetically by the action of ammonia on phosgene,

$$COCl_2 + 4NH_3 = CON_2H_4 + 2NH_4Cl,$$

and is being manufactured on a large scale for use as a fertiliser, apparently by direct coupling of ammonia and carbon dioxide

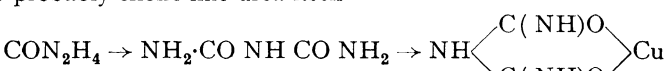
$$CO_2 + 2NH_3 = CON_2H_4 + H_2O.$$

Its properties and methods of preparation, including its synthesis from carbonyl chloride and ammonia, suggest that it should be formulated as **carbamide**, $CO(NH_2)_2$, the amide of carbonic acid, but it is now generally believed to have the " enolic " structure



The name " carbamide " is therefore misleading and should not be used as equivalent to " urea '

Urea crystallises in colourless needles (m -pt 132°), which are soluble in water and alcohol, but insoluble in ether It behaves as a weak monacidic base, *e g* with nitric acid it forms **urea nitrate**, $CON_2H_4,HNO_3$, which is soluble in water, but only sparingly soluble in dilute nitric acid , **urea oxalate**, $CON_2H_4,H_2C_2O_4$, is sparingly soluble in water and is therefore precipitated when oxalic acid is added to a strong solution of urea When heated, urea loses ammonia and gives **biuret**, $NH_2\,CO\,NH\,CO\,NH_2$, this melts at 190°, but on further heating it loses ammonia and gives cyanuric acid $(HCNO)_3$, thus reversing the synthesis of urea from ammonia and cyanic acid (p 651) Addition of copper sulphate to an alkaline solution of biuret gives a red-violet copper salt, the colour of which can be used as a qualitative test for urea (Expt 172) This violet salt is probably enolic like urea itself



When heated with caustic alkalis urea is hydrolysed to ammonia and a carbonate, *e g*

$$CON_2H_4 + 2KOH = K_2CO_3 + 2NH_3$$

It is oxidised to carbon dioxide and nitrogen by nitrous acid, hypochlorites and hypobromites

$$CON_2H_4 + 2HNO_2 = CO_2 + 2N_2 + 3H_2O,$$
$$CON_2H_4 + 3NaBrO = CO_2 + N_2 + 3NaBr + 2H_2O$$

Urea can be estimated by the latter reaction by collecting the nitrogen over caustic potash in a Lunge nitrometer (p 202)

EXPT 172 **Preparation and properties of urea**

(*a*) Fuse an intimate mixture of 20 grams of powdered potassium cyanide and 60 grams of red lead in an iron dish Powder the product and extract with 150 c c of boiling water to dissolve the cyanate, which is then freed from insoluble matter by filtration Stir the solution of cyanate with 10 grams of ammonium sulphate and evaporate the mixture to dryness Boil the solid residue on a water-bath with 25 c c of alcohol, in a flask fitted with a reflux condenser to prevent loss of alcohol At the end of half an hour filter this mixture to remove potassium sulphate, which is insoluble

in alcohol, and evaporate the filtrate to crystallisation The reactions which take place may be represented by the equations

$$Pb_3O_4 + 4KCN = 4KNCO + 3Pb,$$
$$(NH_4)_2SO_4 + 2KNCO = 2(NH_4)NCO + K_2SO_4,$$
$$NH_4NCO \rightleftharpoons CON_2H_4$$

(*b*) Heat some crystals of urea in a test tube Note the smell of ammonia Cool, add a little water and a few drops of copper sulphate solution Then add caustic soda solution in excess Notice the violet colour due to *biuret*

(*c*) To a strong aqueous solution of urea add a few drops of strong nitric acid or a strong solution of oxalic acid Note the formation of crystals in each case and examine them under the microscope

(*d*) To a solution of urea add a little sodium nitrite solution and a few drops of hydrochloric acid Note the vigorous effervescence on warming

(*e*) To a solution of urea add a little sodium hypochlorite solution and observe the evolution of nitrogen

**Oxalic acid**, HO CO CO OH,$2H_2O$, is the simplest dicarboxylic acid (i) It occurs in wood-sorrel, rhubarb, etc , in the form of the **acid potassium oxalate,** $KHC_2O_4$ (ii) It can be prepared in the laboratory by oxidising cane-sugar with ten times its weight of warm concentrated nitric acid (Expt 173) (iii) It is manufactured on a large scale by impregnating sawdust with a concentrated solution of caustic soda and then heating to about 250° in a current of air , the **sodium oxalate,** $Na_2C_2O_4$, thus formed is extracted with water and precipitated as **calcium oxalate,** $CaC_2O_4$, by the addition of lime , the calcium salt is heated with dilute sulphuric acid, and after the removal of calcium sulphate the solution of oxalic acid is evaporated to crystallisation (iv) Sodium oxalate is also manufactured by heating sodium formate, made synthetically from caustic soda and carbon monoxide

$$2H\ CO\ ONa \rightarrow H_2 + (CO\ ONa)_2$$

Oxalic acid crystallises from water as the **dihydrate,** $H_2C_2O_4,2H_2O$, but is converted into the anhydrous acid by heating to 100° , at higher temperatures, *e g* 160°, it decomposes into formic acid and its decomposition products

$$(COOH)_2 \rightarrow H\ CO\ OH + CO_2 \rightarrow CO + CO_2 + H_2O.$$

It is easily oxidised to carbon dioxide and water, *e g* by potassium permanganate (p 426), and gives a mixture of carbon monoxide and carbon dioxide when heated with concentrated sulphuric acid

$$H_2C_2O_4 = H_2O + CO + CO_2$$

EXPT 173 **Preparation and properties of oxalic acid**

(*a*) Place about 25 grams of powdered sugar in a large flask Cover the sugar with 150 c c of concentrated nitric acid, and heat on a water-bath in the fume chamber When the action ceases, evaporate the liquid to a small bulk and allow it to cool, when crystals of oxalic acid will be obtained

(*b*) Dissolve a little oxalic acid in warm water Add a little dilute sulphuric acid and warm the mixture Then add a little potassium permanganate solution The latter is decolorised

(*c*) Heat some crystals of oxalic acid with concentrated sulphuric acid in a test tube Observe what happens and ascertain whether the gas which is evolved will burn

(*d*) Examine some crystals of methyl oxalate Dissolve a little of the substance in water and test the reaction to litmus Repeat the tests (*b*) and (*c*), using methyl oxalate in place of oxalic acid Heat some of the crystals in a test tube, and note the low melting-point and the smell

(*e*) Hydrolyse a little ethyl oxalate as in the case of ethyl acetate (Expt 168, p 730), and test the products

(*f*) To a little ethyl oxalate in a test tube add a strong solution of ammonia, and note the formation of a white precipitate of oxamide

Oxalic acid is a dibasic acid The first carboxyl group to be neutralised is strongly acidic, on account of the influence of the strongly *acylous* COOH group which is attached directly to it , but the second carboxyl group then behaves as a very weak acid, since the *ion* —CO $O^-$ is strongly *basylous* by reason of the electron-repelling effect of the negative charge which it carries The same conclusion follows if we consider that although the first proton is easily transferred to any available base (including water), the second one is liable to be caught by the —CO $O^-$ radical whenever it tries to escape

The salts of oxalic acid include

| | |
|---|---|
| **Potassium oxalate,** | $K_2C_2O_4,H_2O$ |
| **Potassium hydrogen oxalate,** | $KHC_2O_4$ |
| **Potassium quadroxalate,** or " salts of lemon " | $KHC_2O_4,H_2C_2O_4,2H_2O$ |

The last may be regarded as a " double salt " of oxalic acid with the acid oxalate , it is an interesting exception to the rule that the basicity of an acid can be determined by the number of salts produced during its progressive neutralisation by a base , thus we do not regard oxalic as quadribasic, in spite of the fact that in the quadroxalate only *one-quarter* of the displaceable hydrogen is replaced by potassium Reference has already been made to the insolubility of **calcium oxalate,** $CaC_2O_4$ (p 428), and to the use of **potassium ferrous oxalate,** $K_2Fe(C_2O_4)_2,H_2O$, as a developer in photography (p 326)

As a dicarboxylic acid, oxalic acid reacts with phosphorus pentachloride to form **oxalyl chloride,** Cl CO CO Cl It can be esterified in two stages, thus

RO CO CO OH and RO CO CO OR

**Dimethyl oxalate,** $CH_3O$ CO CO $OCH_3$ (m -pt 54°), and **diethyl oxalate,** $C_2H_5O$ CO CO $OC_2H_5$ (b -pt 185°), are converted into **oxamide,**

$NH_2$ CO CO $NH_2$ (m -pt 419°),

when heated with concentrated ammonia (Expt 173*f*, p 750).

**Malonic acid**, $CH_2(CO\,OH)_2$, the homologue of oxalic acid, is synthesised by heating a solution of potassium chloroacetate with potassium cyanide to form potassium cyanoacetate, which is then hydrolysed to malonic acid by boiling with hydrochloric acid

$$Cl\,CH_2{\cdot}CO\,OK \xrightarrow{KCN} CN\,CH_2\,COOK \xrightarrow[HCl]{H_2O} HO\,CO\,CH_2\,CO\,OH$$

The acid, which melts at 132°, loses carbon dioxide when heated to 150°

$$CH_2(CO\,OH)_2 \rightarrow CH_3\,CO\,OH + CO_2$$

The instability of two carboxyls attached to the same carbon atom recalls the readiness with which glycols containing two hydroxyl groups on the same carbon atom lose a molecule of water (p 736)

When malonic acid is heated, a small quantity of **carbon suboxide** $C_3O_2$, is also produced by loss of two molecules of water

$$HO\,CO\,CH_2\,CO\,OH \rightarrow O{=}C{=}C{=}C{=}O + 2H_2O$$

Much better yields are obtained by heating ethyl malonate with phosphoric oxide, when ethylene is formed as a second product of dehydration

$$C_2H_5O\,CO\,CH_2\,CO\,OC_2H_5 \rightarrow O{=}C{=}C{=}C{=}O + 2C_2H_4 + 2H_2O$$

The product is a gas (b -pt 7°) which combines with water to form malonic acid, with hydrogen chloride to form **malonyl chloride**, with ammonia to form **malonamide**, and with alcohol to form **ethyl malonate**,

$$O{=}C{=}C{=}C{=}O + 2HX \rightarrow X\,CO\,CH_2\,CO\,X,$$

where X = OH, Cl, $NH_2$ or $C_2H_5$

**Ethyl malonate**, $C_2H_5O\,CO\,CH_2\,CO\,OC_2H_5$, can be prepared directly (without first making the acid) by acting on chloracetic acid with potassium cyanide in alcoholic solution to produce **potassium cyanoacetate**, and then with alchoholic hydrogen chloride to produce ethyl malonate

$$Cl\,CH_2\,CO\,OH \rightarrow \underset{\text{Potassium cyanoacetate}}{CN\,CH_2{\cdot}CO{\cdot}OK} \rightarrow \underset{\text{Ethyl malonate}}{C_2H_5O\,CO\,CH_2\,CO\,OC_2H_5}$$

The central methylene radical of this ester behaves like that in acetoacetic ester (p 731), since both hydrogen atoms can be replaced successively by alkyl groups by treatment first with sodium ethoxide and then with an alkyl halide, as represented by the scheme

$$\begin{matrix} C_2H_5O\,CO \\ C_2H_5O\,CO \end{matrix}\!\!>\!CH_2 \xrightarrow{NaOEt} \begin{matrix} C_2H_5O\,CO \\ C_2H_5O\,CO \end{matrix}\!\!>\!CHNa^* \xrightarrow{RI} \begin{matrix} C_2H_5O{\cdot}CO \\ C_2H_5O\,CO \end{matrix}\!\!>\!CHR$$

$$\xrightarrow{NaOEt} \begin{matrix} C_2H_5O\,CO \\ C_2H_5O\,CO \end{matrix}\!\!>\!CNa\,R \xrightarrow{R'I} \begin{matrix} C_2H_5O\,CO \\ C_2H_5O\,CO \end{matrix}\!\!>\!CRR'$$

* The sodium compounds are derived from the enolic form of the ester and have therefore the structure, $C_2H_5O\,CONa\,CH\,CO\,OC_2H_5$, etc, but for convenience are here shown in the same positions that the alkyl radicals eventually occupy

In view of these reactions malonic ester is an important synthetic reagent, especially for the preparation of homologues of acetic acid Thus the above mono- or di-substituted alkyl esters can easily be hydrolysed to the corresponding dicarboxylic acids, which lose carbon dioxide on heating and give a mono- or dialkyl derivative of acetic acid

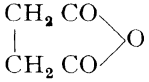
$$RCH(COOC_2H_5)_2 \xrightarrow{H_2O} RCH(COOH)_2 \xrightarrow{HEAT} RCH_2(COOH) + CO_2,$$

$$RR'C(COOC_2H_5)_2 \xrightarrow{H_2O} RR'C(COOH)_2 \xrightarrow{HEAT} RR'CH(COOH) + CO_2$$

**Succinic acid**, HO CO $CH_2$ $CH_2$ CO OH, was first prepared by distilling amber, but it can be synthesised from acetylene through ethylene bromide and cyanide

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| CH<br>‖ | $H_2$ → | $CH_2$<br>‖ | $Br_2$ ——→ | $CH_2$ Br<br>\| | KCN ——→ | $CH_2$ CN<br>\| | $H_2O$ ——→ | $CH_2$ CO·OH<br>\| |
| CH | | $CH_2$ | | $CH_2$ Br | | $CH_2$ CN | | $CH_2$ CO OH |
| Acetylene | | Ethylene | | Ethylene bromide | | Ethylene cyanide | | Succinic acid |

When distilled, the crystalline acid yields an inner **anhydride** containing a ring of four carbon atoms and one oxygen atom



It is also of interest as the parent of the hydroxy acids described below.

## C Malic and Tartaric Acids

**Malic acid**, HO CO CH(OH) $CH_2$ CO OH, contains an asymmetric carbon atom (the one in heavy type) and therefore exhibits optical isomerism The laevo-rotatory acid is present in the juice of many unripe fruits, especially the apple, whilst the dextro-rotatory isomer can be obtained by artificial methods It is a crystalline solid which not only shows the general properties of a dibasic acid, but also some of the properties of an alcohol, *e g* the " alcoholic " hydroxyl group can be acetylated by acetic anhydride

**Tartaric acid**, HO CO CH(OH) CH(OH) CO OH, the acid of sour grapes, is a dihydroxysuccinic acid, which can be reduced to succinic acid by the action of hydrogen iodide It contains *two* asymmetric carbon atoms, and is dextrorotatory , but an optically inactive acid of similar structure is sometimes found as an impurity in the preparation of tartaric acid from grapes, and is distinguished as **racemic acid** Moreover, an optically inactive form of the acid can be synthesised from glyoxal (p 735) through the cyanhydrin, just as lactic acid can be synthesised from acetaldehyde (p 745)

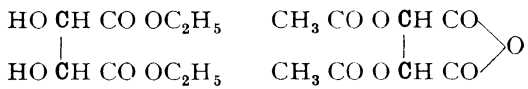
| | | | | |
|---|---|---|---|---|
| CHO<br>\| | $+2HCN$ ——→ | CH(OH) CN<br>\| | $H_2O$ ——→ | CH(OH) CO OH<br>\| |
| CHO | | CH(OH) CN | | CH(OH) CO·OH |

**Derivatives of tartaric acid.**—The principal salts of tartaric acid are

| | |
|---|---|
| **Potassium hydrogen tartrate** | HO CH CO OK<br>\|<br>HO CH CO OH |
| or " cream of tartar " | |
| **Potassium sodium tartrate** | HO CH CO OK<br>\|<br>HO CH CO ONa |
| or " Rochelle salt " | |
| **Potassium antimonyl tartrate** | HO CH CO OK<br>\|<br>HO CH CO O(SbO) |
| or " tartar emetic " | |

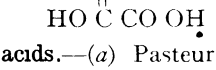
" Cream of tartar " is separated from the " lees " of wine, it is converted into " Rochelle salt " by neutralising with soda and into " tartar emetic " by boiling the solution with antimony oxide

Since the carboxylic and alcoholic hydroxyl groups of tartaric acid are all reactive, a large variety of alkyl, acyl and alkylidene derivatives can be prepared in addition to the simple esters, such as **ethyl tartrate.** Thus acetic anhydride gives **diacetyltartaric anhydride**



Ethyl tartrate — Diacetyltartaric anhydride

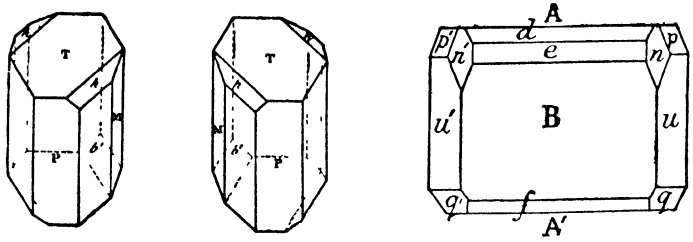
The two atoms of hydrogen which are inert in these reactions can, however, be removed by Fenton's reagent (hydrogen peroxide and a ferrous salt), which converts tartaric acid into **dihydroxyfumaric acid**



**Resolution of racemic acids.**—(*a*) Pasteur found that when **sodium ammonium racemate** was crystallised from water, the crystals were of two sorts, one sort was identical with **sodium ammonium *d*-tartrate,** whilst the other sort (the mirror-image of the first sort) gave solutions of equal and opposite rotatory power and evidently consisted of **sodium ammonium *l*-tartrate** At temperatures above 26°, this separation cannot be effected, since the *d*- and *l*-salts form a " double salt " instead of crystallising separately (Fig 180)

Pasteur showed that the acids, ***d*-tartaric acid** and ***l*-tartaric acid,** derived from these two salts were also of opposite sign and gave crystals which were mirror-images of one another (Fig 181), but that when concentrated solutions of the two acids were mixed, heat was liberated and there was an abundant crystallisation of **racemic acid** It was therefore clear that racemic acid was a sort of " double salt " of *d*- and *l*-tartaric acids The terms RACEMIC MIXTURE and RACEMIC COMPOUND are therefore now used as general expressions to describe those substances which are optically inactive because they contain equal amounts of a *d*- and *l*-constituent Thus, synthetic products (such as lactic acid prepared from acetaldehyde) are always " racemic " because the *d*- and *l*-components are produced in equal amounts in the synthesis

The method of resolution described above can only be applied to *racemic mixtures*, the *d*- and *l*-components of which come out from solution in separate crystals. It is obviously not applicable to *racemic compounds* (such as racemic acid itself or sodium ammonium racemate above 26°), the crystals of which are all of one type, containing equal quantities

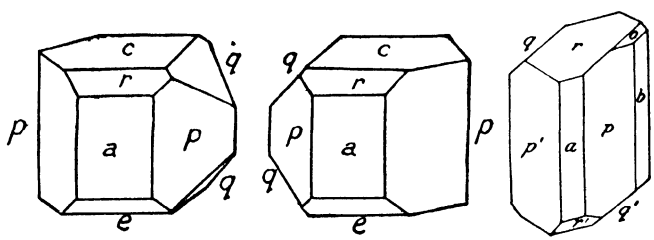



(*a*) Dextrorotatory (*b*) Laevorotatory (*c*) Inactive

FIG 180 (*a*) (*b*) HEMIHEDRAL CRYSTALS OF SODIUM AMMONIUM TARTRATE (Pasteur) (*c*) HOLOHEDRAL CRYSTAL OF SODIUM AMMONIUM RACEMATE (Scacchi)

of the two isomers Its application by Pasteur to sodium ammonium racemate therefore remains almost unique

(*b*) Pasteur also found that the *d*- and *l*-components of racemic acid could be separated from one another by combining them with an *optically active base* As we have already seen, the ordinary salts of *d*- and *l*-tartaric acid are mirror-images of one another, and are therefore identical in every respect except (i) crystalline form, (ii) optical rotatory power The salts




(*a*) Dextrorotatory (*b*) Laevorotatory (*c*) Inactive

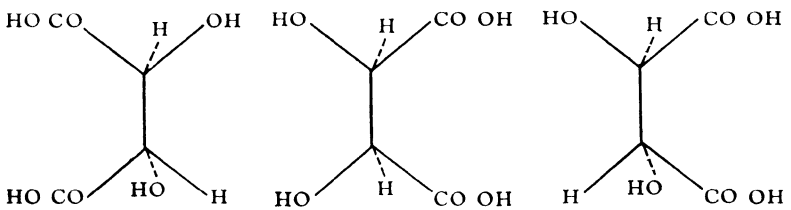
FIG 181 (*a*) (*b*) HEMIHEDRAL CRYSTALS OF TARTARIC ACID (Pasteur) (*c*) HOLOHEDRAL CRYSTAL OF RACEMIC ACID

of *d*- and *l*-tartaric acid with an optically active base, *e g* *d*-cinchonine *d*-tartrate and *d*-cinchonine *l*-tartrate, are, however, no longer mirror-images of one another, since the acid has been inverted by reflection in the mirror whilst the base has not The physical properties of these two salts, including their crystalline form and solubility, are therefore entirely different, with the result that they can be separated from one another in the ordinary way by fractional crystallisation, etc This was done, and the *d*- and *l*-acids were then easily separated in mirror-image forms

This method has been used very widely for the RESOLUTION of racemic acids into their optically active components, with the help of optically active bases, and conversely, but it can also be applied to any other type of coupling Thus racemic *alcohols* are coupled with a dibasic acid, such as sulphuric acid, to form an acid salt, *e g* RO $SO_2$ OH, which can then be resolved into its *d*- and *l*-components by crystallising it with an optically active base; the *d*- and *l*-alcohols are then separated in mirror-image forms by hydrolysis of the two salts

(*c*) Pasteur also found that *d*-tartaric acid was preferentially destroyed by ordinary green mould, *Penicillium glaucum* A solution of racemic acid therefore left a residue of the new *l*-tartaric acid, when a mould was cultivated in it This method can be used in other cases to give one form only of an optically active compound, but does not differ much from the ordinary method of obtaining optically active compounds from plant and animal sources

**Tartaric and *meso*-tartaric acids.**—When tartaric acid is heated in a sealed tube with water at 165° for two days it is converted into an inactive isomer known as ***meso*-tartaric acid** This differs from racemic acid in



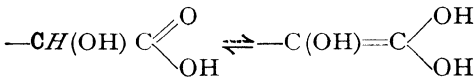

I. *d*-Tartaric acid II *meso*-Tartaric acid III *l*-Tartaric acid

FIG 182 ABSOLUTE CONFIGURATION OF *d*- AND *l*- AND *meso*-TARTARIC ACID

forming a more soluble calcium salt, but above all in the fact that it cannot be resolved into optically active components by any of the preceding methods Whereas, therefore, the inactivity of racemic acid is attributed to EXTERNAL COMPENSATION (whereby the rotations of the *d*- and *l*-components neutralise one another), the inactivity of *meso*-tartaric acid is attributed to INTERNAL COMPENSATION The nature of this compensation is obvious at once from the fact that tartaric acid contains *two* asymmetric carbon atoms In *d*-tartaric acid these two centres co-operate to produce a dextrorotation, and *vice versa* in *l*-tartaric acid , but, since the two halves of the molecule have precisely similar structures, a reversal of sign of either radical would produce a complete neutralisation of optical rotatory power We can therefore assign with certainty the configuration II to *meso*-tartaric acid, since this possesses a plane of symmetry and is identical with its mirror-image The configurations of the *d*- and *l*-acids are less obvious, but can be deduced in the same way as those of amyl alcohol and *iso*-valeric acid (p 744) Thus when viewed from the centre of the molecule the sequence H, OH, COOH is clockwise in *l*-tartaric acid and counterclockwise in *d*-tartaric acid, whilst in *meso*-tartaric acid one sequence is clockwise and the other counterclockwise (It does not

matter which is which, because they can be interchanged by turning the molecule upside down )

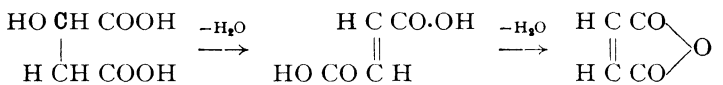
**Mechanism of isomeric change.**—The conversion of tartaric acid into *meso*-tartaric acid and then into a mixture of *meso*-tartaric and racemic acids, is attributed to enolisation of the carboxyl group



This enolisation destroys the asymmetry of the contiguous carbon atom from which the mobile hydrogen atom (shown in italic) is drawn, on reversion to the ordinary form, therefore, either the *d*- or the *l*-radical may be reproduced The formation of the merest trace of enol (accelerated if necessary by an acid or basic catalyst) is therefore sufficient to bring about a condition of dynamic equilibrium, whereby *d*-tartaric acid is converted (by inversion of one radical) into *meso*-tartaric acid, and then (by inversion of the second radical) into *l*-tartaric acid Since *d*- and *l*-tartaric acids have identical energy-contents, they must be present in equal quantities in the final equilibrium, so that the ultimate product should be an inactive mixture of *meso*-tartaric and racemic acids

## D Fumaric and Maleic Acids

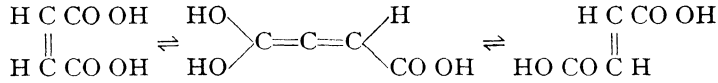
**Preparation and structure.**—When malic acid is heated to 140°-150° it loses a molecule of water and is converted into **fumaric acid**, if heated quickly to 180°, **maleic anhydride** is also produced by loss of a second molecule of water




Malic acid Fumaric acid Maleic anhydride

When dissolved in water, maleic anhydride is hydrolysed to **maleic acid,** which melts at 130°, whereas fumaric acid is still solid at 200° Both acids have the properties and structure of *ethylene dicarboxylic acids*, HO CO CH=CH CO OH, *e g* they both yield disodium salts and dialkyl esters, both combine with two atoms of bromine, and are both reduced to succinic acid by sodium amalgam or zinc They are therefore obviously STEREOISOMERS, containing the same radicals in the same sequence, and therefore represented by the same structural formula, but differing in the way in which the radicals are oriented in space They can, moreover, be converted readily into one another Thus, in contact with concentrated HCl, HBr or HI, solid maleic acid changes into the more stable fumaric acid, but this is reconverted into maleic anhydride when distilled This isomeric change was formerly attributed to addition and removal of HX (the H removed being different from the one just introduced), but the addition compounds are in fact completely stable and removal of HX is impossible under the conditions which prevail.

The conversion of maleic into fumaric acid is therefore attributed (as in the case of the tartaric acids) to enolisation of a carboxyl group, accelerated by the presence of a halogen acid




Maleic acid — Enolic isomeride — Fumaric acid

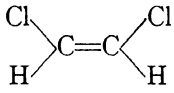
**Stereoisomerism of olefines.**—The isomerism of fumaric and maleic acids was an unsolved problem until van 't Hoff and le Bel suggested, on the basis of the tetrahedral model of the carbon atom, that two carbon atoms linked by a double bond, and therefore having a common *edge* to the two tetrahedra, would not possess the same possibility of FREE ROTATION as two carbon atoms linked by a single bond, and therefore having only an *apex* in common, about which the two tetrahedra could spin quite freely (Fig 7, p 40) Since maleic anhydride yields maleic acid on hydrolysis, it was assigned a *cis*-configuration, in which the two carboxyl groups are on the same side of the plane containing the double bond, so that anhydride-formation is relatively easy A *trans*-configuration, with the two carboxyl groups on opposite sides of the double bond, was then assigned to fumaric acid, the greater stability of which may perhaps be attributed to the mutual repulsion of the carboxyl groups When, however, fumaric acid is distilled, it is wrenched over into the *cis*-configuration, in order to make possible the formation of a cyclic anhydride, and is thus converted into maleic anhydride

This kind of stereoisomerism is not associated with molecular dissymmetry, since the molecule usually possesses a *plane of symmetry*, containing the four radicals of the substituted ethylene , it does not therefore give rise to optical activity and is distinguished as GEOMETRICAL ISOMERISM

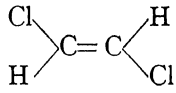
The configurations assigned to fumaric and maleic acids, by reason of their behaviour on dehydration, are confirmed by their behaviour on oxidation to tartaric acid by dilute permanganate Maleic acid, which has a *cis*-configuration, possesses a plane of symmetry which is retained on oxidation , it is therefore oxidised to *meso*-tartaric acid On the other hand, fumaric acid loses its plane of symmetry and is oxidised to racemic acid, *i e* to a mixture of *d*- and *l*- tartaric acids with the dissymmetric configurations shown in Fig 182 Fumaric and maleic acids, however, yield the same succinic acid on reduction, since the conversion of the central double bond into a single bond enables the two carboxyl groups of both reduction products to take up whatever configuration happens to be the most stable Free rotation is in fact a general characteristic of carbon atoms bound by single bonds ; but a long series of compounds is now known in which the radicals on either side of the single bond are so complex that they interlock, and thus give rise to an optical isomerism which can only be explained by the inhibition of free rotation in compounds of this kind

The configurations of fumaric and maleic acids were deduced by chemical methods, but have been confirmed by physical methods. In

other cases physical methods are the only ones available Thus there are two dichlorethylenes with dipole moments as follows




I $\mu = 2\ 5 \times 10^{-18}$ e s u




II $\mu = 0$

It is obvious that the isomer with a zero dipole moment must be II, since this form has a centre of symmetry, so that the component dipoles of the two C-Cl bonds point in opposite directions and therefore cancel out completely.

# CHAPTER LVII

## AMINES, AMIDES AND AMINO-ACIDS

**The amino-radical.**—The univalent AMINO-RADICAL, $NH_2$, plays an important part in organic chemistry, since it is the main source of *basic* qualities, just as the carboxyl group is a main source of *acidic* properties Thus the basic properties of ammonia are retained in its alkyl-derivatives, $CH_3 NH_2$, etc, just as the salt-forming powers of carbonic acid are retained in the carboxylic acids The amino-radical appears in three principal classes of compounds

(i) the AMINES, $R NH_2$,

(ii) the AMIDES, $R CO NH_2$,

(iii) the AMINO-ACIDS, $NH_2 CHR CO{\cdot}OH$

The amines are basic The amides are almost neutral, but exhibit feeble acid and basic properties Finally, the amino-acids are strongly amphoteric, since the amino group yield salts, with acids, whilst the carboxyl group gives salts with bases

### A THE AMINES

**Alkyl-derivatives of ammonia.**—The progressive displacement of the hydrogen atoms of ammonia by alkyl radicals yields

(i) PRIMARY AMINES, *e g* methylamine, $CH_3 NH_2$,

(ii) SECONDARY AMINES, *e g* dimethylamine, $\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!NH$,

(iii) TERTIARY AMINES, *e g* trimethylamine, $\begin{matrix} CH_3 \\ CH_3 \\ CH_3 \end{matrix}\!\!>\!N$

The last can then combine with an alkyl iodide to form

(iv) QUATERNARY AMMONIUM SALTS, *e g* tetramethylammonium iodide, $[N(CH_3)_4]I$

**Preparation of amines.**—(*a*) Derivatives of all the preceding types are formed when an alkyl halide is heated under pressure with alcoholic ammonia, *e g* with methyl iodide the preliminary action is,

$$CH_3{\cdot}I + NH_3 = HI + CH_3 NH_2, \text{ methylamine,}$$

and this is followed by the combination of the hydrogen iodide with some

of the methylamine and unchanged ammonia to form respectively methylamine hydriodide (or methyl ammonium iodide) and ammonium iodide

$$CH_3NH_2 + HI = [CH_3 \cdot NH_3]I,$$
$$NH_3 + HI = NH_4I$$

The unchanged methylamine then reacts with another molecule of methyl iodide to form dimethylamine,

$$CH_3I + CH_3NH_2 = HI + (CH_3)_2NH, \quad \text{dimethylamine,}$$

which is converted partly into dimethylamine hydriodide, $[(CH_3)_2NH_2]I$, by the hydrogen iodide, and partly into trimethylamine, $(CH_3)_3N$, and its hydriodide, $[(CH_3)_3NH]I$, by the action of yet another molecule of methyl iodide Finally, some tetramethyl ammonium iodide is formed by the union of trimethylamine and methyl iodide

$$CH_3I + N(CH_3)_3 = [N(CH_3)_4]I, \quad \text{tetramethylammonium iodide}$$

It is impossible to control the above reactions so that only one amine or its salt is produced, and since the separation of the various amines is extremely tedious, this method of preparing them is of little practical importance

(*b*) Primary amines can be prepared by HOFMANN'S REACTION, *i.e.* by the action of an alkaline hypobromite solution on an amide, *e g*

$$CH_3 \cdot CO \cdot NH_2 + KBrO = CH_3NH_2 + KBr + CO_2$$

This curious reaction, in which a carbonyl radical appears to be bitten out from a molecule of the *amide*, leaving the two residues to unite to form an *amine*, depends on an initial conversion of the amide into a *bromoamide*, $R\,CO\,NH_2 \rightarrow R\,CO\,NHBr$, this then loses hydrogen bromide and the residue appears to undergo isomeric change to an *iso*-cyanate,

$$R \cdot CO\,N < \rightarrow R\,N\,C\,O,$$

from which, as is well known, an amine can be prepared by hydrolysis with potash, $R \cdot N\,N\,O + 2KOH \rightarrow R\,NH_2 + K_2CO_3$ Thus the conversion of acetamide into methylamine may be represented by the following scheme

$$CH_3\,CO\,NH_2 + Br_2 + KOH = CH_3\,CO\,NHBr + KBr + H_2O,$$
$$CH_3\,CO\,N \cdot HBr + KOH = CH_3\,N\,C\,O + KBr + H_2O,$$
$$CH_3\,N\,C\,O + 2KOH = CH_3 \cdot NH_2 + K_2CO_3$$

(*c*) Primary amines can also be prepared by the reduction of nitro-paraffins and alkyl cyanides with nascent hydrogen

$$CH_3\,NO_2 + 6H \rightarrow CH_3\,NH_2 + 2H_2O.$$
$$CH_3 \cdot C \equiv N + 4H \rightarrow CH_3\,CH_2\,NH_2 \text{ (Ethylamine)}$$

Although the first of the above reactions, viz the reduction of a nitro-compound, is seldom used for the preparation of an aliphatic amine, the method is of supreme importance in the case of aromatic amines, since these are almost exclusively prepared by the reduction of the corresponding nitro-compounds (see aniline, p 796)

**Properties of primary, secondary and tertiary amines.**—(*a*) The three ethylamines are gases and their lower homologues are volatile liquids. ney have a pungent, fishy, ammoniacal smell, and are freely soluble in ter, to which they impart a strongly alkaline reaction, since they are en more strongly basic than ammonia

$$CH_3NH_2 + H_2O \rightleftharpoons CH_3NH_3OH \rightleftharpoons CH_3NH_3^+ + OH^-,$$

mpare $$NH_3 + H_2O \rightleftharpoons NH_4OH \rightleftharpoons N_4^+H + OH^-$$

ke ammonia, therefore, they are able to precipitate many metallic droxides from aqueous solutions of their salts, and unite directly with ids to form salts,

$$CH_3NH_2 + HCl = [CH_3NH_3]^+Cl^- \text{ (Methylamine hydrochloride),}$$

nich are usually very similar to the corresponding ammonium salts, for ample, they are readily decomposed by heating with a caustic alkali,

$$[CH_3NH_3]Cl + NaOH = CH_3NH_2 + NaCl + H_2O,$$

mpare $$NH_4Cl + NaOH = NH_3 + NaCl + H_2O$$

Unlike ammonia, however, the amines burn in air and this, incidentally, one of the simplest tests for distinguishing between gaseous methyl- ine and ammonia, which are otherwise very similar

Primary and secondary (but not tertiary) amines can be converted into bstituted amides by the action of acid chlorides or anhydrides, *e g.*

$$CH_3\,CO\,Cl + H_2N\,CH_3 = HCl + CH_3\,CO\,NH(CH_3)$$

Methyl acetamide

$$CH_3\,CO\,Cl + HN(CH_3)_2 = HCl + CH_3\,CO\,N(CH_3)_2$$

Dimethyl acetamide

(*b*) Primary amines (but not secondary and tertiary amines), when ated with chloroform and alcoholic potash, yield an *iso*-cyanide (p. 766) hich can be detected readily by its intolerable odour

$$CH_3\,NH_2 + CHCl_3 + 3KOH = 3KCl + 3H_2O + CH_3\,NC$$

(*c*) Primary, secondary and tertiary amines can be distinguished by eir behaviour towards nitrous acid, just as the three corresponding pes of alcohols can be distinguished by their different behaviour on idation

(i) *Primary amines* give the alcohol and free nitrogen

$$R{:}\dot{N}{:}H_2 + O{:}N{:}OH \rightarrow R{\cdot}OH + N_2 + H_2O.$$

(ii) *Secondary amines* give nitrosamines :

$$\begin{matrix} R \\ R \end{matrix}\!\!>\!N{:}H + HO{:}NO \rightarrow \begin{matrix} R \\ R \end{matrix}\!\!>\!N{\cdot}NO + H_2O.$$

he nitrosamine separates as a yellow oil which is relatively stable, but it in be reconverted into the parent amine, in the form of its hydrochloride, y heating with concentrated hydrochloric acid

(iii) *Tertiary amines* are merely converted into a nitrite, whilst *quaternary ammonium salts* are unaffected.

**Quaternary ammonium salts.**—When ammonia or an amine is heated with an excess of alkyl halide, it is converted into a QUATERNARY AMMONIUM SALT, which can be converted by the action of silver oxide (but not of caustic alkalis) into a QUATERNARY AMMONIUM HYDROXIDE, *e.g.*

$$[N(CH_3)_4]I + AgOH \rightarrow [N(CH_3)_4]OH + AgI.$$

These quaternary hydroxides are comparable in strength with the caustic alkalis, since they are permanently and completely ionised in solution and are not liable to lose their alkaline properties by dehydration as in the case of ammonium hydroxide

$$[N(CH_3)_4]^+OH^-, \text{ contrast } [NH_4]OH \rightleftharpoons NH_3 + H_2O$$

They are therefore comparable in almost every respect with the caustic alkalis, which they resemble in absorbing carbon dioxide from the air to form carbonates, and in liberating ammonia from ammonium salts, etc , but when heated strongly both the salts and the bases decompose with formation of a tertiary amine, *e g*

$$[N(CH_3)_4]OH \rightarrow N(CH_3)_3 + CH_3\,OH\,,\ [N(CH_3)_4]I \rightarrow N(CH_3)_3 + CH_3I.$$

## B THE AMIDES

**The amides** are ACYL-DERIVATIVES of ammonia in which the hydroxyl group of an acid has been replaced by the amino radical, $NH_2$ Thus the fatty acids, RCOOH, yield amides of general formula $R\,CO{\cdot}NH_2$, *e g* ACETAMIDE, $CH_3\,CO\,NH_2$, is the amide derived from acetic acid Dibasic acids, such as oxalic acid $(COOH)_2$, and carbonic acid, $CO(OH)_2$, which contain two "acidic" hydroxyl groups, can form di-amides, namely oxamide, $(CO{\cdot}NH_2)_2$, and urea, $CO(NH_2)_2$, p 747

**Preparation of amides.**—Amides can be prepared by the following general methods

(i) By heating the ammonium salt of a carboxylic acid so that water is expelled

$$CH_3{\cdot}CO{\cdot}ONH_4 \rightleftharpoons H_2O + CH_3\,CO\,NH_2, \text{ acetamide.}$$

The reaction is reversible, but is made to go to completion by distilling off the water from the much less volatile acetamide (Expt 161, p. 713). The method is especially suitable for the preparation of aliphatic amides

(ii) By shaking an excess of concentrated ammonia with the ester of the acid

$$CH_3{\cdot}CO\,OC_2H_5 + NH_3 = C_2H_5{\cdot}OH + CH_3{\cdot}CO{\cdot}NH_2, \text{ acetamide,}$$
$$(CO{\cdot}OC_2H_5)_2 + 2NH_3 = 2C_2H_5\,OH + CO(NH_2)_2, \text{ oxamide.}$$

Oxamide is usually prepared by this method, since, unlike acetamide, it is insoluble and therefore easily separated from the mother liquor by filtration.

(iii) By the action of concentrated ammonia on an acid chloride,

$$CH_3{\cdot}CO{\cdot}Cl + 2NH_3 = NH_4Cl + CH_3\,CO{\cdot}NH_2$$

This, like method (ii), is generally more suitable for the preparation of aromatic amides like benzamide, $C_6H_5CONH_2$, p 790

**Properties of amides.**—The amides are usually colourless solids which have a higher boiling-point than the parent acid, and when the acyl group is small they are usually quite soluble in water

The chief points to note about their chemical properties are

(i) The disappearance of the basic qualities of the amino group under the influence of the contiguous carbonyl group

| | | |
|---|---|---|
| | $CH_3\,CH_2\,NH_2$ | $CH_3{\cdot}CO\,NH_2$ |
| | Ethylamine | Acetamide |
| | (basic) | (almost neutral) |
| compare | $CH_3{\cdot}CH_2\,OH$ | $CH_3{\cdot}CO\,OH$ |
| | (Neutral) | (Acidic) |

Thus the amides form unstable salts with strong acids such as hydrochloric acid, and are sufficiently acidic to yield metallic salts, *e g* yellow mercuric oxide dissolves in aqueous acetamide to form **mercury acetamide,**

$$Hg(NH\,CO\,CH_3)_2$$

(ii) The weakness with which the $NH_2$ group is held in the amides as compared with its stability in the amines Thus it is only necessary to boil an amide with an alkali in order to liberate ammonia and produce a salt of the acid

$$CH_3{\cdot}CO{\cdot}NH_2 + NaOH \rightarrow CH_3\,CO\,ONa + NH_3$$

A similar hydrolysis occurs when an amide is boiled with a dilute acid, *e g*

$$CH_3\,CO\,NH_2 + H_2O + HCl = CH_3\,CO\,OH + NH_4Cl$$

(iii) The formation of a nitrile when they are " dehydrated " by heating with phosphorous pentoxide

$$CH_3\,CO\,NH_2 - H_2O = CH_3CN \text{ (Acetonitrile, p 766)}$$

(iv) The formation of a primary amine when they are treated with an alkaline solution of a hypobromite

$$CH_3\,CO\,NH_2 + 2KOH + KBrO = CH_3NH_2 + K_2CO_3 + KBr + H_2O$$

(v) The liberation of nitrogen and the formation of the parent acid when they are treated with nitrous acid

$$CH_3{\cdot}CO{\cdot}NH_2 + ON{\cdot}OH = CH_3\,CO{\cdot}OH + N_2 + H_2O,$$

compare $\quad CH_3{\cdot}NH_2 + ON{\cdot}OH = CH_3\,OH \quad + N_2 + H_2O$

## C The Amino-acids

**The amino-acids** are formed by inserting $—NH_2$ in place of a hydrogen *in the alkyl radical* of a carboxylic acid, instead of in the hydroxyl radical as in the amides In natural compounds this substitution almost always

takes place on the contiguous α-carbon atom Thus the amino-acids which serve to build up the proteins are of the type

$$NH_2\,CHR\,CO{\cdot}OH,$$

even when R is itself a hydrocarbon chain The parent of the amino-acids is therefore **glycine** (or glycocoll) or **α-aminoacetic acid,**

$$NH_2{\cdot}CH_2{\cdot}CO\,OH$$

This is formed by the hydrolysis of gelatin or glue, but the ammonium salt can be prepared by the action of ammonia on chloracetic acid .

$$Cl\,CH_2\,CO{\cdot}OH + 3NH_3 \rightarrow NH_2{\cdot}CH_2{\cdot}CO{\cdot}ONH_4 + NH_4Cl$$

The acid crystallises in prisms, with a sweet taste, and has many of the physical properties of a salt , but it has no definite melting-point, since when heated it chars before it melts

Glycine exhibits the reactions both of an acid and of a base. Thus, as a carboxylic acid, it forms metallic salts, esters and an amide, *e g.*

| | |
|---|---|
| $(NH_2\,CH_2\,CO\,O)_2Cu,\ H_2O$ | Copper glycine |
| $NH_2\,CH_2\,CO\,OC_2H_5$ | Ethyl glycine |
| $NH_2\,CH_2\,CO{\cdot}NH_2$ | Glycine amide |

On the other hand, it forms a hydrochloride, $\overset{-}{Cl}\,\overset{+}{N}H_3\,CH_2\,CO{\cdot}OH$, and reacts as a primary amine with nitrous acid, liberating nitrogen and forming **glycollic acid,** or **α-hydroxyacetic acid,** $HO\,CH_2\,CO{\cdot}OH$ (p 745)

$$HO{\cdot}N\,O + H_2\,N{\cdot}CH_2{\cdot}CO\,OH \rightarrow HO{\cdot}CH_2\,CO{\cdot}OH + N_2 + H_2O$$

In the absence of acids and bases, there can be little doubt that glycine forms an INTERNAL SALT, *i e* that the acidic carboxyl group transfers a proton to the basic amino group

$$NH_2\,CH_2\,CO\,OH \rightarrow \overset{+}{N}H_3{\cdot}CH_2\,CO\,\overset{-}{O},$$

compare $$NH_3 + CH_3\,CO\,OH \rightarrow \overset{+}{N}H_4 + CH_3{\cdot}CO\,\overset{-}{O}$$

Evidence in support of this " internal salt " formula is found in the fact that, by the action of methyl iodide, *three* atoms of hydrogen can be replaced by methyl groups, *which are all attached directly to nitrogen*

$$\overset{+}{N}H_3\,CH_2\,CO\,\overset{-}{O} + 3CH_3\,I \rightarrow \overset{+}{N}(CH_3)_3{\cdot}CH_2\,CO\,\overset{-}{O} + 3HI$$

EXPT 174 **Preparation and properties of glycine.**

(*a*) *Preparation* —Place 250 c c of o 880 ammonia in a stout jar containing 50 c c of water Then add drop by drop 50 c c of a 50% solution of chloracetic acid from a tap-funnel, the ammoniacal mixture being stirred vigorously by means of a stirrer which is driven by an electric motor or water-turbine Stand the mixture in a fume chamber for twenty-four hours before heating it to drive off the excess of ammonia The last traces of

ammonia can be expelled by blowing in steam. Then add copper carbonate to the hot liquid until no more dissolves, filter and evaporate to crystallisation Filter on to a Buchner funnel the blue needles of **copper glycine,** $(NH_2CH_2COO)_2Cu,H_2O$, which separate, and wash them with a little methylated spirits Dissolve the copper salt in hot water, and regenerate the free acid by passing hydrogen sulphide into the solution until no more copper sulphide is precipitated Filter and evaporate the filtrate to crystallisation

$$Cl\,CH_2\,CO\,OH + 2NH_3 = NH_2\,CH_2{\cdot}CO\,OH + NH_4Cl,$$
$$(NH_2\,CH_2\,CO\,O)_2Cu + H_2S = 2NH_2\,CH_2\,CO\,OH + CuS$$

(*b*) *Properties* —(i) Compare the solubility of glycine in water, alcohol and ether (ii) Place a solution of glycine in two test tubes , to one, add a drop of copper sulphate solution, and to the other a drop of ferric chloride

**Proteins,** which are the predominating nitrogenous constituents of animal and vegetable tissues, are *mixed anhydrides* formed by elimination of molecules of water from chains of α-amino-acids, *e g*

$$NH_2\,CHX\,CO\,OH + NH_2{\cdot}CHY{\cdot}CO{\cdot}OH + NH_2\,CHZ\,CO\,OH$$
$$\rightarrow NH_2\,CHX\,CO\,NH{\cdot}CHY{\cdot}CO{\cdot}NH\,CHZ{\cdot}CO{\cdot}OH + 2H_2O$$

The proteins therefore contain the amphoteric radical —CO NH— linked by —CHX—, —CHY—, —CHZ—, etc , where X Y Z may be $—CH_3$, $—C_4H_9$, $—CH_2\,COOH$, $—CH_2\,CO\,NH_2$, and more complex organic radicals which may contain other elements, such as phosphorus and sulphur The chains thus formed are of great length, since the smallest molecular weight of a protein so far determined is of the order of 35,000 At least twenty amino-acids have been isolated by artificially breaking down protein molecules, and it appears that many of them are essential to animal life Since few of them can be made by animals, it is essential that the vegetable foods on which animals live should be sufficiently varied to include all the essential amino-acids, so that the animal can use them to build up its tissues, after having split them apart (by a reversal of the preceding equation) during digestion

# CHAPTER LVIII

## CYANIDES AND NITRITES

**Cyanides and *iso*-cyanides.**—The preparation and properties of the metallic cyanides have been described in Chapter XIV, together with those of the cyanates and thiocyanates, and the conversion of ammonium cyanate into urea has also been recorded (p 651), as the first synthesis of an organic product from inorganic materials Prussic acid is, however, also of interest as a tautomeric compound (p 732), which reacts as if it had two different structures at the same time, since its esters can be prepared in two isomeric forms These are distinguished as

(*a*) CYANIDES or NITRILES, R CN,

(*b*) *iso*-CYANIDES or *iso*-NITRILES or CARBYLAMINES, R·NC.

(*a*) The *cyanides* or *nitriles* can be prepared

(i) by heating an alkyl halide with potassium cyanide in alcoholic solution at 100°, *e g*

$$CH_3I + KCN \rightarrow KI + CH_3CN \text{ (Methyl cyanide)},$$

(ii) by distilling the amide of a fatty acid with phosphoric oxide, *e g*

$$CH_3CONH_2 \xrightarrow{-H_2O} CH_3CN \text{ (Acetonitrile)}$$

The products obtained by these two methods are described as the CYANIDE of an alkyl radical, and as the NITRILE of a fatty acid, but they are in fact identical, so that methyl cyanide and acetonitrile are synonymous

(*b*) The iso-*cyanides* or *carbylamines* are prepared

(i) by the action of an alkyl iodide on silver cyanide, when an addition compound of the *iso*-cyanide with silver cyanide is first formed, and is then decomposed by distillation with potassium cyanide, thus

$$C_2H_5I + 2AgCN \rightarrow C_2H_5NC,AgCN + AgI$$
$$C_2H_5NC,AgCN + KCN \rightarrow C_2H_5NC + KAgC_2N_2$$

(ii) by heating a primary amine with chloroform and an alcoholic solution of potassium hydroxide, *e g*

$$C_2H_5{\cdot}NH_2 + CHCl_3 + 3KOH \rightarrow C_2H_5NC + 3KCl + 3H_2O$$

The lower cyanides are liquids with an ethereal smell and are miscible with water, but the corresponding *iso*-cyanides are only sparingly soluble in water and have an intolerable odour

EXPT. 175 **Preparation of phenyl *iso*-cyanide.**

Mix in a test tube two or three drops of chloroform, a drop of aniline and a little alcoholic potash Warm gently in the fume cupboard, and notice the intolerable smell of phenyl *iso*-cyanide

**Structure of cyanides and *iso*-cyanides.**—The cyanides and *iso*-cyanides differ in that the alkyl radical is attached to *carbon* in the cyanides and to *nitrogen* in the *iso*-cyanides This can be proved as follows

(*a*) *Cyanides* —(i) The cyanides are prepared from the carboxylic acids by dehydration of the ammonium salt, *e g*

$$CH_3\,CO\,OH \overset{\pm NH_3}{\rightleftharpoons} CH_3\,CO\,ONH_4 \overset{\mp H_2O}{\rightleftharpoons} CH_3\,CO\,NH_2 \overset{\mp H_2O}{\rightleftharpoons} CH_3\,CN$$

The direct attachment of the alkyl carbon to the carboxyl carbon in the acid may be assumed to persist in the amide and nitrile derived from it This is confirmed by the fact that the nitrile can be hydrolysed back to the original acid, by heating with an acid or alkali, as shown by the lower arrows in the preceding scheme

**(ii) The cyanides can be reduced to primary amines, *e g.*:**

$$CH_3{\cdot}CN + 4H \rightarrow CH_3{\bullet}CH_2{\cdot}NH_2, \text{ ethylamine.}$$

The product evidently contains an ethyl radical, since it can also be made by the action of ammonia on ethyl iodide , it is therefore clear that a methyl radical has been converted into an ethyl radical by the direct linkage of an additional carbon atom to it.

(*b*) iso-*Cyanides.*—(i) The *iso*-cyanides are made by attaching an atom of carbon (from chloroform) to a primary amine, in which the *nitrogen* is already linked directly to carbon .

$$CH_3\,NH_2 + CHCl_3 + 3KOH = \dot{C}H_3\,\overset{+}{N} \equiv \bar{C} + 3KCl + 3H_2O.$$

(ii) Unlike the cyanides, the *iso*-cyanides are stable towards alkalis, but they are hydrolysed by acids and by superheated water to formic acid and a primary amine, in which the alkyl radical is attached to *nitrogen*, *e g*

$$C_2H_5{\cdot}NC + 2H_2O \rightarrow C_2H_5\,NH_2 + H\,CO{\cdot}OH.$$

(iii) The structure of *iso*-cyanides is confirmed by the fact that they yield a secondary amine on reduction with nascent hydrogen :

$$CH_3\bar{N} \equiv \overset{+}{C} + 4H = (CH_3)_2NH, \text{ dimethylamine.}$$

**Electronic structure and tautomerism of prussic acid.**—The electronic structure of the cyanide ion, both in potassium cyanide and in silver cyanide, may be represented by the formula,

$$\bar{C} \quad N:,$$

with a negative charge on the carbon atom It can be converted into prussic acid by bringing up a proton, which can attach itself either to carbon or to nitrogen, thus

$$H\,C.\cdot N \quad \text{or} \quad \bar{C} \quad \overset{+}{N}\,H$$

Hydrogen cyanide Hydrogen *iso*-cyanide

Liquid prussic acid is believed to be an equilibrium-mixture of these two isomers, but with only a very small proportion of the *iso*-cyanide

In the alkyl cyanides and *iso*-cyanides, the mobile hydrogen is replaced by an alkyl radical, and the dynamic isomerism of the hydrides becomes static, since there is no indication of any tendency for the alkyl-derivatives to pass into one another under normal conditions, although the *iso*-cyanides revert to cyanides when the vapours are heated to a high temperature

**The ascent and descent of an homologous series.**—(*a*) The formation of a cyanide from an alkyl halide provides an interesting method of ascending an homologous series Thus methyl alcohol can be converted into ethyl alcohol by the following series of changes

$$\text{(i)}\ CH_3{\cdot}OH \xrightarrow{PI_3} CH_3I \xrightarrow{KCN} CH_3CN \xrightarrow{H} CH_3CH_2NH_2 \xrightarrow{HNO_2} C_2H_5OH$$

Other methods of stepping up an homologous series are summarised in the following equations

$$\text{(ii)}\ CH_3OH \xrightarrow{PI_3} CH_3I \xrightarrow{Na} C_2H_6 \xrightarrow{Cl_2} C_2H_5Cl \xrightarrow{H_2O} C_2H_5OH$$

$$\text{(iii)}\ CH_3OH \xrightarrow{PI_3} CH_3I \xrightarrow{Mg} CH_3MgI \xrightarrow{CO_2} CH_3COOMgI \xrightarrow{HCl} CH_3COOH \xrightarrow{PCl_5} CH_3COCl \xrightarrow{H} C_2H_5OH$$

$$\text{(iv)}\ H_2CO \xrightarrow{HCN} H_2C(OH)CN \xrightarrow{HCl} CH_2(OH)CO\,OH \xrightarrow{HI} CH_3COOH \xrightarrow{PCl_5} CH_3COCl \xrightarrow{H} C_2H_5OH$$

(*b*) The reverse process of descending a series is readily effected by utilising Hofmann's method of making amines from amides, *e g*

$$C_2H_5OH \xrightarrow{O_2} CH_3CO\,OH \xrightarrow{NH_3} CH_3CO{\cdot}ONH_4 \xrightarrow{-H_2O} CH_3CO\,NH_2 \xrightarrow{KBrO} CH_3NH_2 \xrightarrow{HNO_2} CH_3OH.$$

**Alkyl nitrites and nitroparaffins.**—When a mixture of ethyl alcohol and dilute sulphuric acid is added to a solution of potassium nitrite and the product is distilled, **ethyl nitrite**, $C_2H_5O\,NO$ (b -pt. 18°), is obtained When, however, ethyl iodide is heated with silver nitrite, **nitroethane**, $C_2H_5{\cdot}NO_2$ (b -pt. 114°), is also produced

**Structures and reactions of the alkyl nitrites and nitroparaffins.**—The ALKYL NITRITES AND NITROPARAFFINS are represented by the following structural formulae .



I Alkyl nitrite II Nitroparaffin

The attachment of the alkyl radical to oxygen in the nitrites and to nitrogen in the nitroparaffins is confirmed by the following facts

(*a*) On reduction with zinc and acetic acid, the nitrites yield an alcohol and ammonia, whilst the nitroparaffins yield an amine, *e g*

$$C_2H_5\,O{\cdot}NO + 6H = C_2H_5\,OH + NH_3 + H_2O$$
$$C_2H_5\,NO_2 + 6H = C_2H_5\,NH_2 + 2H_2O$$

(*b*) The alkyl nitrites are hydrolysed by alkalis to nitrous acid and an alcohol, *e g*

$$C_2H_5\,O\,NO + KOH = C_2H_5\,OH + KNO_2,$$

but the bond between carbon and nitrogen in the isomeric nitroparaffins is too stable to be broken in this way, and the nitroparaffins are rather unexpectedly converted into *salts* These salts were formerly regarded as products of a direct displacement of hydrogen by sodium or potassium *e g* $NO_2\,CH_2\,K$, but this is unlikely, since even the three chlorine atoms in chloroform do not impart any acidity to the one remaining hydrogen atom It is therefore now customary to regard nitromethane as a tautomeric substance, which can react

(i) as $CH_3{\cdot}NO_2$, *e g* when reduced to $CH_3\,NH_2$, and

(ii) as $\overset{-}{C}H_2-\overset{+}{N}\!\!<\!\!\begin{matrix}OH\\O\end{matrix}$ in forming salts such as $\overset{-}{C}H_2-\overset{+}{N}\!\!<\!\!\begin{matrix}\overset{-}{O}\overset{+}{K}\\O\end{matrix}$

Whereas, however, it has proved impossible to isolate two forms of prussic acid to correspond with the alkyl cyanides and *iso*-cyanides, several cases are known in which the salts of aliphatic nitrocompounds liberate the pseudo-nitrocompound when acidified, and only gradually revert to the normal nitrocompound

$$CH_3\,NO_2 \xrightarrow{KOH} \underset{\text{Potassium nitromethane}}{\overset{-}{C}H_2\,\overset{+}{N}O\,O\overset{-+}{K}} \xrightarrow{HCl} \underset{\text{Pseudo nitromethane}}{\overset{-}{C}H_2\,\overset{+}{N}O\,OH} \longrightarrow \underset{\text{Nitromethane}}{CH_3\,NO_2}$$
Nitromethane

Substances such as nitromethane, which are themselves neutral, but yield acids by undergoing isomeric change, are described as PSEUDO-ACIDS

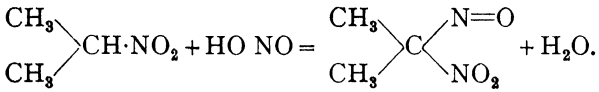
(*c*) The high boiling-point of the nitroparaffins as compared with the isomeric nitrites is in harmony with the presence of a semi-polar double bond in formula II

$C_2H_5\,O\,NO$ (b -pt 18°) $C_2H_5\,NO_2$ (b -pt 114°).

**Primary, secondary and tertiary nitroparaffins.**—The action of nitrous acid on the nitroparaffins is of theoretical interest because it provides a method of determining whether the nitroparaffin is derived from a primary, secondary or tertiary alkyl halide Thus (i) nitrous acid reacts with a ***primary nitroparaffin*** to give a **nitrolic acid**, which reacts with alkalis to give a deep *red* salt, *e g*

$$CH_3{\cdot}CH_2\,NO_2 \xrightarrow{HNO_2} \underset{\text{Ethyl nitrolic acid}}{CH_3\,C\!<\!\begin{matrix}NOH\\NO_2\end{matrix}} \xrightarrow{KOH} CH_3\,C\!<\!\begin{matrix}NOK\\NO_2\end{matrix}$$

(ii) A *secondary nitroparaffin* yields with nitrous acid a **pseudo-nitrol** which gives a *blue* solution, but does not form a salt with an alkali



(iii) Finally, *tertiary nitroparaffins* are not acted upon by nitrous acid Since the alcohols are readily converted into halides and thence into nitroparaffins, the above reaction can be used, in addition to the oxidation test (p. 685), for deciding to which class a given alcohol belongs

# CHAPTER LIX

## AROMATIC HYDROCARBONS

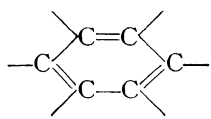
**General considerations.**—AROMATIC COMPOUNDS differ from the ALIPHATIC COMPOUNDS, which have been described in the preceding chapters, in that they contain a much smaller proportion of hydrogen, but without any corresponding development of unsaturation Thus, whereas **dipropargyl**, $HC{\equiv}C\,CH_2\,CH_2\,C{\equiv}CH$ (prepared by the action of potash on diallyltetrabromide), forms silver and copper derivatives like acetylene, and exhibits the unsaturation of a *di*-acetylene, the isomeric hydrocarbon, **benzene**, $C_6H_6$, usually gives substitution products and only forms addition compounds in exceptional cases

Kekulé in 1865 put forward the following three propositions in reference to the structure of aromatic compounds

(i) *All aromatic compounds are derived from a nucleus of six carbon atoms, of which the simplest compound is benzene*, $C_6H_6$ *Derivatives of benzene*, in which its specific character is preserved, are formed by replacing the hydrogen atoms by other groups or radicals (" side-groups ")

(ii) *Benzene has a symmetrical structure* Each atom of carbon is linked with one atom of hydrogen to form a CH group As in the polymethylene compounds, no difference can be detected between the individual C and H atoms, and isomerism is therefore possible only in derivatives with two or more side-groups

(iii) The structure of the benzene nucleus is a closed ring of six carbon atoms, which can be expressed by a regular hexagon If the methods of linkage are the same as in the derivatives of methane, these carbon atoms are linked by alternating single and double bonds

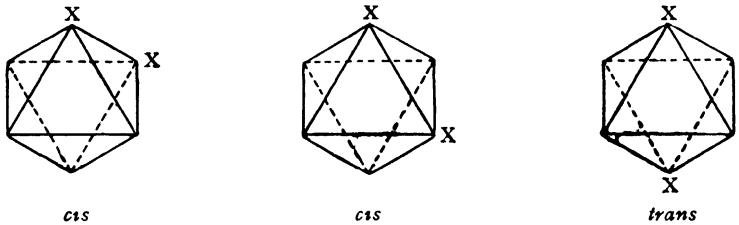


The fourth affinity of the carbon atom is linked to hydrogen in benzene and to other atom groups in benzene derivatives

**Isomerism of derivatives of benzene.**—Kekulé's hexagon, like the tetrahedron of le Bel and van 't Hoff (p 657), was based primarily on the phenomenon of isomerism

(*a*) No isomerism results from the replacement of any *one* of the six hydrogen atoms of benzene by another radical in compounds of the type $C_6H_5X$ This fact rules out all open-chain formulae for benzene, but it can be expressed by representing the hydrocarbon as (i) a ***regular hexagon***, (ii) a ***regular octahedron***, (iii) a ***triangular prism***, since each of these

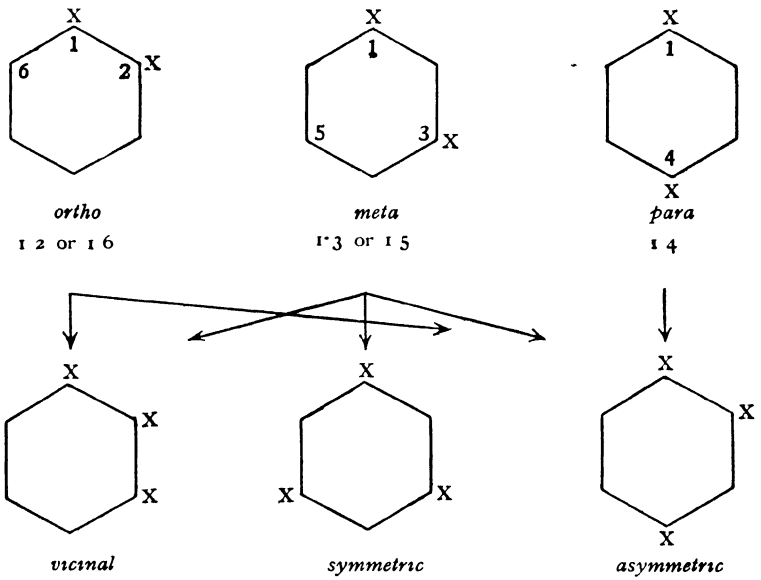
figures has six identical apices, which can be occupied by six identical CH groups.




*cis* *cis* *trans*

FIG 183 THE REGULAR OCTAHEDRON

(*b*) Benzene yields *three* series of *di*-derivatives, $C_6H_4Z_2$, which are distinguished as *ortho*, *meta* and *para* (Fig 184). This can be explained by assigning a hexagonal or prismatic formula to benzene; but the octahedral formula (Fig 183) is ruled out because it only yields *two* series of *di*-derivatives, in which the substituents occupy (i) adjacent or (ii)




*ortho* *meta* *para*

1 2 or 1 6 1·3 or 1 5 1 4

*vicinal* *symmetric* *asymmetric*

FIG 184 ISOMERISM OF *di*- AND *tri*-DERIVATIVES

The atoms of carbon are numbered consecutively from 1 to 6

opposite apices of the octahedron Thus of the three configurations shown in Fig. 183, the first two are identical, whereas all three of the corresponding configurations in Fig 184 are different

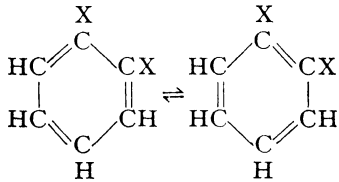
(*c*) Benzene yields three isomeric *tri*-derivatives of the type $C_6H_3X_3$, which are distinguished as *vicinal*, *symmetric* and *asymmetric*. The relationship between the *di*- and *tri*-derivatives, shown by Kekulé's

hexagonal formulae in Fig 184, forms the basis of KORNER'S ABSOLUTE METHOD of identifying *ortho-*, *meta-* and *para*-derivatives of benzene. This method depends on finding out how many *tri*-derivatives can be produced by the introduction of a new substituent into a given *di*-derivative. Thus, when the substituent radicals are all alike, Fig 184 shows that

(i) *para*-diderivatives, which yield only *one* triderivative, are 1 : 4 compounds,
(ii) *ortho*-diderivatives, which yield *two* triderivatives, are 1 2 or 1 : 6 compounds,
(iii) *meta*-diderivatives, which yield *three* triderivatives, are 1 3 or 1 5 compounds.

(*d*) Three-dimensional formulae for benzene, including the regular octahedron and Ladenburg's triangular "prism," are rendered improbable by the fact that some of the *tri*-derivatives would be dissymmetric and therefore capable of existing in optically active forms, which have not yet been observed This result is, of course, merely negative, but positive evidence in favour of the flat hexagon has been provided by modern work on the analysis of crystal structure by X-rays, since this has shown that the twelve carbon atoms of **hexamethylbenzene**, $C_6(CH_3)_6$, are all in a plane

(*e*) In order to maintain the quadrivalency of carbon, Kekulé inserted alternate single and double bonds on the sides of his hexagonal formula (p 771), but (in remarkable agreement with modern theory) he supposed that these bonds were not fixed but mobile, so that two carbon atoms which were linked by a single bond at one instant might be linked by a double bond at the next instant In this way the absence of isomerism due to the orientation of the single and double bonds was explained, *e g* in the *ortho*-derivatives, where isomerism might otherwise occur, according as the carbon atoms 1 and 2 were joined by a single or a double bond



**Preparation and purification of benzene.**—(i) Although it is not so strongly endothermic as acetylene (p 674), the heat of formation of benzene (from *diamond* and hydrogen, but not from *charcoal* and hydrogen) is negative, whereas that of *cyclo*-**hexane**, $C_6H_{12}$, a paraffin-like hydrocarbon, in which six methylene groups are united in a ring, is strongly positive:

$$2C \text{ (diamond)} + H_2 = C_2H_2 - 55{,}000 \text{ cal.}$$
$$6C \text{ (diamond)} + 3H_2 = C_6H_6 - 11{,}000 \text{ cal}$$
$$6C \text{ (diamond)} + 6H_2 = C_6H_{12} + 39{,}000 \text{ cal}$$

Benzene and other aromatic hydrocarbons related to it are therefore stable at high temperatures and provide the principal constituents of

COAL TAR (p 149), from which they are separated by fractional distillation. This distillation yields four fractions :

(i) Light oil (80°-170°) benzene, toluene, xylene
(ii) Middle oil (170°-240°) naphthalene, phenol.
(iii) Heavy or creosote oil (240°-270°) : cresols
(iv) Anthracene oil (270°-400°) anthracene, etc

The light oil (which floats on water) is agitated with sulphuric acid to remove basic impurities, and with caustic soda to remove acidic impurities, such as phenol (p 791). It is then washed with water and fractionally distilled

(ii) The benzene produced in this way always contains *sulphur*, in the form of **thiophen**, $C_4H_4S$, a compound which resembles benzene so closely that it cannot be separated either by distillation or by freezing It can, however, be extracted preferentially by prolonged contact with concentrated sulphuric acid, since thiophen is sulphonated (p 778) much more readily than benzene After this treatment very pure benzene can be obtained by freezing, and then draining the crystals from the mother liquor Benzene completely free from thiophen can be prepared in the laboratory by distilling **calcium benzoate** (from gum benzoin, p. 788) with soda lime $(C_6H_5\ CO\ O)_2Ca + Ca(OH)_2 = 2C_6H_6 + 2CaCO_3$

(iii) The synthesis of benzene by passing acetylene through a red-hot tube has already been described (p 675) It can also be prepared industrially from natural petroleum gas (methane) by a similar method

**Physical properties of benzene.**—Benzene (b -pt 80 5°, f -pt 5 4°, density 0 884 at 20°) is a colourless, volatile oil with a characteristic odour It is almost completely immiscible with water, but it mixes in all proportions with *dry* alcohol and ether, and is a good solvent for many organic substances (including fats and oils) as well as for phosphorus and iodine. In addition to its use as a solvent and as a liquid fuel, benzene is the parent substance for a large range of organic syntheses, and is used as a basis for the preparation of dye-stuffs, antiseptics and drugs

**Chemical properties of benzene.**—(*a*) *General*—(i) Benzene is resistant to attack by oxidising agents, such as permanganate and chromic acid, but it burns with a smoky luminous flame, and is added as an " anti-knock " constituent to motor spirit

(ii) When passed through a hot tube benzene loses hydrogen and gives the hydrocarbon **diphenyl** :

$$2C_6H_6 = C_6H_5\ C_6H_5 + H_2$$

It also decomposes partially into **acetylene**, thus reversing the condensation by which it is most readily synthesised from its elements (p 675)

(*b*) *Addition reactions.*—Unlike the olefines, benzene forms addition compounds only under exceptional conditions, when a maximum of *six* univalent groups is added, in harmony with Kekulé's formula, thus

(i) In presence of nickel (reaction of Sabatier and Senderens) benzene combines with hydrogen to form *cyclo*-**hexane**

$$C_6H_6 + 3H_2 = C_6H_{12}$$

(ii) It combines with ozone to form a **triozonide**, $C_6H_6O_9$, which is hydrolysed by water to hydrogen peroxide and glyoxal (p. 735)

$$C_6H_6O_9 + 3H_2O = 3H_2O_2 + 3H\,CO{\cdot}CO\,H \text{ (Glyoxal)}.$$

(iii) When acted on by chlorine or bromine, in sunlight or in presence of 1% NaOH, benzene yields two stereoisomeric **hexachlorides** (m.-pt. 57° and 310°) and **hexabromides** (m.-pt. 212° and 253°). These are decomposed by heat, and by alcoholic potassium hydroxide or cyanide, to the asymmetric (1 · 2 4) **trichlorobenzene** or **tribromobenzene** (see below)

$$C_6H_6 + 3Cl_2 \rightarrow C_6H_6Cl_6 \rightarrow C_6H_3Cl_3 + 3HCl$$
$$C_6H_6 + 3Br_2 \rightarrow C_6H_6Br_6 \rightarrow C_6H_3Br_3 + 3HBr$$

(*c*) *Substitution reactions*.—(i) In presence of a "halogen-carrier," such as iron or iodine, benzene yields a series of chloro- and bromo-benzenes

$$C_6H_6 \xrightarrow{Cl_2} \underset{\text{Chloro-benzene}}{C_6H_5Cl} \xrightarrow{Cl_2} \underset{\text{Dichloro-benzene}}{C_6H_4Cl_2} \xrightarrow{Cl_2} \cdots \xrightarrow{Cl_2} \underset{\text{Hexachloro-benzene}}{C_6Cl_6},$$

Compare $C_2H_6 \xrightarrow{Cl_2} \underset{\text{Chloroethane}}{C_2H_5Cl} \xrightarrow{Cl_2} \underset{\text{Dichloroethane}}{C_2H_4Cl_2} \xrightarrow{Cl_2} \cdots \xrightarrow{Cl_2} \underset{\text{Hexachloroethane}}{C_2Cl_6}$

These aromatic halogen derivatives are much more stable than those of the aliphatic series. Thus they cannot usually be hydrolysed by alkalis, and do not interact with ammonia to form amines, but they can be made reactive by the introduction of negative radicals, *e.g.*

$$\underset{\text{Picryl chloride}}{C_6H_2(NO_2)_3Cl} + 2KOH \rightarrow \underset{\text{Potassium picrate}}{C_6H_2(NO_2)_3OK} + KCl + H_2O$$
$$C_6H_2(NO_2)_3Cl + 2NH_3 \rightarrow \underset{\text{Picramide}}{C_6H_2(NO_2)_3NH_2} + NH_4Cl$$

(ii) In the FRIEDEL-CRAFTS REACTION, benzene is coupled with organic chlorides, in presence of anhydrous aluminium chloride, to form alkyl and acyl derivatives, with elimination of hydrogen chloride

$$C_6H_6 + CH_3\,Cl \rightarrow HCl + C_6H_5\,CH_3 \text{ (Toluene or methylbenzene).}$$
$$C_6H_6 + CH_3\,CO\,Cl \rightarrow HCl + C_6H_5\,CO\,CH_3 \text{ (Acetophenone or phenyl methyl ketone)}$$

(iii) Nitric and sulphuric acids yield substitution products, in which nitrogen or sulphur is attached directly to carbon, and not through an atom of oxygen

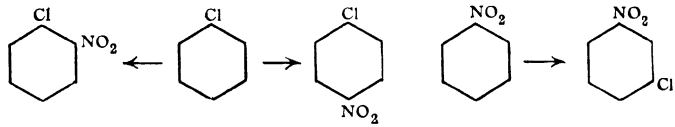
$$C_6H_6 + HO\,NO_2 = H_2O + C_6H_5\,NO_2 \text{ (Nitrobenzene)}$$
$$C_6H_6 + HO\,SO_2OH = H_2O + C_6H_5\,SO_2\,OH \text{ (Benzenesulphonic acid)}$$

The conditions under which these products are formed are set out in Expts. 177 and 178. Under more drastic conditions *two* or *three* nitro or sulphonic groups can be introduced into the same ring (Expt. 177*b*). These groups take up a *meta*-position relatively to one another (1 . 3 or 1 . 3 5). This result is in accordance with a general rule whereby the

first radical to be introduced directs a second substituent either into the *meta*-position or into the *ortho*- and *para*-positions, as follows.

| | |
|---|---|
| *Meta-directing* | $NO_2$,$SO_2$ OH,CO OH, etc |
| *Ortho-para* | Cl,Br,OH,$NH_2$,$CH_3$, etc |

Thus chlorine directs a second chlorine atom or a nitro-group into the *o*- or *p*-position, whilst a nitro-group directs a chlorine atom or a second nitro-group into the *meta*-position. It is therefore possible to prepare *o*- and *p*-chloronitrobenzenes by nitrating chlorobenzene, since chlorine is *o p*-directing, whilst *m*-chloronitrobenzene can be prepared by chlorinating nitrobenzene, since the nitro-group is *meta*-directing.




*ortho* *para* *meta*

EXPT 176 **Properties of benzene and toluene.**

(*a*) Notice the smell of benzene and of toluene, and ascertain their boiling-points. Find out whether they will mix with water, alcohol and paraffin.

(*b*) Samples of chlorobenzene, benzyl chloride and benzylidene dichloride are boiled with caustic soda solution. The alkaline liquors are then acidified with dilute nitric acid, and a solution of silver nitrate is added. Notice what happens in each case.

EXPT 177 **Nitration of benzene**

(*a*) *Nitrobenzene*.—Mix together 100 c c of concentrated sulphuric acid and 80 c c of concentrated nitric acid and cool the mixture, and then add it gradually to 50 c c of benzene in a round-bottomed flask. The flask should be rotated under a tap to mix and cool the ingredients after each addition of acid. When all the acid has been added, heat the mixture for about ten minutes in a water-bath, and shake at intervals to bring the upper layer of benzene and nitrobenzene into intimate contact with the acids. After cooling, run off the lower layer of acid from a separating funnel and pour the nitrobenzene into 100 c c of water. Shake and again separate the lower layer of nitrobenzene with a separating funnel. Wash the latter by shaking it with 50 c c of dilute sodium carbonate, followed by 50 c c of water, and then dehydrate the nitrobenzene by standing it with 10 grams of calcium chloride for a few hours. Distil the product, collecting that portion which comes over between 202° and 208°. The residue of dinitrobenzene in the flask should only be small if the temperature has been kept down during the addition of the acids to the benzene.

(*b*) *m-Dinitrobenzene*.—Add 20 grams of concentrated sulphuric acid to 20 grams of fuming nitric acid in a 250 c c flask. Then add gradually 15 grams of nitrobenzene and heat the mixture for about 20 minutes on a water-bath until a portion of the liquid gives a hard and not a pasty lump

when added to water Pour the hot mixture into 200 c c of cold water and recrystallise the solid from hot alcohol, when the *ortho*- and *para*-isomers (which are formed in very small quantities) remain behind in the mother liquor.

EXPT 178 **Sulphonation of benzene.**

(*a*) Place 10 c c. of concentrated sulphuric acid in a boiling-tube. Add 4 c c of benzene and heat gently with constant shaking until the benzene has dissolved in the acid Cool the product, dilute it with 14 c c of water and add 14 c c of a saturated solution of salt Set aside for half an hour, then filter off the crystals of **sodium benzene sulphonate,** $C_6H_5\,SO_3\,ONa$

(*b*) Equal volumes of benzene and concentrated sulphuric acid are heated for about eight hours, in a flask fitted with a reflux condenser to prevent the loss of benzene Since benzene floats on the acid, the flask is shaken at frequent intervals In order to isolate the sulphonic acid the mixture is diluted with water, and an excess of calcium or barium carbonate is added to remove the free sulphuric acid (compare ethyl hydrogen sulphate), whilst calcium or barium benzenesulphonate remains in solution The sulphonic acid is set free by adding just enough sulphuric acid to precipitate the calcium or barium as sulphate,

$$(C_6H_5\,SO_3\,O)_2Ba + H_2SO_4 = 2C_6H_5\,SO_3\,OH + BaSO_4$$

After filtration the solution is evaporated to a syrup of crude **benzene sulphonic acid.**

(*c*) The alkali salts of benzene sulphonic acid can be prepared by adding an alkali carbonate to the solution of the calcium or barium salts prepared as above

$$(C_6H_5\,SO_3\,O)_2Ba + Na_2CO_3 = 2C_6H_5\,SO_3\,ONa + BaCO_3$$

After filtering off the carbonate precipitate, the filtrate is evaporated to crystallisation

**Preparation and properties of nitrobenzene,** $C_6H_5\,NO_2$.—Nitrobenzene is prepared by the action on benzene of a mixture of nitric and sulphuric acids (Expt 177) $C_6H_6 + HO\,NO_2 = C_6H_5\,NO_2 + H_2O$

The sulphuric acid assists nitration by removing water as fast as it is formed The product is an almost colourless oil (b -pt 211°, f -pt 5 7°, density 1 20) It has an odour of almonds, but is poisonous It burns in air, but is not explosive like picric acid and T N T. (p 779) It can be nitrated and sulphonated in the *meta*-position It is reduced in acid media to **aniline,** $C_6H_5\,NH_2$ (Expt 189), and by neutral reducing agents (aluminium amalgam) to **β-phenylhydroxylamine,** $C_6H_5\,NH\,OH$, whilst alkaline reducing agents yield products containing two benzene rings

$$C_6H_5{\cdot}NO_2 \rightarrow C_6H_5\overset{+}{N}(O^-)N{\cdot}C_6H_5 \rightarrow C_6H_5{\cdot}N{=}N{\cdot}C_6H_5 \rightarrow C_6H_5{\cdot}NH\,NH\,C_6H_5$$

Nitrobenzene — Azoxybenzene — Azobenzene — Hydrazobenzene or diphenylhydrazine

Dinitrobenzene can be reduced in a similar way, the two principal products being *m*-**nitraniline**, $NO_2 C_6H_4 NH_2$, and *m*-**phenylenediamine**,

$$NH_2{\cdot}C_6H_4 NH_2$$

**Preparation and properties of benzenesulphonic acid**, $C_6H_5 SO_2{\cdot}OH$ — Benzenesulphonic acid is prepared by the action on benzene of hot concentrated sulphuric acid (Expt 178)

$$C_6H_6 + H_2SO_4 \rightleftharpoons C_6H_5 SO_2 OH + H_2O.$$

If, however, superheated steam is blown through a mixture of the acid with sulphuric acid, the sulphonic acid is hydrolysed, as shown by the lower arrow in the preceding equation, and benzene is carried over This reversible reaction is general, and can be used to separate aromatic hydrocarbons (*e g* from Borneo petroleum) in a form from which they can easily be recovered

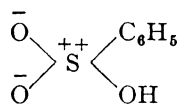
Benzene sulphonic acid is only known as an acid syrup, but **dibromobenzenesulphonic acid**, $C_6H_3Br_2 SO_2 OH$, crystallises well and can be weighed out directly for the preparation of standard acid solutions

All the sulphonic acids are strong electrolytes, and yield neutral crystalline salts They are converted by the action of phosphorus pentachloride into **sulphonic chlorides**, which interact with ammonia to form **sulphonamides** :

$$C_6H_5 SO_2 ONa \xrightarrow{PCl_5} C_6H_5 SO_2 Cl \xrightarrow{NH_3} C_6H_5 SO_2 NH_2,$$

compare $C_6H_5 CO ONa \xrightarrow{PCl_5} C_6H_5 CO Cl \xrightarrow{NH_3} C_6H_5 CO NH_2$

The sulphonic chlorides are less reactive than the chlorides of carboxylic acids, but are valuable reagents for the identification of amines and alcohols , moreover, since the sulphonic chlorides and amides are usually crystalline and have well-defined melting-points, they are often used to identify the hydrocarbons and sulphonates from which they are derived Benzenesulphonic chloride is readily hydrolysed back to the sulphonic acid, which must therefore contain a hydroxyl group , it can also be reduced to **thiophenol**, $C_6H_5 SO_2 Cl \rightarrow C_6H_5 SH$, thus proving that the sulphur atom is attached directly to carbon as in the formula



The sulphonates are also of importance, because they can be converted into phenols (p 791) by fusion with a caustic alkali, and into cyanides by fusion with an alkali cyanide

$$C_6H_5 SO_2 ONa + NaOH = C_6H_5 OH + Na_2SO_3$$
$$C_6H_5 SO_2 ONa + NaCN = C_6H_5 CN + Na_2SO_3$$

**Toluene**, $C_6H_5 CH_3$ —(*a*) *Preparation* —Toluene, the first homologue of benzene, occurs (i) in coal tar, from which it is separated by fractional distillation, and (ii) in Borneo petroleum, from which it is separated by

sulphonation or nitration, leaving a residue of non-aromatic hydrocarbons. It can be synthesised

(i) By Fittig's method from bromobenzene and methyl iodide by the action of sodium

$$C_6H_5Br + CH_3I + 2Na = C_6H_5\,CH_3 + NaBr + NaI$$

(ii) By Friedel-Crafts method from benzene and methyl chloride in presence of anhydrous aluminium chloride

$$C_6H_6 + CH_3Cl \xrightarrow{AlCl_3} C_6H_5\,CH_3 + HCl.$$

Higher homologues, such as **ethylbenzene**, $C_6H_5\,C_2H_5$, can be synthesised by similar methods

(*b*) *Properties* —Toluene resembles benzene, but boils at 110° and has quite a different odour Its chemical properties are modified by the presence of a side-chain as follows

(i) The side-chain can be halogenated and oxidised, *e g*

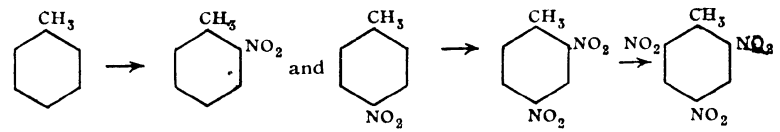
$$\underset{\text{Toluene}}{C_6H_5\,CH_3} \xrightarrow{Cl_2} \underset{\text{Benzyl chloride}}{C_6H_5\,CH_2\,Cl} \xrightarrow{Cl_2} \underset{\text{Benzylidene chloride}}{C_6H_5\,CHCl_2} \xrightarrow{Cl_2} \underset{\text{Benzotri-chloride}}{C_6H_5\,CCl_3}$$

$$\underset{\text{Toluene}}{C_6H_5\,CH_3} \xrightarrow{O} \underset{\text{Benzyl alcohol}}{C_6H_5\,CH_2\,OH} \xrightarrow{O} \underset{\text{Benzaldehyde}}{C_6H_5\,CHO} \xrightarrow{O} \underset{\text{Benzoic acid}}{C_6H_5\,CO\,OH}$$

In practice, toluene is easily oxidised to benzoic acid, *e g* by the action of permanganate , but the intermediate oxidation products are prepared from the chlorides, which are readily hydrolysed, since the halogen in the side-chain resembles that of the aliphatic chlorides and has not the stability of halogens attached to the nucleus Chlorination in the *side-chain* is carried out at the boiling-point and is promoted by sunlight, but in the cold, particularly in the presence of a halogen carrier such as iodine, the *nucleus* is chlorinated in the 2 or 4 position ($CH_3 = 1$) to produce *ortho-* or *para*-chlorotoluene

$$C_6H_5\,CH_3 + Cl_2 \xrightarrow{I_2} C_6H_4Cl\,CH_3 + HCl$$

(ii) The presence of the methyl groups destroys the symmetry of the benzene nucleus and directs the substituents preferentially to the *ortho-* and *para*-positions, as already recorded in the case of the halogens Thus, nitration with a mixture of nitric and sulphuric acids gives *ortho-* and *para*-mononitrotoluene, then 1 2 4 dinitrotoluene and finally 1 2 4 6 trinitrotoluene or T N T :

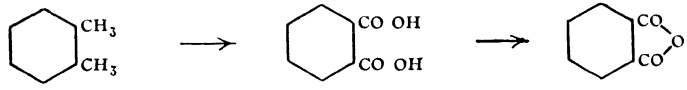



**Toluene** *o*-Nitrotoluene (1 2) *p*-Nitrotoluene (1 4) Dinitrotoluene (1 2 4) Trinitrotoluene (1 2 4 6)

Nitration in the *meta*-position, on the other hand, appears to be impeded by the methyl group, since compounds nitrated in the 3-position are formed only to the extent of about 4%.

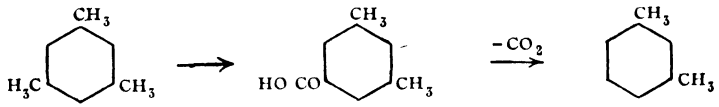
**Xylene,** or dimethylbenzene, $C_6H_4(CH_3)_2$, occurs in coal tar and in Borneo petroleum in three isomeric forms, a fourth isomer, **ethylbenzene,** $C_6H_5\,C_2H_5$, is only known as a synthetic product

(*a*) ***o*-Xylene** (b -pt 142°) can be identified by the fact that it is oxidised to **phthalic acid,** $C_6H_4(CO\,OH)_2$ (m -pt 213°), which differs from its isomers in forming an anhydride




*o*-Xylene (1 2) — Phthalic acid (1 2) — Phthalic anhydride (1 2)

(*b*) ***m*-Xylene** (b -pt 137°) can be identified by preparing it from mesitylene, through mesitylenic acid




Mesitylene (1 3 5 trimethylbenzene) — Mesitylenic acid (1 3 5 dimethylbenzoic acid) — *m*-Xylene (1 3 dimethylbenzene)

Since mesitylene has already been shown to be a symmetrical (1 3 5) trimethylbenzene, it follows that the xylene prepared from it must be a 1 3 dimethylbenzene

(*c*) ***p*-Xylene** (b -pt 137°) can be identified by Korner's method (p 773) as 1 4 dimethylbenzene, since it yields only a single derivative when one additional substituent is introduced, *e g* by bromination, nitration or sulphonation

The determination of the ORIENTATION of the methyl groups in the xylenes may be regarded as typical of the methods used for this purpose, but it can be extended immediately by noting that **terephthalic acid,** HO CO $C_6H_4$ CO OH (which sublimes without melting), is prepared by oxidising *p*-xylene, and must therefore be formulated as 1 4 benzene dicarboxylic acid, whilst **isophthalic acid** (m -pt. >300°), produced by oxidising *m*-xylene, must be the 1 3 acid Since these acids can be prepared from the amines through the cyanides of similar orientation, it is clear that one fundamental determination can be used to settle the orientation of a very wide range of derivatives of benzene

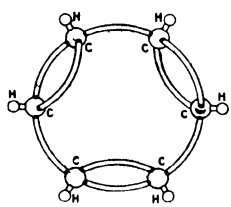
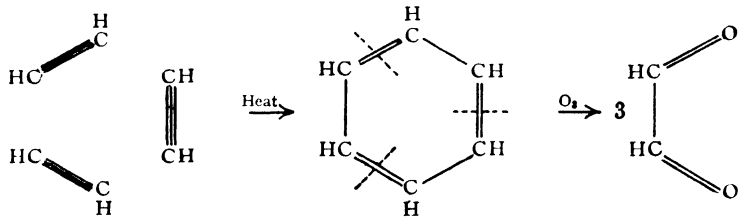


FIG 185 BENZENE RING.

**Structure of benzene.**—The symmetrical ring-structure (Fig 185) assigned to benzene by Kekulé from observations of isomerism (p 771)

is confirmed by its synthesis from acetylene and by its oxidation by ozone to glyoxal as described on page 775.




Acetylene Benzene Glyoxal

Thus, since the six hydrogens in acetylene (3 mols) and the six hydrogens in glyoxal (3 mols) are all equivalent, it is reasonable to suppose that they are all equivalent in benzene

The one difficulty of Kekulé's formula is the absence of isomerism arising from the alternation of single and double bonds, since all the available evidence points to the identity, not only of the six carbon atoms, and of the six hydrogen atoms attached to them, but also of the six linkages by which they are joined into a ring Several courses have been adopted to maintain the six-fold symmetry of the benzene ring

(*a*) Organic chemists have generally " cut the Gordian knot " by writing benzene as a regular hexagon, as in Fig 184, and ignoring the fourth valency of the six carbon atoms This is in many respects the most satisfactory as well as the simplest solution of the problem, but it means (in terms of the electronic theory of valency) that six valency electrons are not yet located

(*b*) Armstrong and von Baeyer proposed a " centric formula " (Fig. 186) with the six spare bonds pointing to the centre of the ring The significance of these centric bonds is not obvious, but they may be regarded conveniently as an intermediate phase in the interconversion of the two forms of Kekulé's formula

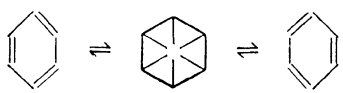


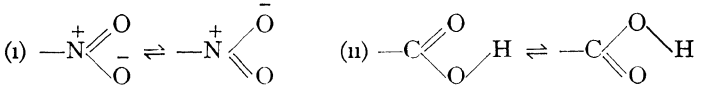
FIG 186 CENTRIC FORMULA

(*c*) J J Thomson joins each pair of carbon atoms by *three* valency electrons (*i e* $1\frac{1}{2}$ bonds) instead of by *two* and *four* alternately

(*d*) Modern physical theory directs attention to the fact that the two forms of the parent hydrocarbon (i) have identically the same energy content, and (ii) can be converted into one another by a mere wandering of electrons, without any movement of the nuclei In these circumstances, the most stable state is one of RESONANCE, in which there is the same probability of finding the single and double bonds in one position as there is of finding them in the other This is substantially identical with the condition postulated by Kekulé in 1865, and may therefore

be regarded for the present as a completely satisfactory solution of the problem

The theory of resonance can be applied equally well (i) to the nitro-group, and (ii) to the carboxyl group, if we assume (as has often been suggested) that the hydrogen atom is placed symmetrically between the two oxygens



Many of the peculiarities of the carboxyl group can be explained in this way, but the theory is *not* applicable to the esters, where the alkyl radical appears to be attached definitely to one particular atom of oxygen The suppression of ketonic properties in the esters as well as in the acids must therefore be explained in some other way

(*e*) In many of the derivatives of benzene, the energy content of the two forms would be different and resonance might then be impossible In cases such as these, it is probable that one form is more stable than the other, but that their interconversion is so easy and rapid that it would be quite impossible to prepare the less stable form by any ordinary chemical process, or to keep it for any appreciable time The second form would then be even more elusive than vinyl alcohol, for instance, since in the latter case the reversion to aldehyde (p 690) involves the migration of a proton, whereas in the present instance it is only necessary for the surplus valency-electrons to migrate round the ring

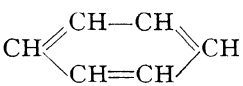
**Aromatic compounds as conjugated systems.**—A CONJUGATED COMPOUND is defined as one which contains a series of alternate single and double bonds Amongst the compounds already described in the preceding chapters, this definition applies to

(i) Acrolein (p 738), $CH_2{=}CH{-}CH{=}O$
(ii) Acrylic acid (p 738), $CH_2{=}CH{-}C(OH){=}O$
(iii) Mesityl oxide (p 706), $(CH_3)_2C{=}CH{-}C(CH_3){=}O$.

The simplest possible example is found in the hydrocarbon

(iv) Butadiene, $CH_2{=}CH{-}CH{=}CH_2$,

but it is essential to recognise that a fully conjugated system is also shown in Kekulé's formula for

(v) Benzene, 

**Mechanism of addition reactions in unsaturated, conjugated and aromatic systems.**—(*a*) *Unsaturated compounds*—We have seen (p 695) that the olefines form addition compounds with reagents which yield an active *cation* (*e g* $H^+$ from HCl, HBr, HI, $H_2SO_4$, $Cl^+$ from ClOH or $Cl_2$; $Br^+$ from $Br_2$, etc), whilst aldehydes and ketones form addition compounds with reagents which yield an active *anion* (*e g*. $CN^-$ from

HCN, $NH_2^-$ from $NH_3$, NaO $SO_2$ $O^-$ from $NaHSO_3$, etc ) Thus the action of bromine on ethylene may be formulated as follows

$$Br_2 + CH_2{=}CH_2 \rightarrow \overset{+}{Br} + \overset{-}{C}H_2{-}\overset{+}{C}H_2 + \overset{-}{Br}$$

$$\rightarrow Br\,CH_2{-}\overset{+}{C}H_2 + \overset{-}{Br} \rightarrow Br\,CH_2\,CH_2\,Br$$

(*b*) *Conjugated hydrocarbons* —Butadiene, $C_4H_6$, can form an addition compound with bromine, but, in spite of the presence of two double bonds, it usually forms only a dibromide and not a tetrabromide Moreover, whilst 20% of the bromine is added in the usual way, to a double bond, giving rise to a 1 2 or 3 4 dibromide, 80% of the bromine goes to form a 1 4 dibromide, leaving a double bond in the 2 3 position

$$\underset{1}{CH_2}{=}\underset{2}{CH}{-}\underset{3}{CH}{=}\underset{4}{CH_2} + Br_2 \rightarrow BrCH_2{-}CH{=}CH{-}CH_2Br$$

To explain this result, we assume, as in the case of ethylene, that the primary reagent is the active cation, $Br^+$ This attacks a terminal $CH_2$ group and transfers its charge to a more distant carbon atom thus

$$\underset{1}{CH_2}{=}\underset{2}{CH}{-}\underset{3}{CH}{=}\underset{4}{CH_2} \xrightarrow{+Br^+} \begin{cases} BrCH_2{-}\overset{+}{C}H{-}CH{=}CH_2 \xrightarrow{+Br^-} BrCH_2{-}CHBr{-}CH{=}CH_2, \\ \qquad\qquad 1\ 2\ \text{Dibromide} \\ BrCH_2{-}\overset{+}{C}H{-}\overset{-}{C}H{-}\overset{+}{C}H_2 \xrightarrow{+Br^-} BrCH_2{-}CH{=}CH{-}CH_2Br \\ \qquad\qquad 1\ 4\ \text{Dibromide} \end{cases}$$

In the first case only the contiguous double bond is ionised by the influence of the active cation, $Br^+$, and its positive charge is therefore transferred (as in ethylene) to the carbon atom 2, where it is neutralised by the negative charge of the anion $Br^-$, forming the 1 2 dibromide In the second case, the ionisation spreads along the chain, so that the carbon atoms 2 and 3 acquire + and − charges, which are neutralised in forming a central double bond, whilst carbon atom 4 acquires an unbalanced + charge, which is neutralised by a $Br^-$ ion, forming the 1 4 dibromide

(*c*) *Benzene* —We have seen (p 774) that the unsaturated character of benzene, as indicated by the three double bonds in Kekulé's formula, is confirmed by the addition of $3Cl_2$, $3Br_2$ and $3O_3$ Nevertheless benzene does not display the activity which is characteristic of an unsaturated hydrocarbon, and still less of a hydrocarbon containing three double bonds in the molecule, since it nearly always gives substitution products This result finds some analogy in the persistence of the central double bond after dibromination of butadiene, which suggests that a " closed " system (in which every double bond may be regarded as central to the other two) would display a similar inactivity , but this explanation is not convincing, since the inactivity of the substituted olefine,

$$BrCH_2\,CH{=}CH\,CH_2Br,$$

must be attributed to the acylous character of the halogens These find no counterpart in benzene, the stability of which is explained much better

by the theory of resonance On the other hand, it is characteristic of aromatic compounds that the influence of a substituent extends far more widely than in saturated aliphatic compounds Thus, whereas benzene itself is almost as resistant to bromination as a saturated hydrocarbon, the ring systems in phenol and in aniline can be brominated instantly

$$C_6H_5\,OH + 3Br_2 \rightarrow 3HBr + C_6H_2Br_3\,OH \quad \text{(Tribromophenol)}$$
$$C_6H_5\,NH_2 + 3Br_2 \rightarrow 3HBr + C_6H_2Br_3\,NH_2 \quad \text{(Tribromoaniline)}$$

This abrupt appearance of reactivity in relatively distant centres can be interpreted as an effect of conjugation, similar to those recorded under (*d*) below

(*d*) *Anomalous addition reactions of carbonyl compounds* —(i) It has already been stated that addition of hydrogen bromide to *acrylic acid* takes place in direct opposition to Markownikoff's rule (p 673) since the product consists entirely of $\beta$- instead of $\alpha$-bromopropionic acid

$$CH_2{=}CH\,COOH \quad \text{gives} \quad CH_2Br\,CH_2\,COOH$$

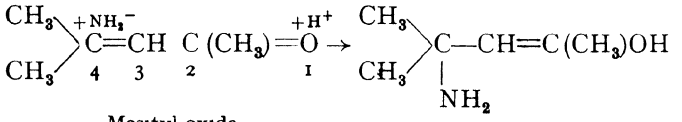
and not $CH_3\,CHBr\,COOH$

This result can, however, be interpreted very easily by assuming a 1 4 addition to the conjugated system, according to the usual rule for the addition of HX to aldehydes and ketones (p 694), whereby hydrogen is added to oxygen and the rest of the molecule to carbon

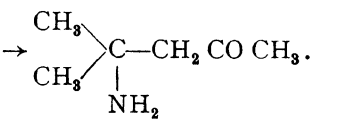
$$\overset{4}{CH_2}{=}\overset{3}{CH}{-}\overset{2}{C}(OH){=}\overset{1}{O} \xrightarrow{+H^+,\ +Br^-} Br\,CH_2{-}CH{=}C(OH)_2 \longrightarrow Br\,CH_2\,CH_2\,CO\,OH.$$

The product is an " enol " which reverts at once to the stable form of $\beta$-bromopropionic acid, of which a quantitative yield is obtained

(ii) The anomalous addition of ammonia to *mesityl oxide* (p 706) can be explained in the same way as due to a 1 4 addition of ammonia to the unsaturated ketone



Mesityl oxide



Diacetonamine

The initial addition product is an enol, which reverts at once to the ketonic form. The final result is the addition of a molecule of ammonia to the double bond of an olefine, which would normally be unresponsive to the action of this reagent

# CHAPTER LX

## AROMATIC ALCOHOLS, ALDEHYDES, KETONES AND CARBOXYLIC ACIDS

### A Aromatic Alcohols

**Benzyl alcohol**, or phenyl carbinol, $C_6H_5\,CH_2\,OH$, was first obtained from benzaldehyde by the Cannizzaro reaction (p 787)

$$2C_6H_5\,CHO + KOH = C_6H_5\,CH_2\,OH + C_6H_5\,CO\,OK$$

Benzaldehyde — Benzylalcohol — Potassium benzoate

It is prepared by boiling benzyl chloride (p 779) with aqueous potassium carbonate

$$2C_6H_5\,CH_2Cl + K_2CO_3 + H_2O = 2C_6H_5\,CH_2\,OH + 2KCl + CO_2$$

It is a colourless oil (b -pt 206°), sparingly soluble in water, which resembles the aliphatic alcohols in its chemical properties, *e g* it forms

(i) **Sodium benzyloxide**, $C_6H_5\,CH_2\,ONa$, with sodium

(ii) **Benzyl chloride**, $C_6H_5\,CH_2\,Cl$, with $PCl_3$

(iii) **Benzyl acetate**, $C_6H_5\,CH_2\,O\,CO\,CH_3$, with acetyl chloride

Like the primary aliphatic alcohols, it is oxidised by chromic acid first to an aldehyde and then to a carboxylic acid

$$C_6H_5\,CH_2\,OH \rightarrow C_6H_5\,CHO \rightarrow C_6H_5\,CO\,OH.$$

Benzyl alcohol — Benzaldehyde — Benzoic acid

### B Aromatic Aldehydes

**Benzaldehyde**, $C_6H_5\,CHO$ —(*a*) *Preparation* —Benzaldehyde was first obtained from bitter almonds as a product of hydrolysis of the glucoside **amygdalin**, in which **benzaldehyde cyanhydrin**, $C_6H_5\,CH(OH)\,CN$, is coupled with two molecules of glucose

$$C_6H_5\,CH\begin{cases}CN\\ O\,C_{12}H_{21}O_{10}\end{cases} + 2H_2O \rightarrow C_6H_5\,CHO + HCN + 2C_6H_{12}O_6$$

Amygdalin — Benzaldehyde — Glucose

It can be made, like the aliphatic aldehydes, by distilling a mixture of calcium benzoate and formate

$$(C_6H_5\,CO{\cdot}O)_2Ca + (H{\cdot}CO{\cdot}O)_2Ca = 2C_6H_5{\cdot}CO{\cdot}H + 2CaCO_3.$$

It is prepared, however, by converting toluene into (i) benzylidene chloride and hydrolysing by boiling with milk of lime

$$C_6H_5\,CHCl_2 + Ca(OH)_2 = C_6H_5\,CHO + CaCl_2 + H_2O,$$

or (ii) benzyl chloride and boiling with aqueous copper or lead nitrate, when hydrolysis and oxidation take place together

$$2C_6H_5\,CH_2\,Cl + Pb(NO_3)_2 = 2C_6H_5\,CHO + PbCl_2 + 2HNO_2$$

(*b*) *Properties* —Benzaldehyde is a colourless oil (b -pt 179°) with an odour of almonds It resembles the aliphatic aldehydes in the following respects

(i) Although it does not reduce Fehling's solution, it reduces ammoniacal silver nitrate, and is readily oxidised to benzoic acid by exposure to air (Expt 179)

$$C_6H_5\,CHO + Ag_2O = C_6H_5\,CO\,OH + 2Ag$$

(ii) By the action of phosphorus pentachloride it is converted into benzylidene (or benzal) chloride without liberation of hydrogen chloride

$$C_6H_5\,CHO + PCl_5 = C_6H_5{\cdot}CHCl_2 + POCl_3.$$

(iii) It forms addition compounds with hydrogen cyanide and with sodium bisulphite

$$C_6H_5\,CHO + HCN = C_6H_5\,CH(OH)\,CN$$
$$C_6H_5\,CHO + NaHSO_3 = C_6H_5\,CH(OH)\,SO_2\,ONa$$

(iv) It can be coupled with bases, including aniline, hydroxylamine, phenyl hydrazine, etc

$C_6H_5\,CH\,O + H_2\,N\,C_6H_5 = H_2O + C_6H_5\,CH{=}N\,C_6H_5$ (Benzylidene aniline)

$C_6H_5\,CH\,O + H_2\,N\,OH = H_2O + C_6H_5{\cdot}CH{=}N\,OH$ (α-Benzaldoxime)

$C_6H_5\,CH\,O + H_2\,N\,NH\,C_6H_5 = H_2O + C_6H_5\,CH\,N\,NH\,C_6H_5$ (Benzylidene phenylhydrazine)

The following points of contrast appear to depend on the direct attachment of the —CHO radical to the aromatic nucleus

(i) The aldehydic hydrogen can be replaced directly by chlorine

$$C_6H_5\,CHO + Cl_2 = HCl + C_6H_5{\cdot}CO\,Cl \text{ (Benzoyl chloride)}$$

(ii) With ammonia, benzaldehyde does not form an addition compound like acetaldehyde, but a substitution product (Expt 179, *d*) like formaldehyde

$$3C_6H_5\,CHO + 2NH_3 = 3H_2O + (C_6H_5{\cdot}CH)_3N_2 \text{ (Hydrobenzamide)}$$

(iii) The aldol type of condensation (which depends on splitting off a hydrogen atom from a methyl group) cannot take place with benzaldehyde, and neither acids nor alkalis bring about the polymerisation of

benzaldehyde, but, in presence of potassium cyanide, benzaldehyde is polymerised to **benzoin** :

$$2C_6H_5\,CHO = C_6H_5\,CH(OH)\,CO\,C_6H_5$$

Benzoin is a ketone-aldehyde, for which an aliphatic analogue can be found in acetoin (p 707), although this cannot be prepared by direct polymerisation from acetaldehyde

(iv) On the other hand, the condensation of acetaldehyde to crotonaldehyde (p 697) finds a close analogy in PERKIN'S REACTION, whereby aromatic aldehydes form unsaturated aldehydes, ketones and acids by condensation with the methylene radical of saturated aliphatic aldehydes, ketones and acids Thus in presence of acetic anhydride, benzaldehyde condenses with acetaldehyde and with sodium acetate to form **cinnamic aldehyde** and **sodium cinnamate** respectively

$$C_6H_5\,CHO + CH_3\,CHO = H_2O + C_6H_5\,CH\,CH\,CHO \quad \text{(Cinnamic aldehyde)}$$

$$C_6H_5\,CHO + CH_3\,CO\,ONa = H_2O + C_6H_5\,CH\,CH\,CO\,ONa \quad \text{(Sodium cinnamate)}$$

(v) Although benzaldehyde is not polymerised by acids or alkalis, caustic alkalis bring about a remarkable transformation, known as the CANNIZZARO REACTION, whereby two molecules of benzaldehyde are converted by mutual oxidation and reduction into one molecule of benzyl alcohol (p 785) and one molecule of a benzoate

$$2C_6H_5\,CHO + KOH = C_6H_5\,CH_2\,OH + C_6H_5\,CO\,OK$$

EXPT 179 **Properties of benzaldehyde**

(*a*) To a few c c of benzaldehyde in a test tube add an equal volume of a concentrated solution of sodium bisulphite and shake the mixture well Notice the formation of crystals of an addition compound

(*b*) Try the effect of warming a little benzaldehyde with an ammoniacal solution of silver nitrate, and with Fehling's solution

(*c*) Place a little benzaldehyde on a watch glass and leave it exposed to the air for a day Examine the product Is it acid to litmus ?

(*d*) Mix 1 c c of benzaldehyde and 4 c c of 0 88 ammonia in a test tube and cork up After a day or so crystals of hydrobenzamide, $(C_6H_5\,CH)_3N_2$, will separate

(*e*) Add a hot alcoholic solution of benzaldehyde (1 gram in 5 c c of alcohol) to a similar weight of phenyl hydrazine dissolved in 5 c c of hot glacial acetic acid Wash the crystalline mass of benzaldehyde phenylhydrazone with a little alcohol and then recrystallise it from hot alcohol and determine the melting-point (158°)

## C THE AROMATIC KETONES

**Aromatic ketones** can be made, like the aliphatic ketones, by distillation of the appropriate calcium salts, but they are usually prepared directly

from an aromatic hydrocarbon by coupling it with an acid chloride in presence of aluminium chloride (FRIEDEL-CRAFTS REACTION, p 775), *e g*

$$C_6H_6 + Cl\,CO\,CH_3 = HCl + C_6H_5\,CO\,CH_3 \text{ (Acetophenone)}$$

$$\left.\begin{aligned} C_6H_6 + Cl\,CO\,C_6H_5 &= HCl + C_6H_5\,CO\,C_6H_5 \\ 2C_6H_6 + Cl\,CO\,Cl &= 2HCl + C_6H_5\,CO\,C_6H_5 \end{aligned}\right\} \text{(Benzophenone)}$$

The condensation-product of ketone and catalyst is decomposed with water, and the ketone is then separated, dried and purified by distillation

**Acetophenone** (m -pt 20°) and **benzophenone** (m -pt 49°) form cyanhydrins, but not bisulphite compounds They can be coupled in the usual way with bases to form oximes, hydrazones, etc They can also be reduced to secondary alcohols and pinacones, and oxidised to benzoic acid, *e g.*

$$C_6H_5\,CO\,CH_3 + 4O = C_6H_5\,CO\,OH + CO_2 + H_2O$$

Like other aromatic compounds, they differ from their aliphatic analogues in that the benzene nucleus can be sulphonated, nitrated, etc

## D AROMATIC CARBOXYLIC ACIDS

**Benzoic acid**, $C_6H_5\,CO\,OH$, is the aromatic analogue of acetic acid It occurs free in " gum benzoin " and can be separated from it by sublimation, but it can also be prepared by the usual methods, *e g*

(i) From *benzyl alcohol* and *benzaldehyde* by oxidation

$$C_6H_5\,CH_2\,OH \rightarrow C_6H_5\,CHO \rightarrow C_6H_5\,CO\,OH$$

(ii) From *benzonitrile* by hydrolysis with an acid or alkali

$$C_6H_5{\cdot}CN + 2H_2O + HCl = C_6H_5\,CO\,OH + NH_4Cl$$

(iii) From *bromobenzene* by combining with magnesium in ethereal solution to a Grignard reagent, carbon dioxide is then passed in and the addition compound is decomposed with dilute acid

$$C_6H_5\,Mg\,Br + CO_2 = C_6H_5\,CO\,O\,Mg\,Br$$
$$C_6H_5\,CO\,O\,Mg\,Br + HCl = C_6H_5\,CO\,OH + MgBrCl$$

(iv) From *toluene* (or any other mono-alkyl derivative of benzene) by the action of permanganate

$$C_6H_5\,CH_3 + 2KMnO_4 = C_6H_5\,CO\,OK + KOH + 2MnO_2 + H_2O$$

(v) In practice it is manufactured by chlorinating toluene, and then hydrolysing the resulting benzotrichloride with boiling milk of lime or with water under pressure

$$2C_6H_5\,CCl_3 + 4Ca(OH)_2 = (C_6H_5\,CO\,O)_2Ca + 3CaCl_2 + 4H_2O.$$

EXPT 180 **Properties of benzoic acid.**

(*a*) Test the solubility of benzoic acid in cold water, in hot water and in caustic soda. To the latter solution add dilute hydrochloric acid and notice the precipitate which is formed.

(*b*) Heat a mixture of sodium benzoate and soda-lime in a test tube and cautiously smell the vapour which is evolved

Benzoic acid crystallises from hot water in needles which melt at 121°, but it also sublimes very readily It has all the usual properties of a carboxylic acid, but is three times stronger than acetic acid, on account of the acylous character of the phenyl radical It also differs from acetic acid in that the carboxyl group is attached to a carbon atom which does not carry an atom of hydrogen, so that many of the reactions of acetic acid are impossible in the case of benzoic acid. On the other hand, the nucleus can be chlorinated, brominated, nitrated or sulphonated , but it is noteworthy that whereas toluene gives *ortho-* and *para*-derivatives, benzoic acid yields *m*-chlorobenzoic acid, *m*-nitrobenzoic acid, etc On heating with soda-lime it yields benzene (Expt 180, *b*)

$$C_6H_5\,CO\,OH + 2NaOH = C_6H_6 + Na_2CO_3 + H_2O$$

**Benzoyl chloride,** $C_6H_5{\cdot}CO{\cdot}Cl$, is prepared by mixing benzoic acid with about 5% more than the theoretical quantity of phosphorus pentachloride: $C_6H_5{\cdot}CO\,OH + PCl_5 = C_6H_5\,CO\,Cl + POCl_3 + HCl$ When the evolution of hydrogen chloride has ceased, the benzoyl chloride (b -pt 198°) is separated from the phosphorus oxychloride (b.-pt 107°) by distillation

Benzoyl chloride can also be prepared by heating benzoic acid for about an hour on a water-bath with an excess of thionyl chloride, $SOCl_2$, in a flask fitted with a reflux condenser

$$C_6H_5\,CO\,OH + SOCl_2 = C_6H_5\,CO{\cdot}Cl + SO_2 + HCl$$

The sulphur dioxide and hydrogen chloride escape as gases and the excess of thionyl chloride (b -pt 78°) is then easily separated from the benzoyl chloride (b -pt 198°) by fractional distillation This method of obtaining an acid chloride is a general one and is especially useful for the preparation of those acid chlorides which have boiling-points close to that of phosphorus oxychloride, since in such cases if the phosphorus pentachloride method is used, it is difficult to separate the resulting acid chloride from the phosphorus oxychloride

Benzoyl chloride is a colourless fuming liquid which shows a general resemblance to acetyl chloride in its properties, although it is much less reactive Thus it is hydrolysed *slowly* by cold water,

$$C_6H_5\,CO{\cdot}Cl + H_2O = C_6H_5{\cdot}CO{\cdot}OH + HCl.$$

Whilst acetyl chloride reacts violently with water even in the cold :

$$CH_3\,CO{\cdot}Cl + H_2O = CH_3\,CO\,OH + HCl$$

Benzoyl chloride will react with hydroxy-compounds, ammonia, primary and secondary amines to form compounds which are analogous to those given by acetyl chloride (p 711), *e g*

$$C_6H_5\,CO{\cdot}Cl + C_2H_5\,OH = HCl + C_6H_5{\cdot}CO\,OC_2H_5 \text{ (Ethyl benzoate)}$$

$$C_6H_5{\cdot}CO\,Cl + 2NH_3 = NH_4Cl + C_6H_5\,CO\,NH_2 \text{ (Benzamide)}$$

$$C_6H_5{\cdot}CO\,Cl + C_6H_5NH_2 = HCl + C_6H_5NH\,CO\,C_6H_5 \text{ (Benzanilide)}$$

The above type of substitution, in which a hydrogen atom belonging to

the molecule of an organic compound is replaced by the benzoyl radical, $C_6H_5{\cdot}CO—$, is described as BENZOYLATION, and is clearly analogous to ACETYLATION, namely, the replacement of a hydrogen atom by the acetyl radical, $CH_3\,CO—$, p 711. Both processes are used in the investigation and identification of hydroxy-compounds, primary and secondary amines, etc Thus, the existence of five hydroxyl groups in the fructose molecule, $C_6H_{12}O_6$, is established by the fact that five hydrogen atoms can be replaced by five acetyl radicals, whilst the identity of a compound such as phenol, $C_6H_5OH$, can be established with certainty by preparing the benzoyl derivative and determining its melting-point (Expt 183, p. 792)

It is important to realise that benzoylation is often more suitable than acetylation in the identification of compounds The reasons are (i) acetyl chloride is so readily hydrolysed that acetylation has to be carried out as a rule in absence of water (this is also true for acetic anhydride which is used for acetylation, though the hydrolysis of this compound is much slower), whilst benzoylation can be carried out in aqueous media, (ii) benzoyl derivatives not only have higher melting-points than the corresponding acetyl derivatives, but are usually much less soluble, and can therefore be more easily isolated and purified

In the Schotten-Baumann method, benzoylation is carried out by shaking a slight excess of benzoyl chloride with a solution or suspension of the hydroxy or amino-compound in an aqueous solution of caustic soda (Expt 183, p 792) The alkali not only combines with the hydrogen chloride set free in the action,

$$XH + C_6H_5\,CO\,Cl = C_6H_5COX + HCl$$

(where $X = C_6H_5O—$, $C_6H_5NH—$, etc), but also decomposes any excess benzoyl chloride which remains over

$$C_6H_5CO\,Cl + 2NaOH = C_6H_5COONa + NaCl + H_2O$$

**Benzoic anhydride**, $(C_6H_5CO)_2O$, is prepared by heating a mixture of benzoyl chloride and sodium benzoate

$$C_6H_5\,CO\,Cl + Na\,O\,CO\,C_6H_5 = NaCl + (C_6H_5\,CO)_2O.$$

compare $$CH_3\,CO\,Cl + Na\,O\,CO\,CH_3 = NaCl + (CH_3{\cdot}CO)_2O,$$

It is a crystalline solid (m -pt 42°), which resembles acetic anhydride in its chemical properties

**Benzamide**, $C_6H_5{\cdot}CO\,NH_2$, is prepared most conveniently by the action of benzoyl chloride on ammonium carbamate

$$C_6H_5\,CO{\cdot}Cl + (NH_3)_2CO_2 = C_6H_5\,CO\,NH_2 + NH_4Cl + CO_2$$

It is a white solid (m -pt 128°) and is soluble in hot water It resembles acetamide in its chemical properties, *e g* it gives **phenyl cyanide** or benzonitrile, $C_6H_5\,CN$, on dehydration with phosphoric oxide, and yields ammonia and sodium benzoate when heated with caustic soda .

$$C_6H_5{\cdot}CO\,NH_2 + NaOH = C_6H_5{\cdot}CO\,ONa + NH_3,$$

compare $$CH_3{\cdot}CO{\cdot}NH_2 + NaOH = CH_3{\cdot}CO\,ONa + NH_3$$

# CHAPTER LXI

## PHENOLS AND AROMATIC AMINES

**General considerations.**—**Benzyl alcohol**, $C_6H_5\,CH_2\,OH$, and **benzylamine**, $C_6H_5\,CH_2\,NH_2$, resemble the aliphatic alcohols and amines in all their essential properties, but special properties appear in **phenol**, $C_6H_5\,OH$, and in **aniline**, $C_6H_5\,NH_2$, in which the hydroxyl and amino groups are attached directly to the aromatic nucleus In particular, (i) the acylous character of the phenyl group makes the phenols more acidic than the alcohols, as is indicated by the names "carbolic acid," "picric acid," etc, which have been applied to some of them, conversely, aniline is a much weaker base than ammonia and the aliphatic amines, (ii) the fact that the carbon atom to which the OH group is attached does not carry any hydrogen atoms rules out a large range of reactions corresponding to the oxidation of alcohol to acetic acid, (iii) on the other hand, the OH or $NH_2$ group makes the nucleus extremely sensitive to substitution (p 784), finally (iv) the stability of the diazo-derivatives, prepared by the action of nitrous acid on the aromatic amines, provides a very important contrast with the aliphatic amines, and forms the basis for a large range of organic syntheses

### A Phenols

**Phenol**, or carbolic acid, $C_6H_5\,OH$, and the homologous **cresols** (or methyl phenols), $CH_3\,C_6H_4\,OH$, are important constituents of coal tar

(i) They are extracted from a middle fraction of coal tar (b -pt 170°-230°) by the action of caustic soda, as **sodium phenate**, $C_6H_5\,ONa$, and **sodium cresylate**, $CH_3\,C_6H_4\,ONa$, from which they are liberated by the action of sulphuric acid or carbon dioxide

$$2C_6H_5\,ONa + CO_2 + H_2O = 2C_6H_5\,OH + Na_2CO_3$$

The resulting oil gives on distillation, (1) a phenol fraction which crystallises on cooling, and (2) a cresol fraction which remains liquid

(ii) Phenols can be made on a large scale by fusing benzenesulphonates with an alkali hydroxide

$$C_6H_5\,SO_2\,ONa + 2NaOH = C_6H_5\,ONa + Na_2SO_3 + H_2O$$

In this drastic operation, however, isomeric changes are liable to take place; thus **resorcinol**, or *m*-dihydroxybenzene, $C_6H_4(OH)_2$, is produced by potash fusion, not only from benzene-*m*-disulphonic acid, but also from *o*-, *m*- and *p*-monochlorophenols

(iii) Phenols are also obtained by decomposing diazo-compounds (p 800)

$$C_6H_5N_2OH \rightarrow C_6H_5OH + N_2$$

Phenol is a colourless solid, which develops a pink coloration on exposure to air It melts at 42° and boils at 181° It is miscible in all proportions with water above 66 5°, but forms two layers at lower temperatures (Fig 133, p 499) It has a characteristic smell and burning taste, and is both poisonous and antiseptic Its aqueous solutions give a violet coloration with ferric salts It has the chemical properties of a weak monobasic acid, but exhibits in a modified form most of the reactions of an alcohol It is chiefly remarkable, however, because the hydroxyl group imparts an intense reactivity to the aromatic ring, which is in complete contrast to the inertness of this system in benzene Thus phenol reacts immediately with bromine-water to give a precipitate of 1 2 4 6 **tribromophenol**, $C_6H_2Br_3OH$

EXPT 181 **Properties of phenol**

(*a*) Melt some phenol by immersing the bottle in warm water Pour a little of the oil into a test tube, add a little water and shake the mixture well Notice the formation of two layers Add a little caustic soda and shake again The phenol dissolves

(*b*) To a fairly strong solution of phenol in caustic soda solution add a little dilute sulphuric acid Notice the separation of phenol as an oily layer

(*c*) Repeat the last experiment, using a stream of carbon dioxide in place of dilute sulphuric acid

(*d*) Make a solution of phenol in warm water To one part of it add a drop of ferric chloride , note the change of colour and the effect of adding (i) dilute hydrochloric acid, (ii) acetic acid To the other part, add bromine-water and note the precipitation of tribromophenol

EXPT 182 **Liebermann's reaction.**

(*a*) Put a crystal of sodium nitrite into a few c c of concentrated sulphuric acid and warm very gently Then add a very small quantity of phenol Notice the changes of colour produced on warming and on diluting the warmed solution with water To the diluted solution add caustic soda solution and observe the effect

(*b*) Repeat this experiment, using a nitrosamine (p 762) instead of sodium nitrite

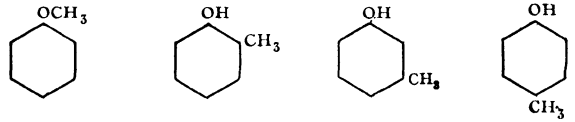
EXPT 183 **The Schotten-Baumann reaction**

This reaction depends on the use of benzoyl chloride, *in presence of an alkali*, to eliminate hydrochloric and benzoic acids from the product Place 5 grams of phenol and 30 c c. of water in a wide-mouthed bottle fitted with a stopper Add 10 c c. of 10% KOH and 2 c c of benzoyl chloride and shake vigorously Repeat this about three times until the smell of phenol has disappeared Make the product alkaline, then filter off the precipitate of **phenyl benzoate**, $C_6H_5CO OC_6H_5$, recrystallise it from hot alcohol and determine the melting-point (68°).

**Reactivity of the hydroxyl group in phenol.**—(*a*) Phenol is described as an acid, rather than as an alcohol, because it forms salts which are hydrolysed only reversibly by water, *e g* sodium phenate gives less than 1% of free phenol in a normal solution It is, however, weaker than prussic acid, and incomparably weaker than carbonic acid, by which it is liberated completely from its salts Nevertheless, its acidity can be used to explain why phenol cannot be esterified like the alcohols by the direct action of an acid but must be treated as in Expt 183

(*b*) Ethers, such as **anisole**, or phenyl methyl ether, $C_6H_5 O CH_3$ (an isomer of *o*-, *m*- and *p*-cresol), can be prepared by the action of an alkyl iodide on sodium phenate

$$C_6H_5 ONa + ICH_3 = C_6H_5 OCH_3 + NaI$$




Anisole *o*-Cresol *m*-Cresol *p*-Cresol

(*c*) The hydroxyl group is not readily reduced, but the oxygen can be eliminated by distillation with zinc dust

$$C_6H_5 OH + Zn = ZnO + C_6H_6$$

(*d*) The hydroxyl group can also be displaced by halogens by the action of phosphorus halides, but the products (unlike ethyl chloride) are not hydrolysed by boiling alkalis

$$C_6H_5 OH + PCl_5 = C_6H_5Cl + POCl_3 + HCl$$

**Reactivity of the nucleus in phenol.**—(*a*) *Halogens* —(i) In complete contrast to the paraffins, which are attacked only slowly even by chlorine in sunlight, and to benzene itself, which requires a halogen-carrier to promote the replacement of hydrogen by halogens, phenol is attacked immediately by chlorine and yields a trisubstitution product, 1 2 4 6 **trichlorophenol**, $C_6H_2Cl_3 OH$, in which the *para*-position and both *ortho*-positions are occupied by chlorine in accordance with the rule given on p 776

(ii) In the same way, bromine-water precipitates phenol quantitatively as 1 2 4 6 **tribromophenol** A volumetric estimation of phenol can indeed be carried out by adding a known amount of standard bromine-water and estimating the excess of bromine after an interval of about 10 minutes

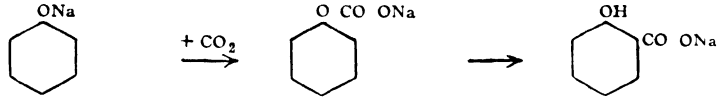
(iii) Even iodine will enter the nucleus under similar mild conditions, since **iodophenol**, $C_6H_4I OH$, is produced by adding a mixture of iodine and iodic acid to a solution of phenol in dilute potash

$$5C_6H_5 OH + 2I_2 + HIO_3 = 5C_6H_4I OH + 3H_2O$$

(*b*) *Nitric acid* —In accordance with the rules given on p 776, dilute nitric acid converts phenol into a mixture of *ortho*- and *para*-**nitrophenols**, $NO_2 C_6H_4 \cdot OH$, whilst strong nitric acid in presence of sulphuric acid yields the explosives D.N.P , or 1 2 · 4 **dinitrophenol**, and finally **picric**

**acid**, or 1 2 4 6 **trinitrophenol** (p 795), in which all the *ortho-* and *para-*positions are nitrated

(*c*) *Carbon dioxide*.—When sodium phenate is heated to 120° with carbon dioxide under pressure, it forms **sodium phenyl carbonate**, $C_6H_5\,O{\cdot}CO\,ONa$, which then undergoes isomeric change to **sodium salicylate**, $HO\,C_6H_4\,CO\,ONa$, where the hydroxyl and carboxyl groups are in the *ortho*-position to one another (KOLBE'S REACTION)




Salicylic acid can also be prepared (as a disodium salt) by boiling a mixture of phenol and carbon tetrachloride with caustic soda (TIEMANN-REIMER REACTION), when substitution again takes place in the *ortho*-position

$$C_6H_5\,OH + CCl_4 + 6NaOH = NaO\,C_6H_4\,CO\,ONa + 4NaCl + 4H_2O$$

If chloroform is used instead of carbon tetrachloride (REIMER REACTION), the product is **salicylic aldehyde**, $HO\,C_6H_4\,CHO$, or *o*-hydroxybenzaldehyde, the characteristic component of "meadow sweet," by the oxidation of which salicylic acid was first prepared

**Salicylic acid**, $HO\,C_6H_4\,CO\,OH$, prepared by the methods described above, crystallises from hot water in needles (m.-pt 150°). Like phenol it gives a violet coloration with ferric chloride, and is a powerful disinfectant, its derivatives are used in medicine and in the preparation of dyes. It unites in one molecule the chemical properties of phenol and of benzoic acid, just as glycollic acid,

$$HO\,CH_2\,CO\,OH,$$

has the properties of an alcohol and of a fatty acid. Thus it gives a **disodium salt** with caustic soda, but a **monosodium salt**,

$$HO{\cdot}C_6H_4\,CO\,ONa,$$

with sodium carbonate, because the phenolic group is too weakly acid to decompose a carbonate. Again, on esterification with methyl alcohol and sulphuric acid, it gives **methyl salicylate**, $HO\,C_6H_4\,CO\,OCH_3$ (the chief constituent of OIL OF WINTERGREEN), the hydroxyl group of which can be methylated by the action of methyl iodide and potash to form **methyl methylsalicylate**, $CH_3O\,C_6H_4\,CO{\cdot}OCH_3$, from this, **methylsalicylic acid**, $CH_3O\,C_6H_4\,CO\,OH$ (an isomer of methyl salicylate), is produced by hydrolysis. **Acetylsalicylic acid**, $CH_3\,CO{\cdot}O\,C_6H_4{\cdot}CO\,OH$, prepared by the action of acetyl chloride on salicylic acid, is well known in medicine as ASPIRIN. Finally the carboxyl group can be eliminated, just as in the case of benzoic acid, by heating salicylic acid with soda-lime

$$2HO{\cdot}C_6H_4{\cdot}CO\,OH + 3Ca(OH)_2 = Ca(OC_6H_5)_2 + 2CaCO_3 + 4H_2O.$$

EXPT 184 **Properties of salicylic acid.**

(*a*) Dissolve a little salicylic acid in warm water, and add a solution of ferric chloride. Observe the colour.

(*b*) Heat a mixture of salicylic acid or one of its salts with soda-lime, and notice the smell of phenol

(*c*) To a solution of salicylic acid in caustic soda add dilute hydrochloric acid The acid is precipitated

EXPT 185 **Preparation and properties of picric acid**

(*a*) Heat 3 grams of phenol with 10 c c of concentrated sulphuric acid in an evaporating basin on a water-bath until a clear solution of **phenol-sulphonic acid,** $HO\,C_6H_4\,SO_2\,OH$, is obtained Pour this very gradually into 10 c c of fuming nitric acid in a boiling-tube, the operation being carried out in a fume chamber, as oxides of nitrogen are evolved freely When the reaction subsides, heat the mixture on a water-bath for about half an hour, and then pour it into about 200 c c of cold water Wash the solid picric acid on a filter with cold water and recrystallise it from hot water containing a little sulphuric acid Dry the yellow crystals in a steam oven and determine their melting-point (122°) Recrystallise a portion from absolute alcohol, is there any difference in the product?

(*b*) Examine the action of picric acid on a strong solution of sodium carbonate

(*c*) Dissolve about equal quantities of picric acid and naphthalene in hot alcohol, mix the solutions and note the formation on cooling of yellow crystals of **naphthalene picrate,** $C_{10}H_8,C_6H_2(NO_2)_3OH$

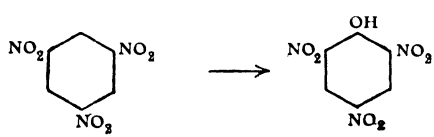
(*d*) Dip pieces of wool, silk and cotton fabric into an aqueous solution of picric acid and note the effect of washing each piece in hot water

**Picric acid,** $(NO_2)_3\,C_6H_2\,OH$, prepared as described in Expt 185, is a yellow solid (m -pt 122°), which can be crystallised from hot water, to which it imparts a strongly acid reaction It is remarkable in that it forms molecular compounds with hydrocarbons, such as benzene and anthracene It also acts upon silk and wool, which are dyed a yellow colour without the use of a mordant Unlike phenol, picric acid will decompose carbonates to give well-defined salts which (like the parent acid) explode violently on percussion Its acid character is also confirmed by the fact that **picryl chloride,**

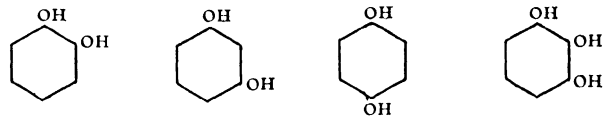
$$(NO_2)_3\,C_6H_2Cl,$$

prepared by the action of phosphorus pentachloride on the acid, is not inert like the chlorobenzenes, but has the activity of an aliphatic chloride, since it can be hydrolysed back to the parent acid and interacts with ammonia to form **picramide,** $(NO_2)_3\,C_6H_2\,NH_2$

The symmetrical structure of picric acid is established by the fact that it can be prepared by oxidising symmetrical trinitrobenzene with potassium ferricyanide



**Polyhydric phenols**, such as **quinol** and **pyrogallol**, are similar to phenol in many of their properties, but are much more easily oxidised Thus quinol (or hydroquinone) is used as a photographic developer, and alkaline pyrogallol for removing and estimating oxygen in gaseous mixtures.




Catechol (*ortho*) Resorcinol (*meta*) Quinol (*para*) Pyrogallol (*vicinal*)

EXPT 186 **Resorcinol**

(*a*) To a solution of resorcinol in water add a few drops of ferric chloride solution, and observe the colour

(*b*) Heat a mixture of resorcinol and phthalic anhydride very gently over a small flame Cool the product, dissolve it in a little caustic alkali and pour the solution into a large beaker of water Notice the brilliant green fluorescence of the resulting fluorescein

EXPT 187 **Quinol**

To a solution of quinol in water add a solution of ferric chloride, and warm the mixture Notice the colour changes and the pungent smell of the resulting quinone

EXPT 188 **Pyrogallol.**

To a solution of pyrogallol in water add a little caustic soda solution and shake the mixture Notice how rapidly it darkens owing to the absorption of oxygen

## B AROMATIC AMINES

**Aniline**, $C_6H_5NH_2$, the simplest amine of the aromatic series, was first prepared by distilling indigo It is made in the laboratory by reducing nitrobenzene with tin and hydrochloric acid (Expt 189), and on a large scale by reduction with iron borings in presence of a little hydrochloric acid

$$C_6H_5NO_2 + H_2O + 2Fe = C_6H_5{\cdot}NH_2 + Fe_2O_3$$

The reduction is effected by blowing steam into the mixture in a large tank fitted with a condenser, and returning the distillate so long as it still contains nitrobenzene Lime is then added and the aniline separated by steam distillation as a lower oily layer The acid is needed to start the reduction, but is set free again because ferric chloride is readily hydrolysed to ferric oxide (compare the rusting of iron in presence of carbonic acid, p 357)

Pure aniline is a colourless oil (b.-pt 184°, density 1·022), which readily becomes brown on exposure to air It exhibits in a modified form the reactions of a primary aliphatic amine, but differs in forming relatively

stable diazo-compounds (p 799), like phenol it is also remarkable for the intense reactivity which the substituent imparts to the nucleus

EXPT 189 **Preparation and properties of aniline**

(*a*) Twenty-five grams of nitrobenzene and fifty grams of granulated tin are placed in a 750 c c round-bottomed flask, which is fitted with a reflux water-condenser (Fig 187) 100 c c of concentrated hydrochloric acid are then added in portions of about 20 c c, care being taken to allow the reaction to subside before adding the next portion of acid If the reaction becomes very violent the flask must be cooled in a bath of cold water When all the acid has been added, the mixture is heated on a water-bath for ten minutes, the reflux condenser is then removed and the heating continued until the vapour issuing out of the flask has only a faint smell of nitrobenzene In this way the reduction is almost completed and any unchanged nitrobenzene is vaporised The liquid in the flask is diluted with 50 c c of water and then made strongly alkaline by the cautious addition of caustic soda, 80 grams in 100 c c of water A great deal of heat is liberated during the addition of the alkali, so that it is necessary to cool the flask in cold water The dark oil which floats on the surface is crude aniline

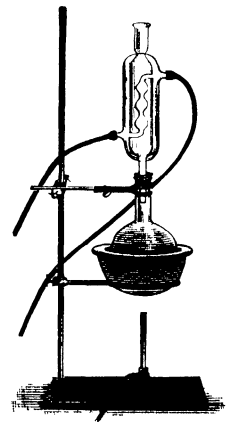


FIG 187 PREPARATION OF ANILINE

(*b*) The aniline is expelled from the flask by steam distillation (see p 502), because the heterogeneous mixture " bumps " badly if it is heated directly by a burner Steam is generated by boiling water in an oil-can (*a*) (Fig 188), which is fitted with a cork carrying a delivery tube and a safety-tube

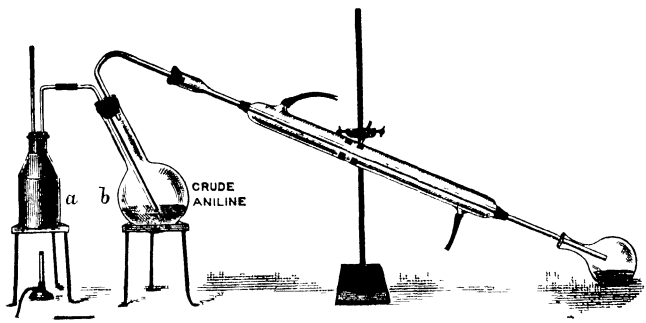



FIG 188 STEAM DISTILLATION

The latter reaches nearly to the bottom of the can The steam is forced through the crude aniline in the flask (*b*), by means of a bent tube, fitted as in the diagram The outlet tube is connected with a Liebig's condenser

The distillation is continued until the distillate is no longer turbid, *i e* until it contains virtually no aniline The distillate is then shaken with salt (20 grams per 100 c c distillate), and when the latter has dissolved, the mixture is shaken vigorously in a separating funnel with 50 c c of ether *N B —See that all flames are extinguished as ether is dangerously inflammable* The lower aqueous layer is run into a conical flask preparatory to another ether extraction, whilst the ether layer which contains most of the aniline is run into a 250 c c flask containing 20 grams of coarsely powdered caustic potash The second ether extraction is then carried out in precisely the same way as before, and the ether layer added to the first one The reason for adding the ether in two portions of 50 c c rather than in *one* portion of 100 c c should be clear from the distribution law (p 565), try question 18, p 836 The addition of the salt lowers the solubility of the aniline in water, and therefore increases the efficiency of the ether extraction The flask containing the ether extract is securely corked and left for several hours in order that the caustic potash may remove the water that is present Calcium chloride cannot be used for drying aniline because it forms an addition compound with it (*cf* ammonia, p 182) The dry aniline-ether solution is filtered *via* a fluted filter paper into a 250 c c distilling flask, which is then fitted with a thermometer graduated to 200°, water-condenser and receiving flask, just as in the purification of ether, Expt 164, p 722 The ether is then distilled off by immersing the flask in a bath of hot water (60°), which must be reheated in the fume chamber from time to time When all the ether has distilled off, the water-condenser is replaced by an air-condenser and test tube as receiver, and the flask is heated over a burner The fraction which boils at 181-185° is almost pure aniline and is therefore collected separately

(*c*) Shake a few drops of aniline with a little water in a test tube, and note how sparingly soluble it is Add a little dilute hydrochloric or sulphuric acid and shake again Notice the effect Notice also what happens when a solution of sodium hypochlorite is added to the aqueous solution of aniline

(*d*) Examine the action of bromine-water on a solution of aniline in hydrochloric acid

(*e*) Recall, but do not repeat, the carbylamine test (Expt 175, p 766)

**Aniline as a primary amine.**—(*a*) Aniline is a very weak base, which does not turn red litmus completely blue, and only precipitates the weaker metallic hydroxides, *e g* those of Al, Fe, Zn, from their salts, but it forms crystalline salts, *e g* **aniline hydrochloride**, $[C_6H_5NH_3]^+Cl^-$, and **aniline sulphate**, $[C_6H_5{\cdot}NH_3]_2^{++}SO_4^{--}$, which have a strongly acid reaction in solution, on account of hydrolysis (p 627) It also forms double salts, such as the **platinichloride**, $[C_6H_5{\cdot}NH_3]_2^{++}PtCl_6^{--}$, which is almost insoluble in water

(*b*) Aniline forms secondary and tertiary amines with aliphatic and aromatic halides (p 799), but quaternary ammonium salts are only formed when at least one of the radicals is aliphatic

(*c*) Aniline is readily attacked by acetyl chloride to give acetanilide,

$$C_6H_5{\cdot}NH_2 + CH_3\,CO\,Cl = C_6H_5{\cdot}NH\,CO\,CH_3 + HCl,$$

but this amide is usually prepared in the laboratory by heating aniline acetate, just as acetamide, $CH_3\,CO\,NH_2$, is prepared by heating ammonium acetate (Expt 161, p 713)

$$\underset{\text{Aniline acetate}}{[C_6H_5\overset{+}{N}H_3]\bar{O}\,CO\,CH_3} \rightarrow \underset{\text{Acetanilide}}{C_6H_5\,NH\,CO\,CH_3} + H_2O,$$

compare · $[\overset{+}{N}H_4]\bar{O}{\cdot}CO\,CH_3 \rightarrow H_2N\,CO\,CH_3 + H_2O$

Acetanilide is a colourless solid which may be crystallised from hot water It is hydrolysed, like acetamide, by boiling with acids or alkalis,

$$C_6H_5\,NH\,CO\,CH_3 + NaOH = C_6H_5\,NH_2 + NaO\,OC\,CH_3,$$

though the reaction with alkalis takes place less readily than is the case with acetamide Acetanilide is much less reactive than aniline and is therefore often used to make derivatives that cannot easily be prepared from aniline itself on account of its excessive reactivity Thus monochloroanilines, $Cl\,C_6H_4\,NH_2$, mononitroanilines, $NO_2\,C_6H_4\,NH_2$, etc, are prepared by the action of chlorine, nitric acid, etc, on acetanilide, followed by hydrolysis to get rid of the acetyl group

(*d*) Aniline is oxidised by per*mono*sulphuric acid to **nitrosobenzene**, $C_6H_5\,NO$

(*e*) The carbylamine reaction has already been described in Expt. **175**; the reactions with nitrous acid are described in Expt 190 below

**Reactivity of the nucleus in aniline.**—(*a*) Like phenol, aniline can be precipitated from solution by chlorine or bromine, and can be titrated against bromine-water The products are 1 2 4 6 **trichloro-** and **tribromoaniline**, $C_6H_2Cl_3{\cdot}NH_2$ and $C_6H_2Br_3\,NH_2$

(*b*) Aniline can be sulphonated in the *para*-position by heating the acid sulphate at 200°, when it loses water and gives ***p*-sulphanilic acid**.

$$[C_6H_5{\cdot}NH_3]O\,SO_2\,OH \rightarrow NH_2\,C_6H_4\,SO_2\,OH + H_2O$$

(*c*) Aniline is oxidised by chromic acid to **quinone**, a volatile yellow solid, which is reduced by sulphurous acid to the colourless dihydric **phenol**, known as **quinol** or **hydroquinone** (p 796) ·

$$\underset{\text{Aniline}}{C_6H_5{\cdot}NH_2} \rightarrow \underset{\text{Quinone}}{O{=}C\begin{cases}CH{=}CH\\ CH{=}CH\end{cases}C{=}O} \rightarrow \underset{\text{Quinol}}{HO{\cdot}C_6H_4{\cdot}OH}$$

**Preparation of secondary and tertiary amines from aniline.**—(*a*) *Aliphatic derivatives.*—Aniline can be methylated by heating it with methyl alcohol and hydrogen chloride under pressure.

$$\underset{\text{Aniline}}{C_6H_5{\cdot}NH_2} \rightarrow \underset{\text{Methylaniline}}{C_6H_5{\cdot}NH\,CH_3} \rightarrow \underset{\text{Dimethylaniline}}{C_6H_5\,N(CH_3)_2}$$

The products are secondary and tertiary bases, but are abnormal in two respects: (1) They are liable to undergo isomeric change during the

process of preparation, and thus to yield derivatives of aniline in which the ring is methylated instead of the side-chain.

$$\underset{\text{Methylaniline}}{C_6H_5{\cdot}NH\,CH_3} \rightarrow \underset{\text{Toluidine}}{CH_3\,C_6H_4\,NH_2}.$$

(ii) Not only does monomethylaniline yield a yellow nitrosamine, $C_6H_5\,N(CH_3)NO$, (compare Liebermann's reaction, p 792), but dimethylaniline yields a green **nitrosodimethylaniline**, $NO\,C_6H_4\,N(CH_3)_2$, in which a nitroso-group has entered the nucleus in the *para*-position

Quaternary ammonium salts, such as $C_6H_5\,N(CH_3)_3I$, can also be prepared and converted into bases by the action of moist silver oxide

(*b*) *Aromatic derivatives* —**Diphenylamine**, $(C_6H_5)_2NH$, is prepared by heating aniline and aniline hydrochloride in a closed vessel at 250°

$$C_6H_5\,NH_3Cl + C_6H_5\,NH_2 = (C_6H_5)_2NH + NH_4Cl$$

It melts at 54° and is insoluble in water It forms a nitrosamine, but (on account of the acylous character of the phenyl group), it is such a feeble base that its salts are decomposed by water On the other hand, metallic potassium yields a **potassium-derivative**, which interacts with bromobenzene to form **triphenylamine**, $N(C_6H_5)_3$

$$(C_6H_5)_2NK + C_6H_5Br = (C_6H_5)_3N + KBr$$

This compound (which can also be prepared directly from aniline, potassium and bromobenzene), does not form salts with acids

**Diazotisation.**—When sodium nitrite is added to an ice-cold acidified solution of an aniline salt (Expt 190), a DIAZONIUM SALT is produced, which can be precipitated by the addition of alcohol or ether

$$C_6H_5\,NH_3Cl + NaNO_2 + HCl = C_6H_5\,N_2\,Cl + NaCl + 2H_2O$$

Although these diazonium salts can be isolated, they are explosive when dry, and their solutions readily decompose with liberation of nitrogen, unless ice-cold Their reactions may be described under three headings as follows

(*a*) *Reduction* —An aqueous solution of benzene diazonium chloride is reduced by a solution of stannous chloride in hydrochloric acid to **phenylhydrazine hydrochloride**, from which **phenylhydrazine** itself can be separated with caustic soda, extracted with ether, dried over solid potassium carbonate and distilled:

$$C_6H_5\,N_2{\cdot}Cl + 4H = C_6H_5\,NH\,\overset{+}{N}H_3\overset{-}{Cl}.$$

(*b*) *Elimination of nitrogen* —(i) When an aqueous solution of a diazonium salt is warmed, **phenol** is produced in poor yield

$$C_6H_5{\cdot}N_2\,Cl + H_2O = C_6H_5\,OH + N_2 + HCl.$$

(ii) When boiled with alcohol, the alcohol is oxidised to aldehyde and the diazo-compound is reduced to benzene with liberation of nitrogen

$$C_6H_5\,N_2Cl + C_2H_6O = C_6H_6 + C_2H_4O + N_2 + HCl.$$

This reaction is accompanied by another in which phenetol (phenyl ethyl ether), $C_6H_5 O C_2H_5$, is formed according to the equation

$$C_6H_5 N_2Cl + C_2H_5OH = C_6H_5 O C_2H_5 + N_2 + HCl$$

The extent to which either of these reactions takes place depends upon the conditions

(iii) The elimination of nitrogen with formation of a halide or cyano-derivative of benzene can be promoted by the addition of a cuprous salt (SANDMEYER REACTION) or of copper powder (GATTERMANN'S METHOD)

$$C_6H_5 N_2 Cl \rightarrow C_6H_5 Cl + N_2 \qquad C_6H_5 N_2 I \rightarrow C_6H_5I + N_2$$
$$C_6H_5 N_2 Br \rightarrow C_6H_5 Br + N_2 \qquad C_6H_5 N_2 CN \rightarrow C_6H_5 CN + N_2$$

The reagents used are as follows .

$C_6H_5Cl$ Copper powder or a solution of CuCl in HCl
$C_6H_5Br$ ,, ,, ,, ,, ,, CuBr in HBr
$C_6H_5I$ Add KI to a cold solution of the diazonium sulphate
$C_6H_5CN$ Add a solution of the diazonium chloride to a solution of copper sulphate in excess of potassium cyanide, containing potassium cuprocyanide, $K_3CuC_4N_4$

By means of these reactions it is possible to effect a very wide range of substitutions and thus to link together the orientations of a large variety of derivatives of benzene, *e g*

$$NO_2 \rightarrow NH_2 \rightarrow OH,\ Cl,\ Br,\ I$$
$$\rightarrow CN \rightarrow COOH \leftarrow CH_3$$

(*c*) *Coupling* —The diazonium ion readily loses nitrogen, but is not otherwise very reactive When, however, the base is released from mineral acids by the addition of sodium acetate, the diazo-hydroxide is found to be an extremely active reagent, which can be coupled with a wide range of phenols, anilines, etc The products are coloured AZO-COMPOUNDS containing the group —N=N— and form the basis for a large range of colours and dye-stuffs ; *e g* **methyl orange** can be prepared by diazotising sulphanilic acid, and then coupling it with dimethylaniline, which has already been shown (by the action of nitrous acid, p. 799) to be reactive in the *para*-position

$$HO SO_2 C_6H_4 N_2 OH + H C_6H_4{\cdot}N(CH_3)_2$$

Diazotised sulphanilic acid — Dimethylaniline

$$\rightarrow HO SO_2 C_6H_4{\cdot}N_2{\cdot}C_6H_4 N(CH_3)_2$$

Methyl orange

**Structure of diazo-compounds.**—If a saturated solution of benzene-diazonium chloride is added to an excess of strong aqueous potash, **potassium diazotate**, $C_6H_5 N_2 OK$, separates in pearly scales, from which the **anhydride**, $C_6H_5 N_2 O N_2 C_6H_5$ (but not the free hydroxide), can be separated by cautious addition of acids, whilst excess of hydrochloric acid reconverts it quantitatively into the diazonium chloride.

It is a remarkable fact that the DIAZONIUM SALTS, *e g* $C_6H_5N_2Cl$, and the DIAZOTATES, *e g* $C_6H_5N_2{\cdot}OK$, both give *neutral* solutions in water The diazo-compound therefore behaves as a strong base towards acids and as a strong acid towards bases Since it is generally recognised that the same substance cannot be at the same time a strong acid and a strong base, the parent diazo-compound is regarded as TAUTOMERIC (p 732), *i e* its derivatives are represented by two different structures Thus the diazonium salts are represented by BLOMSTRAND'S FORMULA, I, in which the basic ion contains a quaternary atom of nitrogen, whilst the diazotates are represented by Kekulé's formula, II, in which the nitrogen is all tervalent These formulae are shown (in an ionised form) below

$$[C_6H_5\overset{+}{N}{\equiv}N]\overset{-}{Cl} \rightarrow C_6H_5N_2OH \rightarrow C_6H_5N{=}N\overset{-}{O}\overset{+}{K}$$

I Diazonium salt Diazo-hydroxide II Diazotate

It is clear that the coupling reactions and the reduction to phenylhydrazine are based upon Kekulé's structure, whilst the elimination of nitrogen from acid solutions appears to be a function of Blomstrand's structure

EXPT 190 **Preparation and properties of benzene diazonium sulphate**

Dissolve 5 grams of aniline in a warm solution of sulphuric acid, prepared by adding 5 c c of the concentrated acid to 50 c c of water in a beaker Cool this solution to 0° by adding a few lumps of ice and then add a solution of sodium nitrite (about 5 grams in 20 c c of water) until a drop of the liquid gives a blue coloration with starch iodide paper, thereby showing the presence of an excess of nitrous acid The nitrite must be added in small quantities at a time and the temperature of the solution must be kept near 0° by adding ice and stirring, otherwise a tarry mass is produced Portions of this solution of benzene diazonium sulphate are then tested as follows

(*a*) Boil in a test tube and note the smell of phenol

(*b*) Add to an alkaline (NaOH) solution of (i) phenol, (ii) β-naphthol, and add more dilute alkali if the mixture is not alkaline Note the colour of the precipitates, which are sodium benzene-azophenate, $C_6H_5NNC_6H_4ONa$ and sodium benzene-azo-β-naphtholate, $C_6H_5NNC_{10}H_6ONa$

(*c*) Add a few drops of aniline and shake, the yellow precipitate consists of **diazoaminobenzene**, $C_6H_5NNNHC_6H_5$,

(*d*) Add to a solution of potassium iodide, nitrogen is evolved and **iodobenzene**, $C_6H_5I$, separates as an oil.

# QUESTIONS

The following abbreviations are used

| | |
|---|---|
| C S | Cambridge Scholarship |
| O S | Oxford Scholarship |
| C H S C | Cambridge Higher School Certificate |
| C W B H S C | Central Welsh Board Higher School Certificate |
| J M B H S C | Joint Matriculation Board Higher School Certificate |
| L H S C | London Higher School Certificate |
| O H S C | Oxford Higher School Certificate |
| O & C H S C | Oxford and Cambridge Higher School Certificate |

## CHAPTERS I-VIII

**1.** Give a short sketch of the development of the atomic theory from the time of Dalton until the present day (O S)

**2** " The theory of chemistry, with all its modern development, is indisputably the theory of Dalton " Discuss and criticise this statement (C H S C)

**3** State the law of constant proportions and the law of multiple proportions Describe the experiments which have been made in order to prove the truth of one of these laws (C H S C)

**4.** State the laws of chemical combination, and give some account of the experimental evidence on which they are based Point out how the atomic theory as developed by Dalton gives a satisfactory explanation of these laws (C S)

**5.** State the law of multiple proportions and show how you would verify it in the cases of (*a*) the oxides of carbon, and (*b*) the oxides of copper (C S)

**6.** State the law of reciprocal proportions Give an account of the experiments by which Stas determined the weight of potassium which is chemically equivalent to a given weight of oxygen (C S)

**7** Define the term " equivalent weight " How can the equivalent weight of iron be determined ? (C H S C)

**8** Explain what is meant by the equivalent weight of (*a*) an element, (*b*) a compound

Describe in outline how you would determine the equivalent weights of (*a*) carbon, (*b*) sodium carbonate (C H S C)

**9.** When asked how to determine the equivalent of zinc, a boy answered " I should take some zinc, dissolve it in concentrated nitric acid, weigh the hydrogen which came off and calculate how many grams of hydrogen I could get out of one gram of zinc "

Criticise this answer, pointing out the errors it contains, and state how you would determine the equivalent of zinc (J M B H S C)

**10.** State the laws of chemical combination, and discuss whether they give any support to the atomic theory (Madras Inter)

**11.** A solution proved by qualitative analysis to contain only the chloride and bromide of a certain metal gave the following results on analysis

(*a*) 25 c c titrated with $N/10$ silver nitrate required 37 5 c c of the latter, and the washed and dried silver salts thus precipitated weighed 0 5935 gram

(*b*) 25 c c evaporated to complete dryness with sulphuric acid left 0 2906 gram of anhydrous sulphate What was the equivalent of the metal and in what proportions were the chloride and bromide present in the solution ?

[Cl = 35 5, Br = 80, Ag = 108, S = 32, O = 16 ] (O S)

**12** State Gay-Lussac's law of the combination of gases by volume

It was at one time stated that this law could be explained by assuming that equal volumes of all gases at the same temperature and pressure contain equal numbers of atoms How was it shown that this assumption was not in agreement with the facts and what hypothesis is now accepted ?

Give the reasoning applied in deducing the relation between the molecular weight of a gas and its density (C W B H S C)

**13** State Avogadro's hypothesis Explain how this hypothesis has been applied to decide the atomic weights of elements of known equivalent weight (C H S C)

**14.** Dalton's formulae included water HO, ammonia NH, ethylene CH, methane $CH_2$, and his atomic weights were H = 1, O = 8, N = 5, C = 6

Explain Dalton's method of arriving at atomic weights and formulae Show how his difficulties were at length overcome and how a reliable method was developed for finding the correct multiple of the equivalent weight to give the atomic weight (C W B H S C)

**15** It was formerly held that equal volumes of elementary gases at the same temperature and pressure contained equal numbers of atoms Discuss briefly this hypothesis in relation to experimental evidence (C S)

**16** Why do you believe in the correctness of Avogadro's hypothesis ? (O S)

**17** Explain concisely why matter is thought to be made up of atoms, why the atom of sulphur is thought to be 32 times heavier than that of hydrogen, and why some elements are believed to exist in the free state in the form of molecules made up of several atoms (O S)

**18** State concisely the experimental evidence and the reasoning which have led to the conclusion that the gram molecular weight of any gas at normal temperature and pressure occupies approximately 22 2 litres (C H S C)

**19** Explain how (*a*) isomorphism of compounds, (*b*) specific heats of elements, have been used in fixing the atomic weights (O H S C)

**20.** A metal $X$, which in its ordinary salts is divalent, forms an oxide which contains 90 66% of the metal When 13 70 grams of this oxide were treated with nitric acid, 13 24 grams of the nitrate of the metal were formed and an insoluble residue weighing 4 78 grams was left This residue was shown by analysis to be another oxide of $X$ containing 86 61% of $X$ From these data calculate the formulae of the two oxides and the atomic weight of the metal $X$

Write an equation for the reaction of the first-mentioned oxide with nitric acid (C W B H S C)

**21** The equivalent weights of elements are determined by analysis State clearly the fundamental principles and reasoning employed in deriving atomic weights from these equivalent weights, and give supplementary methods which confirm the values obtained (C W B H S C)

**22.** An element $X$ forms a volatile chloride which contains 77 48% of chlorine and has a vapour density of 69 (H = 1) It also forms an oxychloride which contains 10 41% of oxygen and 69 39% of chlorine and has a vapour density of 77 (H = 1). The free element has a vapour density of 62 (H = 1)

From these data calculate the atomic weight of the element and the molecular

formulae of the element, its chloride and its oxychloride State clearly any hypotheses you use in the course of your calculations (L H S C)

**23** What data are required for the determination of the atomic weight of an element ? Illustrate your answer by reference to hydrogen, oxygen, sulphur and silver (C S)

**24** A chloride of an element contains 58 7% of chlorine, and the density of the vapour is 91 times that of hydrogen Draw what conclusions you can as to the formula of the compound and the atomic weight of the element (C S)

**25** What is meant by saying that two substances are isomorphous ? How can isomorphism be demonstrated ? How has isomorphism been applied in chemistry ? (C S)

**26** 11 72 grams of a non-volatile oxide were heated with excess of sodium carbonate, and the resulting loss of weight, due to escape of carbon dioxide, was 2 228 grams In another experiment, 0 1037 gram of the element when treated with ammoniacal silver nitrate yielded 0 3657 gram of silver
Derivatives of the element were isomorphous with chromates What conclusions do you draw from these data regarding the equivalent and atomic weights of the element and the formula of the oxide ? (Ag = 108) (C S)

**27** Two oxides of a metal contain 36 8 and 30 38% of oxygen The specific heat of the metal is 0 117 Assign formulae to the two oxides (B I B Sc)

**28** How is it possible to determine the atomic weight of an element whose equivalent weight is known ? Illustrate your answer by reference to the elements carbon and chromium (C S)

**29** How would you endeavour to convince a sceptical but unusually intelligent layman of the existence of atoms and molecules ? (O S)

**30** Define *valency* and give an account of the experimental work and the reasoning involved in the determination of the valency of an element Illustrate your answer by showing how the valencies of (i) bromine, (ii) aluminium, (iii) phosphorus, can be determined

**31** Chemists generally try to express chemical reactions by means of equations Give illustrations of this, explaining how far the equations given actually represent the reactions (i) with respect to the substances actually taking part in the reaction, (ii) quantitatively, (iii) as regards the conditions required to bring about the reaction

**32** What is meant by the valency of an atom ?
" The valency of an atom is the number of components into which the combining power of the atom can be subdivided " How far do you think this statement is correct ? (O & C H S C)

**33** Explain the various types of valency from the standpoint of atomic structure Illustrate your answer by the electronic structure of methane, ammonia, and ammonium chloride (C S)

**34** Explain the terms *molecule* and *valency*
Show how the number of atoms in the molecules of chlorine and nitrogen has been determined (O & C H S C)

**35** Explain what is understood by *oxidation* and *reduction* Give some examples of these processes, with reference to any cases in which the reactions are reversible (C H S C)

**36** Describe briefly the main features of Mendeléeff's periodic classification of the elements, and discuss any improvements which this system of classification has undergone since it was first advanced (C W B H S C)

**37** Give an account of the influence of the concept of atomic number on the periodic classification (C W B H S C)

**38.** The second period of the periodic table is as follows:

| Element | Ne | Na | Mg | Al | Si | P | S | Cl |
|---|---|---|---|---|---|---|---|---|
| Atomic number | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 |
| Atomic weight | 20·18 | 23 00 | 24 32 | 26·97 | 28 06 | 31 02 | 32 06 | 35·46 |
| Isotopes | 22 | 23 | 26 | 27 | 30 | 31 | 36 | 37 |
| | 20 | | 25 | | 29 | | 34 | 35 |
| | | | 24 | | 28 | | 32 | |

Explain this table

Discuss briefly the valency of these elements from the standpoint of the electronic theory (C W B H S C)

## ADDITIONAL PROBLEMS

**39.** 3 00 gm of a mixture of zinc oxide and zinc powder were attacked by an excess of dilute sulphuric acid to give 600 c c of hydrogen, measured over water at 17° C and 750 mm What percentage of the zinc atoms in the mixture were combined with oxygen? [Zn = 65 4, 1 gram hydrogen occupies 11 2 litres at N T P, aqueous vapour = 14 mm at 17° C]

**40** What weight of water would be obtained by heating in a stream of hydrogen 10 0 gm of (*a*) ferrous oxide, (*b*) ferric oxide, (*c*) magnetic oxide of iron, until no further change occurred? [Fe = 56, H = 1 0]

**41.** The chloride of an element was converted quantitatively into the corresponding oxide, when the following figures were obtained 0 1827 gm of the chloride gave 0·1057 gm of the oxide Calculate the equivalent weight of the element [Cl = 35 5] (C S)

**42.** 2 67 gm of the chloride of a metal is heated with concentrated sulphuric acid until a residue of the sulphate of the metal weighing 3 42 gm is obtained Calculate the equivalent of the metal (London Inter Coll Schol Bd)

**43.** Two chlorides of a certain element contained respectively 77 5 and 85 2 per cent of chlorine What conclusions can you draw from these figures? (C S)

**44.** Calculate the percentage composition of a mixture of nitrogen with nitrous and nitric oxides from the following data (*a*) when 50 c c are passed over heated copper, the volume is reduced to 40 c c, (*b*) 1000 c c of the mixture weighs 1 584 gm. [1 litre $H_2$ weighs 0 09 gm All volumes at N T P] (O H S C)

**45.** 100 c c of a mixture of hydrogen, carbon monoxide and carbon dioxide was added to 100 c c of oxygen in a eudiometer After sparking the volume was reduced to 112 5 c c, and the addition of caustic potash caused a further contraction of 50 c c If the residual gas was completely absorbed by alkaline pyrogallol and all the measurements were made at room temperature, calculate the percentage composition of the mixture.

**46.** 20 c c of a gaseous hydride of an element X gave 40 c c of products when decomposed completely into its elements The latter, after mixing with 30 c c of oxygen and sparking for a second, gave a final volume of 25 c c, consisting of element X and excess of oxygen If X is a gaseous element with a value of 1 41 for the ratio $Cp/Cv$, deduce the formula of the hydride What element do you suspect that X is? Mention one physical measurement and one chemical test which would confirm the identity of the hydride Assume that all the above measurements were made at room temperature.

**47.** The equivalent of a volatile metal is 100·3 The specific heat of the metal is 0·033 0·25 gm of the metal occupies 79·5 c c at 500° C and 760 mm Calculate the atomic weight of the metal and the molecular weight of its vapour What value would you predict for the ratio of the specific heat of the metallic vapour at constant pressure to that at constant volume? (O.H.S C)

**48.** 0 256 gm of the sulphate of a certain element yielded 0 525 gm of barium sulphate, when it was treated in aqueous solution with excess of barium chloride The vapour-density of the chloride of the element was about 67 Suggest possible values for the atomic weight of the element What further experiments could be made in order to confirm the value assigned? [O = 16, S = 32, Ba = 137 4 ] (O & C H S C)

**49** A crystalline solid which is isomorphous with potash alum contains water and the following percentages a metal X, 23 41 , aluminium, 4 75 , sulphate radical, 33 80 The specific heat of X is 0 0482 Find the atomic weight of X (London H S C)

**50.** Assuming that the atomic weight of oxygen is 16 00, find the atomic weight of carbon and magnesium, using the following data of percentage composition

Magnesium carbonate Mg = 28 91 , C = 14 22 , O = 56 87

**51.** From the following experimentally determined ratios, calculate the atomic weights of lithium, silver and chlorine, taking the atomic weight of oxygen to be 16 000

LiCl $AgCl = 29\ 579$ 100 00 LiCl $LiClO_4 = 34\ 406$ 86 347
LiCl $Ag = 39\ 299$ 100 00 (C W B H S C)

**52** In an atomic weight determination (*a*) 1 0000 gm of silver gave 1 1485 gm of $Ag_2S$, (*b*) 1 4450 gm of $Ag_2SO_4$ gave 1 0000 gm of silver Calculate the atomic weights of silver and sulphur, assuming the above formulae [O = 16 000 ] (O & C H S C)

**53** From the following data calculate the equivalent weight of the alkali metal M correct to two places of decimals

1 0000 gm of the chlorate of M when heated to constant weight gave 0 6085 gm of the chloride 1 0000 gm of the latter precipitated 1 4460 gm of silver (dissolved in nitric acid) 1 0000 gm of silver combined with 0 3285 gm of chlorine to form silver chloride

The equivalent weight of oxygen is to be taken as 8 00 No atomic weights or other equivalents are to be assumed, but note may be taken of the fact that preliminary experiments have shown the equivalent weight of chlorine to be approximately $35\frac{1}{2}$, and in consequence the chlorate is known to contain 6 equivalents of oxygen for each equivalent of chlorine (C S)

**54.** In a recent series of determinations 11·5783 gm of silver cyanide gave on heating in hydrogen 9 3290 gm silver, and 10 8052 gm of silver cyanate gave 7 7768 gm silver Assuming that the atomic weight of nitrogen is 14 008, find the atomic weights of silver and carbon to two places of decimals referred to O = 16 00 as standard (O S)

**55** The vapour-density of an anhydrous metallic chloride is 40 The sulphate of the metal crystallises with four molecules of water of crystallisation 1 771 gm of the hydrated sulphate on ignition yields 0 251 gm of metallic oxide Calculate the atomic weight of the metal (C S)

**56.** It was found that 2 gm of the oxide of a hexavalent element united with 0 1725 gm of normal ammonium orthophosphate to give a complex compound, there being no other reaction product

One gram of the compound reacted with 0 4902 gm of sodium hydroxide to form water, disodium hydrogen orthophosphate and the normal sodium and ammonium salts of the acid which is derived most simply from the oxide Suggest an empirical formula for the compound

[NaOH = 40 00 $(NH_4)_3PO_4 = 149{\cdot}0$ ] (C S)

**57.** Calculate the weight of pyrolusite, containing 60% by weight of manganese dioxide, which would be required to liberate sufficient chlorine from hydrochloric acid to make 10 gm of anhydrous ferric chloride from the metal Assume that 10% of the available chlorine is wasted

**58.** The chloride of a metal is completely hydrolysed by water into an insoluble oxide and hydrochloric acid

0 313 gm of this chloride, after treatment with water, needed 19 2 c c of a solution of sodium hydroxide containing 1 gm in 100 c c , for neutralisation of the hydrochloric acid formed

0 230 gm of the chloride expelled 21 8 c c of air from a Victor Meyer vapour-density apparatus, measured at 15° C and 741 mm pressure

Calculate the equivalent weight of the metal, and the molecular weight of the chloride What conclusions can you draw about the atomic weight of the metal and the formula of the chloride? (C H S C )

## CHAPTERS IX-X

**1** What led to the discovery of the existence of the inert gases, and how were they isolated ? Discuss the value of the inert gases to science and industry

**2** Write a brief essay on *either* " The discovery and characteristics of the inert gases " or " The atom " (C W B H S C )

**3** Describe the methods by which argon was isolated from the atmosphere Discuss the theoretical and experimental reasons for assigning to this gas a monatomic molecule (C H S C )

**4** Discuss the position of hydrogen in the periodic classification

**5** How is a continuous supply of hydrogen prepared in the laboratory ? What do you understand by the term " nascent " hydrogen , what suggestions have been put forward to account for the fact that it is a more powerful reducing agent than ordinary hydrogen ?

**6** Explain, giving experimental details, how you would prepare a sample of pure hydrogen, using commercial sulphuric acid as your source How could the purity of the gas be tested ? (O & C H S C )

**7** How is hydrogen prepared on the large scale ? Point out the impurities likely to be found in the gas prepared by each of the methods you describe Calculate the weight of iron that would be required to generate by the action of sulphuric acid enough hydrogen to fill a spherical balloon of 10 metres diameter at 10° C , and 750 mm pressure [Fe = 56 ] (C S )

**8** What methods are used for preparing hydrogen (*a*) in the laboratory, (*b*) on a manufacturing scale ?

State briefly the conditions under which hydrogen reacts with (*a*) nitrogen, (*b*) chlorine, (*c*) oxygen (O & C H S C )

**9** What are the common impurities in tap-water ? How may they be detected and removed ? Describe how you would estimate the amount of any one of them present (O S )

**10** Why are some waters called hard ?

Describe briefly the chemical reactions which occur in the principal processes used for softening hard water on a large scale (O & C H S C )

**11** What do you understand by " temporary " and " permanent " hardness How would you determine the proportion of each in a specimen of hard water ?

**12** Give an account of the part played in chemistry by water To what extent is the simple formula $H_2O$ insufficient to describe the properties of water ? (C S )

**13.** Give an accouut of experiments which have been carried out on the composition of water, pointing out their importance in advancing chemical theory (O & C H S C )

**14** How may the composition of water, (*a*) by weight, (*b*) by volume, be determined ? (C S )

**15** On what evidence is the molecular formula for hydrogen peroxide based ? What is the relation of hydrogen peroxide to the oxides $BaO_2$, $MnO_2$, $PbO_2$, $Na_2O_2$ ?

Describe what you would expect to observe when a solution of hydrogen peroxide is added in excess to the following (*a*) lead hydroxide in excess of sodium hydroxide solution, (*b*) barium hydroxide solution (C S)

**16** How may hydrogen peroxide be prepared in aqueous solution ? What are the approximate strengths of the solutions usually met with ? How may the strength of a solution be determined ?

Describe the action of a solution of hydrogen peroxide on (*a*) lead sulphide, (*b*) silver oxide, (*c*) manganese dioxide, (*d*) an acidified solution of potassium dichromate (J M B H S C)

**17** Describe the preparation of pure hydrogen peroxide What products are formed and under what conditions when hydrogen peroxide reacts with (*a*) potassium permanganate, (*b*) lead sulphide, (*c*) manganese dioxide, (*d*) colloidal platinum, (*e*) potassium iodide ? (L H S C)

**18** Give an account of the properties of hydrogen peroxide 25 c c of a potassium permanganate solution, containing 6 grams per litre, were required to react with 20 c c of a solution of hydrogen peroxide in the presence of dilute sulphuric acid Calculate the volume of oxygen measured at 20° C and 750 mm pressure which would be liberated from 100 c c of the hydrogen peroxide solution by the action of finely divided platinum (C H S C)

**19** What do you know of the structural formula of hydrogen peroxide ? 10 c c of a given solution of hydrogen peroxide gave 22 4 c c of oxygen (measured at N T P) when heated with colloidal platinum How many grams of hydrogen peroxide were there per litre of solution ?

## CHAPTERS XI-XII

**1** Discuss the properties of the alkali metals and their compounds Do you consider that their properties show any analogies with the coinage metals ?

**2** What products may be obtained on the industrial scale by electrolytic methods using common salt as raw material ? Give the principal features of the different methods employed, indicating the best conditions for obtaining the several products (C W B H S C)

**3** Describe the manufacture of sodium starting from brine For what purposes is metallic sodium used ?

Describe briefly the preparation and properties of (*a*) sodium bicarbonate, (*b*) sodium nitrite, (*c*) sodium silicate, (*d*) sodium sulphide (J M B H S C)

**4** Starting from common salt, give *one* process by which each of the following substances can be prepared (*a*) sodium bicarbonate, (*b*) sodium hydroxide, (*c*) sodium (J M B H S C)

**5** Give a brief account of the preparation of sodium carbonate by the present-day commercial process Explain the importance of the by-products of the reactions employed

How would you distinguish between solutions of sodium carbonate and sodium bicarbonate ? (C W B H S C)

**6** Starting from sodium hydroxide, how could you prepare specimens of *four* of the following (*a*) metallic sodium, (*b*) sodium nitrate, (*c*) sodium carbonate, (*d*) sodium bicarbonate, (*e*) sodium bisulphate ?

Describe the action of heat (if any) on (*b*), (*c*) and (*d*) (J M B H S C)

**7** 4 35 grams of a mixture of sodium chloride and anhydrous sodium carbonate were dissolved in distilled water and the solution made up to 100 c c 20 c c of this solution required 75 5 c c of decinormal sulphuric acid to react completely with the sodium carbonate Calculate the percentage composition by weight of the original mixture. (J M B H S C)

**8.** Describe the manufacture, properties and uses of sodium hydroxide

**9.** How is magnesium manufactured Starting from magnesium, how would you prepare pure specimens of (*a*) magnesium oxide, (*b*) magnesium nitride, (*c*) anhydrous magnesium chloride, (*d*) magnesium carbonate ?

**10.** A white powder is suspected to contain barium and magnesium carbonates How would you verify this, and how would you estimate the amount of one of the metals present ? (O S)

**11** What are the chief compounds of calcium which occur in Nature ? Describe the preparation of calcium from one of them and the preparation of any three calcium compounds of commercial importance (L H S C)

**12** If, in a country where water power is available, a large salt deposit containing sodium, potassium, and magnesium chlorides is known to exist, what chemical industries could be established ? (C H S C)

**13** Give the relative positions of magnesium, calcium, and zinc in the periodic table, and show the truth of the statement, " The properties of magnesium are in some respects intermediate between those of calcium and zinc " (C H S C)

**14** Calcium and zinc are included in the same group of the periodic system of classification How far is this justified by the principal properties of these elements and of their chief compounds ? (O & C H S C)

**15** How are calcium, calcium oxide and calcium carbide prepared ? Describe the action of water on each of these substances and state how you would investigate the composition of the products in each case (C S)

**16** How is quicklime manufactured ? State its properties and uses (Calcutta Inter)

**17** How would you prepare a specimen of pure quicklime ? What experiments would you make to show (*a*) that it is a chemical individual, (*b*) that it is the oxide of a metal, (*c*) that it contains 28 53% of oxygen ? (C S)

**18** What compounds does calcium form with the elements nitrogen and hydrogen ? Describe briefly their preparation and properties How does nitrogen react with calcium carbide, and what is the practical importance of this reaction (O S)

**19** What happens (*a*) when limestone is heated (i) in a closed vessel, (ii) in the open, and (*b*) when quicklime is allowed to remain in contact with carbon dioxide at ordinary temperature ? How are the reactions involved related to one another ? (J M B H S C)

**20** Describe the manufacture and uses of calcium carbide How can this substance be converted into a useful fertiliser ? (C H S C)

## CHAPTER XIII

**1.** Do you consider that the classification of boron with aluminium in the same group of the periodic table is justified ?

**2** Describe the characteristic properties of boron How can this element be prepared from borax ? (C S)

**3.** Give an account of the manufacture and properties of borax Of what use is this compound in qualitative analysis How would you prepare a crystalline specimen of boric acid from borax ?

**4.** How is boric acid obtained ? Describe its properties and uses How may the following substances be obtained from it, boron trioxide, boron, boron nitride, boron hydride ? Give a short account of their properties (O S)

**5.** Describe briefly the preparation (*a*) of aluminium starting from bauxite, *or* (*b*) of sodium starting from sodium chloride.

Describe the behaviour of aluminium hydroxide in the presence of (*a*) hydrochloric acid, and (*b*) sodium hydroxide solution Give *two* other examples of similar behaviour (J M B H S C)

**6** Explain clearly how aluminium is extracted from its ores Give an account of the properties of this metal, showing how its uses depend upon these properties (O H S C)

**7** Describe the extraction of aluminium from its ores What reactions occur between (*a*) aluminium and potash, (*b*) ammonium alum and sodium sulphide, in presence of water ? (C S)

**8** Give an account of the industrial uses of aluminium and its compounds Starting from aluminium, how would you prepare specimens of (*a*) aluminium chloride, (*b*) aluminium sulphide, (*c*) potash alum ?

## CHAPTERS XIV-XV

**1** What is meant by allotropy ? Give a short description of the allotropic modifications of carbon and mention their chief uses (Calcutta Inter)

**2** Show that the elements of Group IV of the periodic system (the carbon family) become increasingly metallic with rising atomic weight (L H S C)

**3** The atomic weight 12 has been assigned to carbon Summarise the theoretical and experimental grounds upon which this value is based, and sketch the apparatus necessary for the determination of the equivalent weight of this element (C H S C)

**4** Describe one method for the preparation of pure carbon monoxide in the laboratory Of what commercial gas mixtures is carbon monoxide an important constitutent and for what purposes are these mixtures used ?

50 c c of a mixture of carbon monoxide, carbon dioxide and hydrogen was exploded with 20 c c of oxygen The volume measured at the original room temperature and pressure was 37 c c , and after treatment with sodium hydroxide solution 3 c c Calculate the composition by volume of the original mixture (J M B H S C)

**5** Describe the preparation and properties of carbon monoxide Give details of the processes by which carbon monoxide can be converted into carbon dioxide and carbon dioxide into carbon monoxide (Calcutta Inter)

**6** How would you prepare a specimen of pure carbon monoxide ? How, and under what conditions, does carbon monoxide react with (*a*) sodium hydroxide, (*b*) nickel, (*c*) chlorine, (*d*) hydrogen ? On what evidence has the molecular formula CO been assigned to this gas ?

**7.** How would you determine the composition by weight of carbon dioxide ? What precautions would you take to secure accurate results ? Sketch the apparatus used for the purpose (Calcutta Inter)

**8** Give an account of the properties and industrial uses of carbon dioxide How would you prove that its molecular formula is $CO_2$ ?

**9.** Give as full an account as you can of the natural phenomena which follow from the fact that carbon dioxide is soluble in water to form a weakly acid solution How would you determine the amount of carbon dioxide present per litre in water through which a current of gas has been passed ? (Oxford Prelim)

**10.** Describe the manufacture of carbon disulphide Compare and contrast its properties with those of carbon dioxide How would you show that one is an endothermic and the other an exothermic compound ? (C W B H S C)

**11** Give an account of the action of steam on red-hot carbon and show how the reaction has been adapted for industrial use Name the constituents of water-gas, and indicate briefly how you would determine their proportions in a sample of the gas. (L H.S C)

**12.** How is coal-gas manufactured and purified? What products (besides coal-gas) are produced in the manufacture of coal-gas? (C H S C)

**13** Coal-gas and water-gas are two gaseous fuels derived from coal Give in outline the methods by which they may be prepared, and compare and contrast their compositions (C H S C)

**14** 10 c c of a gaseous carbon compound, exploded with 10 c c of oxygen, gave 10 c c of carbon dioxide and no other product, and 5 c c of oxygen were left Find the molecular formula of this compound

Of what practical importance is it? Describe its manufacture on the large scale How would you detect traces of it in a room in which a gas fire was burning? (O H S C)

**15** Give an account of the structure of the Bunsen flame and state the conditions necessary for its production Explain how you would investigate the chemical changes taking place in the flame, (i) when it is burning properly, (ii) when it has " struck back " (C S)

**16** Discuss the relationship of silicon to carbon and boron, by considering the properties of the elements and their compounds

**17** Boron and silicon are said to resemble one another closely, though they are in different groups of the periodic table What experimental evidence is there for or against this statement? Can you suggest any theoretical explanation? (O S)

**18** Describe fully the physical and chemical properties of silicon In what forms does silicon occur in nature? (Allahabad Inter)

**19** Starting from sand, how would you prepare specimens of (*a*) silicon tetrafluoride, (*b*) barium silicifluoride, (*c*) hydrated silica, (*d*) water-glass?

**20** Describe briefly the preparation and purification of tin from its principal ore, and consider the chemical properties of this element in the light of its position in the periodic system (O S)

**21** Starting from tin, how would you prepare specimens of (*a*) stannic oxide, (*b*) stannous sulphide, (*c*) stannous chloride, (*d*) stannic chloride? Mention the chief characteristics of these substances

**22** Compare and contrast the properties of tin and lead and their chief compounds Do you consider that they show any similarities to antimony and bismuth and their compounds?

**23** Metallic tin can be dissolved in nitric acid of a certain concentration without evolution of any gas, and the solution formed contains ammonium nitrate

$$4Sn + 10HNO_3 = 4Sn(NO_3)_2 + NH_4NO_3 + 3H_2O$$

How would you carry out an experiment to test this equation by finding the amount of ammonia obtainable from the solution produced by dissolving a known weight of tin? (O H S C)

**24** What is the chief natural source of lead? Give an account of its extraction from this source

Describe the following substances, and state how they may be obtained from lead (*a*) red lead, (*b*) litharge, (*c*) white lead (J M B H S C)

**25** How would you prepare from metallic lead specimens of (*a*) litharge, (*b*) red lead, (*c*) lead dioxide? By what tests could you distinguish between these oxides? (C H S C)

**26** Red lead, $Pb_3O_4$, is stated to behave towards hot dilute nitric acid as if it were $2PbO + PbO_2$ and towards hot concentrated hydrochloric acid as a peroxide Describe how you would (*a*) test these statements experimentally, (*b*) verify the formula $Pb_3O_4$ for red lead (O H S C)

**27** Lead chloride, $PbCl_2$, is sparingly soluble in water at 15° C but readily soluble in water at 100° C Describe fully how, starting with metallic lead, you

would (*a*) prepare a solution of this salt saturated at a given temperature (*e g* 18° C), and (*b*) determine the amount of chloride ion present per litre of this solution (O H S C)

**28** Give an account of the chemistry of the lead accumulator (C H S C)

**29** Give an account of the methods you would adopt for the preparation of any *four* compounds of lead if you were provided with the metal and the ordinary laboratory reagents (O & C H S C)

**30.** How would you prepare a specimen of lead peroxide from lead? How would you estimate the purity of your specimen? (O S)

## CHAPTER XVI

**1** Describe how you would obtain nitrogen, (*a*) from the atmosphere, (*b*) from chemical sources Comment on the differences you would expect to find in samples of the gas prepared from these two sources (C S)

**2** Do you consider that nitrogen is an inert element?

**3** Write a concise account of *two* methods for the fixation of atmospheric nitrogen

Explain the great importance of nitrogen fixation (J M B H S C)

**4** Give an account of the reactions in which the element nitrogen combines directly with other elements and compounds, and indicate how these reactions are applied on the manufacturing scale (C W B H S C)

**5** Compare and contrast the preparation and properties of one important hydride of nitrogen, with those of one important hydride of phosphorus (C H S C)

**6** Give an account of the methods used commercially to prepare ammonia from atmospheric nitrogen

Outline the evidence on which the formula $NH_3$ is based (L H S C)

**7** Explain fully why the formula $NH_3$ is given to ammonia, describing the experiments by which you would obtain the necessary data to establish it (O H S C)

**8** Give a brief account of the preparation of ammonia from nitrogen and hydrogen

How would you prepare from ammonia (*a*) nitrogen, (*b*) nitric acid, (*c*) hydrazine sulphate? (C H S C)

**9** Give the evidence for the belief that the group $NH_4$ is present in ammonium compounds

Illustrate by means of typical reactions the properties of these compounds (J M B H S C)

**10** How is dry ammonia prepared in the laboratory? What are the chemical and physical properties of this gas? (Calcutta Inter)

**11** How has the formula of ammonia been determined? What reasons are there for supposing that ammonia gas combines chemically with water?

What reactions occur between an aqueous solution of ammonia and (*a*) chlorine, (*b*) a solution of sodium hypochlorite, (*c*) mercurous chloride, (*d*) silver chloride? (O S)

**12.** In general, there is a close resemblance between ammonium and potassium salts Give examples of this resemblance, and also a series of equations (with notes) to illustrate the fact that striking differences of behaviour are sometimes observed What conclusions may be drawn as to the cause of these differences? (C S)

**13.** What is the action of heat upon (*a*) lead nitrate, (*b*) sodium nitrate? How would you verify your statements by quantitative experiments? (O S)

**14.** How would you determine the composition of nitrous oxide ? Give details of the experiment and calculation How would you distinguish this gas from oxygen ? (C S)

**15.** Find the composition of nitrous oxide from the following data volume of gas taken, 10 c c , after addition of hydrogen, 28 c c , after explosion, 18 c c , after addition of oxygen, 27 c c , after second explosion, 15 c c
(Calcutta Inter )

**16** Give an account of the preparation and properties of (*a*) nitrous oxide, (*b*) nitric oxide How would you determine the percentage of nitrous oxide in a mixture of these two gases ?

**17** Describe the preparation of pure samples of (*a*) nitrous anhydride, $N_2O_3$, (*b*) nitrogen peroxide, $N_2O_4$, (*c*) nitric anhydride What products are obtained by passing gaseous nitrogen peroxide into milk of lime ?

**18** Describe a method for the preparation of pure nitric oxide How has the constitution of this gas been established ? Compare and contrast the properties of this gas with those of carbon monoxide (C H S C)

**19** Give an account of the changes of colour of nitrogen peroxide which occur when (*a*) the pressure, (*b*) the temperature, is varied How may they be explained ? What experiments would you make to confirm your explanation ?
(C S)

**20** How would you prepare from concentrated nitric acid samples of three oxides of nitrogen Outline the experiments and give the reasoning necessary to confirm the molecular formula of any one of these oxides (C S)

**21** Describe how you would prepare a specimen of nitrogen peroxide and determine its vapour density
The vapour density of nitrogen peroxide at 70° C and atmospheric pressure is 27 7 in terms of hydrogen as unity Calculate the percentage dissociation of the gas (O & C H S C)

**22** Describe carefully how nitric acid is manufactured from (*a*) atmospheric nitrogen, (*b*) Chile saltpetre

**23** Give an outline of *one* method for the preparation of nitric acid on a large scale Outline the principal uses of this acid (C H S C)

**24** What is the action of nitric acid upon the following substances (*a*) iodine, (*b*) copper, (*c*) arsenic, (*d*) tin ? In any two of these reactions describe how you would isolate a solid product in a pure state (L H S C)

**25.** The formula for a molecule of nitric acid is $HNO_3$ On what evidence do you base your belief (*a*) that the acid is composed of hydrogen, nitrogen and oxygen but no other element ; (*b*) that the acid contains these elements in the proportion indicated by the formula , (*c*) that this, the simplest formula of the acid, is also the molecular formula ? (J M B H S C)

**26** 1 064 grams of a specimen of sodium nitrate were dissolved in dilute sulphuric acid and completely reduced by nascent hydrogen Excess of caustic soda was added and the ammonia distilled into 50 c c of 0 6 N sulphuric acid After this operation the latter required 45 6 c c of 0 4 N caustic soda for neutralisation Calculate the percentage purity of the sodium nitrate What result would you expect if the impurity were sodium nitrite ? (C W B H S C)

**27.** Explain the importance of carbon and nitrogen in the life-cycle of plants and animals (C W B H S C)

**28.** Discuss the " nitrogen cycle " in nature, and indicate briefly the methods used to restore the nitrogen compounds removed from the soil. (O H S C)

**29** How would you proceed in order to determine what products are formed when a given metal acts on nitric acid ? How would you attempt to isolate a pure specimen of each product ?

**30.** Nitric oxide and oxygen combine in the ratio 4 to 1 by volume over aqueous potassium hydroxide, and in the ratio of 4 to 3 by volume over water Describe any further experiments you think necessary in order to use the above facts in ascertaining formulae for nitrous and nitric acids Give fully the reasoning required (C S)

**31** Describe how you would obtain (*a*) nitrogen, (*b*) oxygen from nitric acid Suggest a method by which the percentage amount of either of these elements in nitric acid could be determined (O S)

**32** Describe experiments showing the oxidising action of nitric acid How may ammonia, nitrogen and oxides of nitrogen be prepared from nitric acid ? (Madras Inter)

**33** What is the action of nitric acid upon (*a*) tin, (*b*) ferrous sulphate, (*c*) hydrochloric acid, (*d*) phosphorus ? State briefly in each case the conditions of reaction (O S)

**34** How may the oxides of nitrogen be prepared from nitric acid ? What are their reactions with water ? (O S)

**35** Give an account of the preparation, properties and probable constitution of nitrous acid

**36** How may sodium nitrite be prepared ? Describe some qualitative experiments which illustrate the differences between nitrites and nitrates (Camb 1st M B)

**37** A basic inorganic compound *X*, containing nitrogen, gives on treatment with nitrous acid a colourless gas, which is unaltered on mixing with air, and dissolves in approximately its own volume of water at 0° What would you suspect the gas to be ? Having regard to the behaviour of ammonia with nitrous acid, what deductions can you make as to the chemical composition of *X* ? (C S)

## CHAPTERS XVII-XVIII

**1.** From a consideration of the properties of phosphorus, arsenic, and bismuth, and their compounds, show that increase in the atomic weights of members of this group is accompanied by a diminution of their non-metallic character (O & C H S C)

**2** What is the main source of phosphorus ? Outline the process of manufacturing white and red phosphorus How can red phosphorus be converted into white phosphorus ? Compare phosphine with hydrogen sulphide and with ammonia (C W B H S C)

**3** How is yellow phosphorus prepared on the large scale ? Starting with yellow phosphorus, how would you prepare (*a*) phosphine, (*b*) phosphorus oxychloride, (*c*) magnesium pyrophosphate ? (L H S C)

**4** Describe *two* methods for the preparation of yellow phosphorus, starting from a natural phosphate

How should yellow phosphorus be treated so as to obtain (*a*) phosphorus trioxide, (*b*) phosphorus pentachloride, (*c*) metaphosphoric acid, (*d*) red phosphorus ? (J M B H S C)

**5.** Give an account of the allotropy of phosphorus Describe shortly the preparation and properties of three phosphorus compounds (O S)

**6.** Phosphorus forms two chlorides State how you would (i) prepare them, (ii) determine their composition and molecular formulae (iii) illustrate their chemical differences (C S)

**7.** Given a solution of phosphoric acid, how would you prepare specimens of its three sodium salts ? Give an account of their properties and explain the principles involved in their preparation (O & C H S C)

**8** Starting from phosphorus, how would you prepare solutions containing phosphorous and phosphoric acids respectively, and how would you prove that you had obtained them ? (O S)

**9** Describe the preparation and properties of the hydrides and chlorides of *either* phosphorus *or* arsenic

What is the action of (*a*) phosphine, (*b*) arsenic trihydride on a solution of silver nitrate ? (C H S C)

**10.** Describe the preparation of the chlorides of phosphorus, and explain the action of water upon them

A determination of the vapour density of the higher chloride at ordinary pressure gave a value of 73 5 How is this fact explained ? What modification of the method would you suggest so as to obtain a normal value for the vapour density, and why ? (C W B H S C)

**11** What do you know of the sources and properties of the element arsenic ? A " weed killer " is suspected to be a solution of sodium arsenite How would you test it for arsenic, and how determine the amount of arsenic present per c c ?

**12** How is arsenic hydride prepared ? How would you discover whether a sample of hydrogen contained this compound ? (Camb 1st M B)

**13.** How can a solution of sodium arsenite be obtained ? What reactions take place when such a solution is treated with (*a*) chlorine, (*b*) hydrogen sulphide, (*c*) hydrochloric acid ? (Camb 1st M B)

**14** Compare the properties of the oxides, sulphides, chlorides and hydrides of arsenic and antimony, and mention any points of particular interest

**15** It is said that nitrogen is a typical non-metal and that bismuth is a typical metal Do you agree ?

## CHAPTERS XIX-XX

**1** How would you prepare a specimen of pure oxygen ? In what ways do you think that oxygen and sulphur are analogous ?

**2** Discuss some method for classifying the oxides of the elements Illustrate your answer by examples showing the characteristics of each class (O S)

**3** Describe the distinctive properties of (*a*) acidic oxides, (*b*) basic oxides, (*c*) amphoteric oxides Explain fully how you would prepare in pure form *one* oxide of each type and *two* salts derived from each of these oxides (C W B H S C)

**4** How would you prepare a sample of ozonised oxygen ? Draw a neat sketch of the apparatus you would use and mention the properties of the gas When 150 c c of a sample of ozonised oxygen were treated with turpentine the volume was reduced by 36 c c What changes, if any, would you notice when another 150 c c of the same mixture is heated until no further change is noticeable and finally cooled to the original temperature and pressure ? (Mysore, 1st C)

**5** How may ozone be prepared, and how is its formula arrived at ? What is the action of ozone on (1) lead sulphide, (2) potassium iodide, (3) an unsaturated hydrocarbon ?

**6** Give an account of one method of preparing ozone, and state the grounds upon which the formula $O_3$ is assigned to it How can the presence of ozone in air be detected, and how would you determine the percentage of ozone in a mixture of oxygen and ozone ? (C S)

**7.** How can the percentage by volume of oxygen in the atmosphere be determined ? Describe how any *two* of the constituents of the atmosphere can be prepared from it in a fairly pure state (C H S C)

**8.** Explain fully an experiment *you* would carry out to show that air is a mixture, not a compound, of nitrogen and oxygen (O.H S C.)

**9.** Describe with full experimental details one method for determining the proportions by volume of oxygen and nitrogen in the air How would you determine the proportion of carbon dioxide present in the air of an ordinary living-room ? (O H S C)

**10** Describe the three types of allotropy and give examples of each type (C S)

**11** Describe the allotropic forms of sulphur, and discuss the conditions governing their stability (C W B H S C)

**12** Summarise the evidence for the statements that sulphur (*a*) can exhibit several valencies, (*b*) is in many respects closely analogous to oxygen (O S)

**13** How would you collect and purify a specimen of hydrogen sulphide ? How would you prove that (*a*) the gas contains hydrogen and sulphur, (*b*) its molecular formula is $H_2S$ ? (Madras Inter)

**14** Describe two independent methods of determining the concentration of hydrogen sulphide in a given dilute aqueous solution of that gas (O S)

**15** How would you prepare, from sulphur, a reasonably pure specimen of hydrogen sulphide ? How would you show experimentally that this compound is (*a*) a reducing agent, (*b*) a very weak dibasic acid ? (O H S C)

**16** How is hydrogen sulphide prepared in the laboratory ? Describe its chief properties, particularly its action on solutions of (*a*) copper sulphate, (*b*) zinc sulphate, (*c*) ferric chloride, (*d*) sulphur dioxide (J M B H S C)

**17** Describe the preparation of hydrogen sulphide in a state of purity State and explain the reactions of hydrogen sulphide with (*a*) zinc sulphate solution, (*b*) dilute nitric acid, (*c*) concentrated sulphuric acid, (*d*) iodine and water (C S)

**18** How would you prepare a specimen of sulphur dioxide as pure as possible ? How has the formula of this substance been arrived at ? (O & C H S C)

**19** How is sulphur dioxide prepared in the laboratory ?
Describe its chief properties and particularly its action on (*a*) water, (*b*) potassium permanganate solution, (*c*) sodium hydroxide solution, and (*d*) lead peroxide (J M B H S C)

**20.** Explain fully what reasons there are for thinking that combination takes place between sulphur dioxide and water What is the action of the solution on solutions of (1) potassium permanganate, (2) barium hydroxide, (3) cupric chloride, (4) chlorine ? Give equations (O S)

**21** From one gram of lead 1 077 grams of lead oxide and 1 154 grams of lead sulphide can be obtained respectively One gram of lead sulphide heated with fuming nitric acid gives 1 268 grams of lead sulphate Show how from these data the percentage composition of the anhydride of sulphuric acid can be obtained
Point out any assumption made in your calculation and explain how you would attempt to justify it experimentally (C S)

**22** When anhydrous aluminium sulphate is strongly ignited, alumina is formed, and a colourless gas is evolved which is partially absorbed by aqueous alkalis Describe how you would carry out such an experiment quantitatively, so as to obtain information on the composition of sulphuric anhydride (C S)

**23.** Why do you believe that the formula of sulphuric acid is $H_2SO_4$ ? Suggest with reasons a structural formula (O S)

**24.** Tabulate the oxides of sulphur and the oxyacids and sodium salts (normal and acid) derived from them so as to bring out their relation to each other Correlate the strength of these acids with their oxygen content and show by comparison with other elements to what extent this relation is general
How is sodium thiosulphate prepared and what is its behaviour with acids, with silver chloride, and with iodine ? (C.W B H S.C.)

**25.** From what sources and by what means is sulphuric acid prepared on a large scale ?
Outline the principal uses of this acid (C H S C.)

**26** What experiments would you carry out to prepare from sulphuric acid, (*a*) sulphur dioxide, (*b*) sulphur, (*c*) sulphuryl chloride ?
Give the structural formula of sulphuric acid and outline the evidence on which it is based (L H S C)

**27.** Describe the manufacture of sulphuric acid by the contact process. Can you mention any difficulties that manufacturers had to overcome before the process was a success ? What advantages does this process possess over the lead chamber process ? (O H S C)

**28.** Describe a commercial process for converting sulphur into sulphuric acid (O & C H S C)

**29** Sulphuric acid may act as (*a*) an acid, (*b*) an oxidising agent, and (*c*) a dehydrating agent Describe and explain *two* experiments to illustrate each of these functions (J M B H S C)

**30** A crystalline solid proved to have the percentage composition sodium 14 28, hydrogen 6 21, sulphur 9 94, oxygen 69 56 On prolonged heating to a certain temperature it lost 55 9 % in weight and left a solid residue of percentage composition sodium 32 39, sulphur 22 53, oxygen 45 07

Show what conclusions can be drawn as to the substances concerned How would you verify your conclusions ? (O H S C)

**31.** Describe in outline *two* processes by which sulphuric acid is manufactured What products are obtained when each of the following substances is heated with concentrated sulphuric acid (*a*) carbon, (*b*) potassium iodide, (*c*) a mixture of calcium fluoride and sand ? (J M B H S C)

## CHAPTER XXI

**1.** How is fluorine prepared ? Give reasons for the procedure adopted
Give a concise account of the chemistry of this element and its more important compounds, noting briefly the features that accord with the group-properties, and paying special attention to the marked deviations therefrom (C W B H S C)

**2** What is the chief naturally occurring compound of chlorine ? From what natural sources and in what way may this compound be prepared in the pure state ? How may chlorine be obtained from it ? (Give *two* methods)
(J M B H S C)

**3.** Give an account of three methods which have been used for the manufacture of chlorine Mention four industrial uses of chlorine

**4.** What do you know about the compounds which (*a*) chlorine, (*b*) fluorine, form with hydrogen ?
A normal solution of hydrogen chloride behaves as a " strong " acid, but a normal solution of hydrogen fluoride acts as a " weak " acid Explain what this statement means and describe how, given such solutions, you would show it to be true (O H S C)

**5.** How would you isolate chlorine from (*a*) bleaching powder, and (*b*) sodium chloride ?
What are the chief properties of this element, and how could you use it to prepare (*a*) anhydrous ferric chloride, and (*b*) a solution of sodium hypochlorite ?
(J M B H S C)

**6.** The oxidation of hydrogen chloride by oxygen is represented as follows

$$2HCl + \tfrac{1}{2}O_2 \rightleftharpoons Cl_2 + H_2O\,(\text{vapour}) + 14{,}000 \text{ calories}$$

Explain the meaning of this equation, and describe briefly how the reaction is carried out commercially Discuss the theoretical principles involved
(C W B H S.C.)

**7** Under what conditions does chlorine react with (*a*) ammonium hydroxide, (*b*) tin, (*c*) aluminium, (*d*) sulphur dioxide, and (*e*) carbon monoxide? Describe in *one* case how you would isolate a pure product (C H S C)

**8.** Describe how you would prepare a pure specimen of chlorine from rock-salt What evidence is there for thinking that chlorine reacts with water according to the equation.

$$H_2O + Cl_2 \rightleftharpoons HCl + HClO$$

**9.** Give an account of the laboratory preparation of (*a*) gaseous hydrogen chloride, (*b*) a solution of hydrochloric acid How would you detect small quantities of free chlorine in hydrochloric acid? How would you remove this impurity? (C H S C)

**10** How is hydrochloric acid manufactured, and for what purposes is it used? How would you establish that its molecular formula is HCl?

**11** Give a brief account of the preparation and properties of the oxides of chlorine

**12** How can bleaching powder be prepared, and for what purposes is it used? (C H S C)

**13** What do you think is the correct formula for bleaching powder? How would you determine the percentage of available chlorine in a specimen of this compound? What happens when bleaching powder is boiled (*a*) alone, (*b*) with a suspension of litharge?

**14** When potassium chlorate is acted upon by moist oxalic acid at 60° C, a mixture of carbon dioxide and an oxide of chlorine is evolved The oxide of chlorine can be liquefied by cooling to 0° C On exposing this oxide, in the gaseous state, to light, it decomposes into chlorine and oxygen When the gaseous mixture, formed by the decomposition of 50 c c of this oxide, was shaken with excess of potassium iodide solution, 50 c c of oxygen remained, and the iodine liberated required 22 3 c c of $N/10$ thiosulphate for its titration

Deduce a formula for the oxide of chlorine, and an equation for its production from potassium chlorate and oxalic acid

[Gaseous volumes are given as reduced to *STP*]

**15** Describe the methods of manufacture of chlorates and perchlorates How would you distinguish between solutions containing perchlorates, chlorates and hypochlorites? (C S)

**16.** Compare the methods which can be employed for the preparation of the halogen acids, and point out the differences in properties of these acids which determine the choice of methods used in their preparation (O S)

**17** What is the chief source of bromine and how is it obtained in the pure state?

Contrast this element and its compounds with the elements chlorine and iodine and their compounds (C H S C)

**18** Describe the preparation of bromine on the commercial scale How and under what conditions does bromine react with (*a*) phosphorus, (*b*) hydrogen, (*c*) sulphur dioxide, (*d*) sodium carbonate, (*e*) sodium thiosulphate? (L H S C)

**19.** Give a brief summary of the principal properties of bromine and consider these in the light of its position in the periodic classification (O S)

**20.** Bromine is said to react with sodium thiosulphate in dilute aqueous solution according to the equation

$$Na_2S_2O_3 + 5H_2O + 4Br_2 = 2NaHSO_4 + 8HBr$$

What experiments would you make to prove that the reaction written above does actually take place and that the reaction is quantitative? (O & C H S C)

**21.** Give an account of the extraction of iodine from its natural sources What are the chief impurities you would expect to find in commercial iodine, and how would you purify a sample? (O C H S.)

**22** How is iodine prepared from the salt deposits in Chile ?
Describe and discuss the reactions between concentrated sulphuric acid and the sodium halides (C H S C)

**23** Name *two* natural sources of iodine and indicate the reactions by which iodine is obtained from them
What is the action of iodine on (*a*) sodium hydroxide solution, (*b*) hydrogen sulphide solution, (*c*) sodium thiosulphate solution, (*d*) potassium iodide solution, (*e*) phosphorus ? (J M B H S C)

**24** Compare and contrast the properties of the halogens and include in your treatment of the subject references to (*a*) the methods of their preparation, and (*b*) the preparation and properties of their compounds with hydrogen (J M B H S C)

**25** How would you investigate the interaction occurring between iodine and sodium thiosulphate in presence of water in order to establish as completely as possible what reaction takes place ? (C S)

**26** Starting with solid iodine, how would you prepare (*a*) a standard solution of iodine, (*b*) potassium iodide, (*c*) iodine pentoxide ?

**27** Describe a laboratory method for the preparation of hydriodic acid State its properties and uses How would you distinguish iodides from chlorides and bromides ? (Calcutta Inter)

**28** What experiments would you perform to show that iodic and hydriodic acids react together according to the equation $HIO_3 + 5HI = 3I_2 + 3H_2O$ ? How would you make use of this reaction to determine the strength of a given solution of sulphuric acid ? (L H S C)

**29** The periodic classification indicates that a member of the halogen group of elements probably remains to be discovered If a new substance were suspected to be this element, describe (*a*) what experiments you consider should be made to prove that it should be rightly regarded as a halogen, (*b*) the most appropriate method of fixing its atomic weight (C S)

## CHAPTERS XXII-XXIV

**1** Discuss the chemical relationships of the metals copper and zinc, pointing out in what respects they resemble one another and in what respects they differ (O H S C)

**2.** What are the chief ores of copper ? Describe how the metal is extracted on the large scale from *one* of these ores
Starting with metallic copper, how would you prepare in the laboratory (*a*) copper sulphate, (*b*) cuprous chloride, (*c*) cuprous thiocyanate, (*d*) cuprammonium hydroxide ? (L H S C)

**3** Write a brief account of the metallurgy of copper Describe how you would prepare the following compounds in the laboratory from metallic copper cuprous oxide, cupric sulphate crystals, cuprous chloride, cupric chloride crystals (C W B H S C)

**4** How would you prepare from copper carbonate specimens of (*a*) black copper oxide, (*b*) copper sulphate crystals, (*c*) cupric chloride, (*d*) red copper oxide (cuprous oxide) ? (C H S C)

**5** Describe *shortly* how the following compounds can be prepared from metallic copper (*a*) anhydrous cupric chloride, (*b*) a crystalline specimen of cuprous chloride, (*c*) cuprous sulphide
Compare the properties of the cuprous salts with those of the corresponding silver salts (C H S C)

**6.** Starting from copper, describe concisely how you would prepare (*a*) copper sulphate, (*b*) cuprous oxide How does the latter oxide differ from cupric oxide ?

**7.** Describe *two* methods by which silver can be extracted from argentiferous lead, and discuss briefly the theoretical principles on which the methods are based (O H S C)

**8** How may pure silver be prepared from an alloy of copper and silver? Write equations to show the action on a solution of cupric sulphate and on a solution of silver nitrate of (*a*) potassium iodide, (*b*) potassium cyanide, (*c*) ammonium thiocyanate Name the colours of the precipitates (C H S C)

**9.** Describe and discuss the use made of silver nitrate as a reagent in the laboratory (C S)

**10** Name the important ores of zinc How is the metal extracted and purified? State its properties and uses (Calcutta Inter)

**11** Discuss how far the chief compounds of calcium, zinc and mercury justify the inclusion of these metals in one group (O S)

**12** Give an account of the properties and uses of the more important inorganic compounds of mercury Starting from metallic mercury, how would you prepare mercuric oxide, mercurous chloride, mercuric chloride? (O H S C)

**13** From what sources, and how, is mercury obtained? What do you know about the purification of this metal? Give an account of any two compounds of it which you consider to be of interest (O S)

**14** Mercury reduces potassium dichromate in presence of hydrochloric acid In an experiment so conducted that one compound only of mercury was produced, one gram of the metal reduced 50 c c of decinormal potassium dichromate solution From the data decide whether a mercurous or a mercuric compound is formed What other experiments would you make to confirm your conclusion? [Hg = 200 6] (O S)

## CHAPTERS XXVI-XXVII

**1** What are the chief mineral sources of iron? Describe the chemical reactions which take place in the various zones of the blast furnace (Madras Inter)

**2** What are the main differences in the composition, properties, and use of cast iron, wrought iron, and steel? (Calcutta Inter)
Explain the methods used for converting cast iron into (1) wrought iron, and (2) steel

**3** Describe, without giving technical details, the essential processes by which wrought iron is obtained from an ore To what properties is the usefulness of iron due? (O & C H S C)

**4** "Iron is bivalent in the ferrous salts and tervalent in the ferric salts" Explain clearly what you understand by this statement
Describe how, starting with metallic iron, you would prepare ferrous and ferric sulphates By what reactions could you distinguish the two salts? (O H S C)

**5** If you were given a supply of iron wire, what experiments would you make to show that the compounds of iron with oxygen obey the law of multiple proportions? (C S)

**6** A metallic-looking solid is suspected to be iron pyrites Describe qualitative experiments to test this supposition How would you determine the percentage of iron in a sample? (O & C H S C)

**7.** How would you examine, qualitatively and quantitatively, the reactions between nitric acid and ferrous sulphate solution? (O S)

**8.** Given a substance known to be iron oxalate, describe and explain how you would find its formula (O S)

**9** Discuss the classification of chromium with sulphur in Group VI in the periodic table With what other elements does chromium show analogies?

**10** Give an account of the uses of chromium Starting with potassium dichromate, how would you prepare specimens of (*a*) chrome alum, (*b*) chromic sulphate, (*c*) chromyl chloride, (*d*) chromium trioxide (O S)

**11.** Describe the manufacture, properties and uses of chromium

**12.** Describe in detail the laboratory preparation of *either* potassium dichromate from chromite, ($FeO,Cr_2O_3$), *or* potassium permanganate from pyrolusite. What slight modifications of your method are made in the large-scale methods, and why ? Mention *three* uses of the substance you choose (O H S C)

**13.** Give an account of the properties and reactions of the chromates and dichromates Explain the action of potassium chromate as an indicator in the titration of chlorides by silver nitrate (C S)

**14.** Manganese occurs in the same group of the periodic table as the halogens On what grounds can you justify its position and what resemblances does manganese show to elements in other groups ? (O S)

**15** How is potassium permanganate obtained ? Describe the chief properties of this substance How has its formula been shown to be $KMnO_4$ ? (O & C H S C)

**16** Manganese dioxide is readily dissolved by aqueous sulphur dioxide How would you investigate experimentally whether the following equation adequately represents the reaction which occurs $MnO_2 + SO_2 = MnSO_4$ ? (O & C H S C)

**17** It is stated that manganese and carbon form, at high temperatures, a carbide, $Mn_3C$, which is decomposed by water into manganese hydroxide, methane and hydrogen Given a supply of the compound, how would you propose to verify its composition and to determine the equation for its decomposition by water ? (O S)

## General Questions on Chapters I-XXVII

**1** " It is impossible to infer what will be the qualities of a compound from the qualities of its constituents " (Sir Humphry Davy) Comment on this statement and say how far you consider it to be true at the present day (J M B H S C)

**2** Explain briefly the grounds on which the formulae of any two well-known compounds are established, and show how the general chemical behaviour of the compounds is in accordance with these formulae (C H S C)

**3.** What experiments would you make to find out whether a basic oxide of a metal was MO or $M_2O_3$ ? (O S)

**4** The simplest formulae for nitrogen peroxide, water and carbon monoxide are $NO_2$, $H_2O$ and CO respectively How far do these formulae agree with the physical and chemical properties of these compounds ? (C S)

**5** Discuss the position of (*a*) hydrogen, (*b*) nickel in the natural classification of the elements

**6.** Explain what is meant in reference to chemistry by (*a*) a law, (*b*) a hypothesis, and (*c*) a theory
Illustrate your answer by reference to (*a*) the law of constant composition, Boyle's law and the law of Dulong and Petit, (*b*) Avogadro's hypothesis, and (*c*) the atomic and ionic theories (J M B H S C)

**7.** " In the case of every successful scientific theory the time must come when its first easy triumphs become exhausted and what prominently confronts the investigator are its outstanding defects and difficulties " (Larmor) Discuss the above statement by reference to *either* the theory of phlogiston *or* periodic classifications of the elements (J M B H S C)

**8** What do you understand by the term " reduction " ? How may the following reductions be brought about (*a*) ferric chloride to ferrous chloride, (*b*) carbon dioxide to carbon monoxide, (*c*) cupric chloride to cuprous chloride ? (C H S C)

**9.** What is meant by (*a*) an oxidising agent, (*b*) a reducing agent? Give equations to illustrate the use of three typical agents of each class (O S)

**10.** Many cases are known in which a compound of an element at an intermediate stage of oxidation decomposes on suitable treatment into two other compounds, one in which the element is at a lower, and the other in which it is at a higher, stage of oxidation Give some examples of this behaviour, indicating the conditions suitable to the changes Discuss any points of interest arising from your examples (C S)

**11.** What is meant by acidity and basicity? In what terms may the equivalent of an acid and of a base be defined? Give examples to illustrate your answer

**12** Classify the following substances as oxidising or reducing agents, giving two examples of the action of each chlorine, hydrogen sulphide, hydrogen peroxide, nitric acid, sulphur dioxide (Camb 1st M B)

**13** Explain what is meant by the following terms (*a*) oxidation, (*b*) oxidising agent, (*c*) available oxygen How would you determine experimentally whether a given substance is an oxidising agent or not? (Camb 1st M B)

**14** Discuss how the tendency of the atom of an element X to bind or release a hydrogen ion

$$X - H \rightleftharpoons X^- + H^+,$$
$$[-XH]^+ \rightleftharpoons X + H^+,$$

depends (*a*) on the position of X in the periodic table, (*b*) on other atoms or groups which may be attached to X (C S)

**15** What are the chief physical and chemical properties by which metals are distinguished? Illustrate your answer by contrasting a typical metal with a typical non-metal (O & C H S C)

**16.** Explain what considerations decide the classification of a particular element Illustrate your answer by discussing the case of *either* magnesium *or* phosphorus (O H S C)

**17** Divide the following elements into three groups in the way which you consider accords best with their chemical relationships fluorine, oxygen, iron, chromium, manganese, aluminium Give reasons for your choice, and point out any analogies which are ignored by your classification (C S)

**18.** If you were given an element and were required to determine to what group of elements it was most closely related, state in general how you would proceed

If the element were one of the following, state what experiment you would make and what results you would expect to obtain iron, mercury, arsenic (C S)

**19.** What substances are commonly used in the laboratory as drying agents? For what purposes would each of them be specially suitable, and upon what does its efficiency depend? (O S)

**20.** How would you determine the amount of water in a hydrated salt? What difficulties might arise, and how could they be overcome? (O S)

**21.** Discuss the methods used to separate from their ores metals whose oxides cannot be reduced by carbon (C W B H S C)

**22.** Describe what occurs when an aqueous solution of sodium carbonate reacts with (*a*) chlorine, (*b*) sulphur dioxide, (*c*) a solution of barium chloride, (*d*) a solution of aluminium sulphate, (*e*) ammonium chloride (L H S C)

**23.** Describe the action, if any, of sodium hydroxide solution and of nitric acid on the following substances zinc, iodine, phosphorus, lead sulphide (C H S C)

**24.** Illustrate and discuss the statement that when a caustic alkali acts upon a non-metal simultaneous oxidation and reduction of the non-metal takes place (C S)

**25** Certain elements react with sodium hydroxide Give as many examples of such reactions as you can, and classify them according to type (C S)

**26** Define normal salt, acid salt, basic salt, double salt, complex salt Give one example of each Describe in detail how you would prepare a crystalline specimen of sodium hydrogen sulphate, starting from sodium hydroxide and sulphuric acid (Camb 1st M B)

**27** Give a short account of the preparation (*one* method only), chief chemical characteristics, and uses of any *three* of the following substances sodium silicate, sodium peroxide, cuprous chloride, bleaching powder, aqua regia (C W B H S C)

**28** Starting with a solution of crude brine, how would you prepare pure crystalline specimens of (*a*) sodium chloride, (*b*) sodium carbonate, (*c*) Glauber's salt, (*d*) sodium chlorate (Madras Inter)

**29** (*a*) What conclusions respecting the nature and composition of quicklime can be drawn from the fact that one gram of quicklime neutralises 35 7 c c of a normal acid solution ?

(*b*) What conclusions respecting the composition of an oxyacid of sulphur can be drawn from the following fact the volume of an oxidising agent which oxidises a given amount of its sodium salt to sulphate is three times that of another oxidising agent of equivalent strength which oxidises it to sulphite ? (C S)

**30** Describe with full experimental details how you would prepare a specimen of potash alum, starting from potassium hydroxide and aluminium

What metals are found to form alums and what special properties are exhibited by crystals of these substances ?

How would you determine the percentage weight of iron in a specimen of ferric alum ? (J M B H S C)

**31** How would you prepare from potash alum pure specimens of (i) potassium chloride, (ii) aluminium chloride, (iii) sulphuric acid ? (C S)

**32** Summarise what you consider to be the most important facts in the chemistry of one of the following elements from the point of view of its position in the Periodic Table (*a*) silicon, (*b*) lead, (*c*) zinc (O S)

**33** Give a brief account of the chemistry of *two* of the following (*a*) the manufacture of water-gas, (*b*) the setting of plaster of Paris, (*c*) the charging and discharging of a lead accumulator, (*d*) water softening (O & C H S C)

**34** Describe in detail how you would prepare (*a*) pure silica from glass, (*b*) pure aluminium oxide from china clay (O H S C)

**35** You are given a gas which may be a mixture of two or more of the gases oxygen, nitrogen, carbon monoxide, and carbon dioxide Explain how you would prove the presence or absence of each of these gases in the mixture and indicate how the percentage amount of each gas present by volume may be estimated (C W B H S C)

**36** Describe what is observed and the reactions which occur when the following substances are heated separately in test tubes (*a*) lead nitrate, (*b*) crystalline ferrous sulphate, (*c*) ammonium nitrate, (*d*) washing soda, (*e*) crystalline copper sulphate (J M B H S C)

**37** What is the action of heat on (*a*) nitrates, (*b*) sulphates, and (*c*) ammonium salts ?

Calculate the percentage loss in weight when magnesium ammonium phosphate ($MgNH_4PO_4.6H_2O$) is heated to redness (L H S C)

**38.** State the conditions under which *two* of the following pairs of substances react, and explain, in each case, what are the principal circumstances upon which the final result depends . (*a*) nitrogen and hydrogen, (*b*) hydrogen and iodine, (*c*) steam and carbon. (O & C H S C)

**39** You are given mixtures of the following gases (*a*) nitrogen and carbon dioxide, (*b*) hydrogen and sulphur dioxide, (*c*) ammonia and oxygen Indicate how you would separate them and obtain pure samples of each (Calcutta)

**40** Describe how you would treat a given quantity of ammonium chloride in order to isolate as much as possible of each of the elements of which it is composed

**41** "The metallic properties of the elements increase with increasing atomic weight" Discuss this statement and exemplify it with reference to the elements nitrogen, phosphorus, arsenic and antimony (C S)

**42** What products are formed when (*a*) arsenic trisulphide is dissolved in yellow ammonium sulphide, (*b*) the resulting solution is acidified, (*c*) a solution of mercuric nitrate is treated with potassium iodide solution gradually to excess, (*d*) a solution of manganous sulphate is treated with sodium hydroxide solution and subsequently shaken with air Explain the reactions which occur in each case (C W B H S C)

**43** What do you understand by a peroxide? What general methods for preparing them do you know? Describe in detail the preparation of a pure specimen of lead peroxide from metallic lead State briefly how you would show that your product was pure (O H S C)

**44** What chemical industries may be developed in a country rich in water power where the available minerals are coal, limestone, and iron pyrites? (C H S C)

**45** Describe the changes which take place when (*a*) sulphur is heated, (*b*) sodium hydroxide is added in excess to a solution of potash alum, (*c*) hydrogen sulphide gas is passed into a solution of ferric chloride, (*d*) ammonium dichromate is heated Explain the reactions which occur in (*b*), (*c*) and (*d*) (J M B H S C)

**46** State briefly the chief features of *three* commercial catalytic processes Explain as fully as you can the principles underlying *one* of these processes (J M B H S C)

**47** Why are the elements chlorine, bromine, and iodine considered to be "naturally" classified together? What could be said for, and against, classifying sulphur and phosphorus together? (O H S C)

**48** Give *three* distinct and general methods for preparing metallic chlorides Describe with experimental details how you would prepare all the anhydrous chlorides of (*a*) iron, (*b*) copper, (*c*) magnesium (J M B H S C)

**49** How would you prepare the anhydrous chlorides of oxygen, boron, phosphorus, iron and chromium? Describe the action of water on these substances (C S)

**50** Give an account of the action of water on the chlorides of the elements State reasons for thinking that this action gives a satisfactory distinction between metals and non-metallic elements or otherwise (O H S C)

**51.** Given sodium chloride, slaked lime, potassium carbonate, and such other reagents as you might require, how would you prepare (*a*) a solution containing potassium hypochlorite, (*b*) a crystalline specimen of potassium chlorate? How would you determine the percentage of hypochlorite in the solution from (*a*), and how would you verify the purity of the sample of chlorate obtained in (*b*)? (O H S C)

**52.** How are perchlorates, persulphates, and permanganates prepared? Write down what you consider to be the structural formulae of these substances, with any remarks on valency which you consider to be applicable (C W B H S C)

**53.** How would you determine the percentage composition of any two of the following (*a*) a mixture of potassium chloride and potassium chlorate, (*b*) a mixture of ammonium sulphate and ammonium nitrate, (*c*) a mixture of litharge, (PbO), and red lead ($Pb_3O_4$)? (O S)

**54.** A reddish-brown gas is being slowly evolved in a reaction How would you decide whether it was bromine or nitrogen peroxide ? If it were bromine, how would you estimate the amount evolved from a given quantity of the reaction mixture ? (O S)

**55** Describe how you would prepare the following substances and comment on any features of interest chromyl chloride, carbonyl chloride, nickel carbonyl (O S)

**56.** Discuss, for *two* of the following pairs of elements, the statement that " in each pair the elements and their compounds show such similarities in properties and reactions that they may be considered to belong to the same family " (*a*) copper and mercury, (*b*) magnesium and zinc, (*c*) carbon and tin, (*d*) iron and aluminium (C H S C)

**57** Describe in detail how you would prepare reasonably pure laboratory specimens of *three* of the following copper sulphate from copper, copper oxide from copper, iodine from potassium iodide, ferrous sulphate from iron turnings, sodium phosphate from phosphorus (O H S C)

**58** In the potential series of the metals, magnesium and zinc precede hydrogen, while copper and silver follow that element Explain, by a consideration of properties and reactions, how the general chemical behaviour of these metals is in accordance with this arrangement (O & C H S C)

**59** Give an account of the corrosion which takes place when iron, copper, zinc and lead are exposed to the atmosphere

**60** Give an account of the general chemical reactions involved in the smelting of metals from oxide and from sulphide ores Mention any cases which arise where the general method does not apply, say why it does not, and briefly indicate the necessary modifications (O H S C)

**61.** Describe briefly *one* laboratory method for making each of *three* of the following compounds (*a*) ferric alum, (*b*) sodium thiosulphate, (*c*) potassium permanganate, (*d*) aluminium chloride

Describe a *quantitative* experiment to test the purity of *one* of the substances selected (O & C H S C)

**62** How do you account for the following facts ?

(*a*) Iron immersed in copper sulphate solution is coated with copper

(*b*) Iodine is liberated from sodium iodate by the action of a solution of sodium bisulphite

(*c*) Aluminium hydroxide dissolves in sodium hydroxide solution and is precipitated from this solution by the addition of ammonium chloride

(*d*) Glass is etched by a solution of hydrofluoric acid (L H S C)

**63.** Describe and explain the changes which the following substances undergo when exposed to the atmosphere (*a*) ferrous sulphate crystals, (*b*) phosphorus pentoxide, (*c*) iron, (*d*) quicklime Describe how you would determine the extent of the change in any *one* case (J M B H S C)

**64.** Give an account of the reactions which take place between the following pairs of substances, stating in each case the conditions under which the reactions occur (*a*) stannous chloride and mercuric chloride, (*b*) arsenic trioxide and nitric acid, (*c*) sand and coke, (*d*) ferrous sulphate and potassium cyanide. (L H S C)

## Chapters XXVIII-XXXII

**1** Give an account of the uses of (*a*) borax, (*b*) concentrated sulphuric acid, (*c*) ammonium chloride, in qualitative analysis, explaining the theory of the use of each (O H S C)

**2** The following pairs of elements are closely associated in the periodic table (*a*) calcium and magnesium, (*b*) tin and lead, (*c*) iron and manganese Describe the

methods applied for the separation of the elements in each of the pairs in qualitative analysis, and explain the principles upon which such separations are based (C W B H S C)

**3.** Explain, giving suitable equations, how the presence of *traces* of the following impurities may be detected in the following substances (*a*) sodium sulphate in sodium sulphite, (*b*) iron in zinc, (*c*) calcium phosphate in calcium carbonate, (*d*) acetylene in coal gas (C H S C)

**4.** How may the following separations in qualitative analysis be effected (*a*) iron from manganese, (*b*) lead from tin, (*c*) silver from mercury in the mercurous state? Comment upon the reactions involved (C S)

**5.** Give reasons for taking the precautions (in italics) in the following paragraphs

(*a*) In the separation of zinc and manganese the sulphides are dissolved in dilute hydrochloric acid and *the solution is boiled* before adding caustic soda solution to precipitate the manganese

(*b*) The separation of iron, aluminium, and chromium as hydroxides is carried out *by adding ammonium chloride* and then ammonium hydroxide to the solution of the chlorides

(*c*) In the separation of nickel and cobalt, potassium cyanide solution in excess is added to the solution of the chlorides of these metals and *the solution is boiled for five minutes in an open dish* Bromine water and caustic soda solution are then added when nickel only is precipitated (L H S C)

**6** Explain fully the chemical reactions which are utilised to distinguish between the following pairs of ions, when present together in a solution (*a*) Cu and Cd , (*b*) Zn and Al , (*c*) Ca and Mg (O S)

**7.** Explain the reactions which are used to distinguish (1) zinc from manganese, (2) cobalt from nickel, (3) arsenic from antimony, (4) a chloride from a bromide, (5) a hypochlorite from a chlorate (O S)

**8** Give an account of *either* the occurrence and mutual transformations of allotropic forms of the elements, *or* the classification of cations (metallic radicals) for purposes of qualitative analysis (O H S C)

**9.** You are provided with a white crystalline solid and are told that it is sodium chloride, bromide, or iodide How would you discover which of these it was, and how would you determine the solubility of the salt at 15° C ?
(C W B H S C)

**10.** How would you attempt to identify a simple salt in the " dry " way ? When are dry tests of particular value ?

**11.** How may the following separations in qualitative analysis be effected (*a*) manganese fron zinc, (*b*) arsenic from antimony, (*c*) antimony from tin, (*d*) calcium from strontium ?
Comment upon the reactions involved

**12.** How would you identify and separate the constituents in the following gaseous mixtures (*a*) carbon dioxide and sulphur dioxide, (*b*) chlorine and carbon monoxide, (*c*) hydrogen chloride and hydrogen sulphide, (*d*) nitric oxide and nitrogen.

**13.** What is a " normal " solution ?
2·5 grams of a mixture of ammonium chloride and sodium chloride are weighed out into a flask and 50 c c of a solution of caustic soda (containing 24 grams per litre) are added The solution is boiled until all the ammonia has been expelled, and the excess of caustic soda is then titrated with 20 6 c c of a solution of sulphuric acid containing 38 grams per litre Calculate the percentage of ammonium chloride in the original mixture of ammonium chloride and sodium chloride
(C H S C)

**14** State clearly what you mean by the expression " a normal solution " 20 grams of silver nitrate are dissolved in water and the solution diluted to 1 litre 50 c c of this solution are added to 25 c c of a solution of sodium sulphide, when silver sulphide is precipitated as follows

$$2AgNO_3 + Na_2S = Ag_2S + 2NaNO_3$$

The silver sulphide is filtered off and washed, and the excess of silver nitrate in the filtrate and washings is titrated with decinormal potassium thiocyanate solution, of which 12 7 c c are required Calculate the normality of the sodium sulphide solution (L H S C)

**15** Describe exactly how you would prepare and standardise a solution of an oxidising agent and explain how, having established the normality of such a solution, you could make use of it to standardise (*a*) a thiosulphate solution, (*b*) a solution of a mineral acid (O S)

**16** (*a*) Equal volumes of a solution containing a compound of an element which can exist in different states of valency was found to reduce 10 c c of 0 09 N-iodine solution, 18 c c of 0 1 N-ferric sulphate solution, and 25 c c of 0 108 N-potassium permanganate solution respectively The last of these oxidises the element to the pentavalent state What do you deduce from these results ?

(*b*) A given volume of a solution of ferric sulphate when reduced by zinc required 30 c c of $N/10$ permanganate for titration When the same volume of the same solution of ferric sulphate was reduced by another metal 45 c c of $N/10$ permanganate were required What can you say about this metal ? (O & C H S C)

**17** Describe the preparation of (*a*) ferrous ammonium sulphate, (*b*) potassium permanganate, (*c*) potassium dichromate Give an account of the chief uses of these substances in volumetric analysis What weight of each must be taken per litre to give decinormal solutions ? (C W B H S C)

**18** Supposing that it was desired to analyse volumetrically a solution containing ferric chloride and hydrochloric acid, describe fully the methods you would adopt, including the preparation and standardisation of the necessary stock solutions (C W B H S C)

**19.** Describe briefly a volumetric method for the estimation of iron in a ferric salt

3 476 grams of potassium permanganate are dissolved in water and the solution made up to 1 litre 5 88 grams of an unknown salt containing ferrous iron are weighed out, dissolved in water, and the solution made up to 100 c c It is found that 20 c c of the salt solution decolorises 27 25 c c of the permanganate solution What was the percentage of ferrous iron in the salt ? (C W B H S C)

**20** How would you prepare a crystalline specimen of potassium permanganate from manganese dioxide ?

Manganese can be estimated in acid solution by oxidising it to permanganic acid, using sodium bismuthate The excess of bismuthate is then removed by filtration A known volume of ferrous sulphate solution is added in excess, and this excess is back-titrated with standard potassium permanganate

The following results are from a laboratory notebook

| | |
|---|---|
| Weight of manganese salt | = 0 1 gram |
| Volume of arbitrary ferrous solution | = 50 0 c c |
| Volume of potassium permanganate | = 21 0 c c |
| Weight of potassium permanganate per litre | = 3 00 grams |
| Volume of permanganate equivalent to 20 c c of arbitrary ferrous solution | = 14 55 c c |

What was the percentage of manganese in the salt ? (C H S C)

**21** What methods can you suggest by which the weight of available oxygen in one gram of potassium permanganate (in acid solution) could be determined without using chemical formulae or atomic weights ?

Give experimental details of the method you would prefer (C S)

**22** Describe the preparation of accurately decinormal solutions of (*a*) iodine, (*b*) sodium hydroxide, (*c*) potassium quadroxalate ? For what purposes are the above solutions used ?

**23** How would you estimate volumetrically, (*a*) the strength of a solution or potassium cyanide, (*b*) potassium iodide in presence of potassium chloride, (*c*) the percentage of iron in a ferrous solution containing oxalic acid ? (C S)

**24** How would you analyse quantitatively solutions containing (*a*) ferrous iron and oxalic acid, (*b*) sodium chloride and potassium bromide, (*c*) sodium chloride and sodium hypochlorite ? (C S)

**25** (*a*) 25 c c portions of a solution containing 7 3 grams per litre of potassium quadroxalate, $KHC_2O_4$ $H_2C_2O_4$ $2H_2O$, were titrated under the usual experimental conditions with (i) decinormal sodium hydroxide, (ii) decinormal permanganate What volumes of these standard solutions were required ?

(*b*) Metallic tin in presence of hydrochloric acid is oxidised by potassium dichromate solution to stannic chloride What volume of N/10 dichromate would be required by 0 40 gram of tin ? (O & C H S C)

**26** How would you show that chloroform contains chlorine, that cane-sugar contains hydrogen and that acetamide contains nitrogen ? (O S)

**27** How can the elements nitrogen, sulphur, and iodine be detected in organic compounds ? Describe the quantitative determination of nitrogen (C W B H S C)

**28** Give an account of the reactions of sulphuric acid with organic compounds (O H S C)

**29** Discuss the different types of reaction that occur between organic substances and nitric acid (O H S C)

## CHAPTER XXXIII

**1** What are the laws deduced from the behaviour of gases under varying conditions of temperature and pressure ? How is this behaviour to be explained ? (Sheffield Inter)

**2** State Charles's law Describe an instrument that employs this principle to measure temperature and explain how it is used

Chlorine for sterilising drinking water is supplied under pressure in steel cylinders A medical text-book gives the pressure in such cylinders as 54 lb per square inch at 32° F and 216 lb per square inch at 122° F If this be so, does chlorine behave as a perfect gas ? (Manchester Inter)

**3** In what manner are the specific heats of gases affected according as the experiments are carried out at constant pressure or at constant volume ? How is the ratio of the two specific heats connected with the atomicity of a gas ? (C S)

**4** How may the states of matter be classified ? Illustrate your answer by reference to sulphur and water (C S)

**5** What is Graham's law of diffusion ? Show how advantage is taken of this law in the determination of the relative densities of gases

The speeds of diffusion of carbon dioxide and ozone were found by Soret to be as 0 29 is to 0 271 The relative density of carbon dioxide is 22 when $H_2 = 1$ What is the relative density of ozone ? (Bombay Inter)

**6** " The molecular weight of a substance is numerically equal to the weight in grams of it which occupies in the state of vapour 22 4 litres at 0° and 760 mm "

Give the experimental facts and reasoning on which this statement is based (O & C H S C)

**7.** Calculate the average velocity and kinetic energy of a molecule of carbon dioxide at 0° C and 1000° C, given that $R = 0\ 0821$ litre-atmosphere, and Avogadro's number, $N = 0\ 606 \times 10^{24}$

**8.** The equation $pV=RT$ represents the behaviour of a perfect gas Give some account of the deviations from this equation which are observed experimentally How are these deviations accounted for by van der Waals' equation ? (C S)

**9** Oxygen, under pressures not exceeding a tenth of an atmosphere, and at ordinary temperatures, behaves as a perfect gas Explain fully what you understand by this statement (O S)

**10.** What is meant by the expression " a perfect gas " ? Explain, in this connexion, the following statements

(*a*) The pressure exerted by a gas at constant volume varies directly as its absolute temperature

(*b*) For the gram-molecular weight, $PV=RT$

(*c*) The value of $R$ in this expression is approximately 2 cal per ° C (Oxford Prelim )

**11** Explain what is meant by (*a*) molecular weight, and (*b*) vapour density What is the relation between them ?

Describe fully *one* method for the determination of the vapour density of a volatile liquid (J M B H S C)

**12** Describe, with an explanatory sketch of the apparatus, a method for determining the molecular weight of a volatile substance

0 175 gram of a volatile substance displaced 19 c c of air collected over water at 15° C and 740 mm pressure What is its molecular weight ? [Pressure of aqueous vapour at 15° C = 12 7 mm ] (C H S C)

**13** What methods are available for the determination of vapour densities ? Describe carefully how you would determine the density of a substance like ether by the aid of one of them Of what value or importance is a knowledge of the vapour density of such a substance ? (Sheffield Inter )

**14** What do you understand by the term " specific heat " ? What deductions can be drawn from the values of the specific heats of (*a*) metals, (*b*) gases ? (C S)

## CHAPTER XXXIV

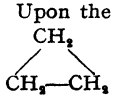
**1.** What do you understand by " the critical temperature " of a gas ? (C S)

**2.** Describe qualitatively the changes in volume which would be observed if the pressure on a given mass of carbon dioxide were gradually increased from 1 to 1000 atmospheres at each of the following temperatures 25°, 32°, 40°, 50°, 100° C The critical temperature and pressure of carbon dioxide are 31° C and 73 atmospheres (Sheffield, B Sc )

**3.** Discuss the deviations gases show from simple gas laws Explain how this behaviour is useful in the method introduced by Linde for liquefying gases (Bombay, B A )

**4** What do you understand by the terms " additive " and " non-additive " physical properties, when applied to atoms (or groups of atoms) in chemical combination ?

" Molecular volume," measured under suitable conditions, may be assumed to be an additive property The following are the " molecular volumes " of four hydrocarbons $CH_4$ 73, $C_2H_6$ 112, $C_3H_8$ 151, $C_3H_4$ 101

A hydrocarbon, the empirical formula of which is $C_3H_6$, is found to have a " molecular volume " of 140 Upon the basis of the above facts, which of the formulae $CH_3.CH=CH_2$ or  do you consider better represents the molecule ? (C S)

## CHAPTER XXXV

**1.** What do you understand by " a crystal " ? Indicate briefly some of the directions in which the study of crystals has been of use to chemistry (O H S.C )

**2.** What is a crystal? Give a short account of the properties characteristic of the crystalline state, mentioning any observations about crystalline form that have been of theoretical importance in chemistry Why is crystallisation a good method of purifying many substances? (O & C H S C)

**3** What evidence is there for the occurrence of diffusion in solids? In terms of the kinetic theory describe how diffusion may occur in (*a*) gases, (*b*) liquids, (*c*) solids

## CHAPTER XXXVI

**1** Henry's law says that "the solubility of a gas is proportional to the pressure" It also states that "the volume of a gas dissolved is independent of the pressure" Explain this paradox (Bombay, Inter)

**2.** How would you determine as accurately as possible the amount of carbon dioxide that dissolves when a current of the gas is bubbled through water at room temperature Give full experimental details

What grounds have we for thinking that combination takes place between carbon dioxide and water? (O H S C)

**3.** Enunciate and explain Dalton's *law of partial pressures* A certain weight of a mixture containing sodium carbonate and sodium formate in the proportion of one to three was treated with sulphuric acid, and the mixture of gases evolved was collected over water at 10° C and 750 mm of mercury Calculate the partial pressures of the constituents of the gaseous mixture, assuming the gases are insoluble in water Tension of aqueous vapour at 10° C = 9 2 mm of mercury (J M B H S C)

**4** State Henry's law of solubility of gases in liquids What explanation is offered for the fact that the law is not obeyed for solutions of ammonia, carbon dioxide, and chlorine in water?

Devise an experiment for the determination of the solubility of oxygen in water (C W B H S C)

**5** How is the solubility of a gas in a liquid affected by (*a*) temperature, (*b*) pressure?

How would you determine the solubility of (*a*) carbon dioxide, (*b*) nitrogen, in water? (O & C H S C)

**6** How may the solubility of a gas in a liquid be determined?

What is the absorption coefficient and how may it be modified when (*a*) mixed gases, (*b*) solutions instead of pure liquids are employed?

The concentrations of chlorine gas $C_1$ in millimols per litre over a carbon tetrachloride solution of concentrations $C_2$ at 0° C are as follows

| | | | | |
|---|---|---|---|---|
| $C_1$ - | - 0 0554 | 0 0889 | 0 1341 | 0 1760 |
| $C_2$ - | - 4 454 | 7 490 | 11 035 | 15 200 |

What conclusions can be drawn as to the state of the chlorine in the carbon tetrachloride? (C S)

**7** Describe and explain the operation known as distillation in steam When aniline (mol -wt 93) is steam-distilled, the distillate is found to contain 26 5% by weight of aniline What is the approximate vapour pressure of aniline at the temperature of the distillation? (O & C H S C)

**8** Discuss very briefly and with the aid of diagrams what takes place when a mixture of two liquids is distilled

Naphthalene distils in steam at 98 3° under a pressure of 753 mm , the vapour-pressure of water at this temperature is 715 mm Calculate the proportion of naphthalene in the distillate (C H S C)

**9.** Describe the behaviour of two non-miscible liquids on distillation A mixture of ethylene dibromide and water boils at ordinary pressure at 91°, the vapour-pressure of water at this temperature being 545 mm What will be the percentage composition of the distillate? (C S)

**10** State the phase rule and explain the terms involved Apply the rule to explain the fact that the dissociation of calcium carbonate depends upon the temperature only (Bombay, B A)

**11** How would you distinguish between (*a*) a pure liquid and a constant boiling mixture, (*b*) a pure and an impure specimen of a crystalline solid ? Illustrate your answer by examples (C H S C)

**12.** Propyl alcohol and water are miscible in all proportions The vapour-pressure curve of mixtures of these substances passes through a maximum corresponding to a mixture containing 80% by weight of propyl alcohol The corresponding curve for formic acid-water mixtures passes through a minimum at the mixture containing 73% of formic acid Compare the behaviour on distillation of aqueous solutions containing 50% of formic acid and propyl alcohol respectively (Sheffield, B Sc)

**13** Describe in some detail how you would determine the solubility at the room temperature of crystalline sodium carbonate, $Na_2CO_3$, $10H_2O$
What do you consider is the chief source of error in the determination, and how would you avoid it as far as possible ? (O H S C)

**14** What do you understand by the terms (*a*) saturated solution, (*b*) supersaturated solution ? How would you prepare a saturated solution of copper sulphate at room temperature in water and prove that it was saturated ? (O & C H S C)

**15** What experiments would you make to determine the solubility of potassium chloride in water at different temperatures ?
The solubility of potassium chloride at 15° C and 100° C is 32 4 and 56 7 grams per 100 grams of water, the solubility of potassium iodide is 140 and 208 at the same temperatures and in the same units Explain, with the aid of a diagram, how a knowledge of these facts assists in the purification of potassium chloride from small quantities of potassium iodide (C H S C)

## CHAPTER XXXVII

**1** Write a short essay on the mechanism and measurement of osmotic pressure (Sheffield, B Sc)

**2.** Write a brief account of the principal phenomena of osmotic pressure Calculate the osmotic pressure of a 5% solution of cane-sugar at 15° C (H = 1, C = 12, O = 16) (C S)

**3.** In what ways is the behaviour of a substance in the dissolved state similar to its behaviour in the gaseous state ?
Calculate the osmotic pressure at 25° C of a solution containing 5 grams of urea in a litre of solution The molecular weight of urea is 60 (Madras, B A)

**4** Write a brief account of some of the phenomena of osmotic pressure Calculate the osmotic pressure of a 10% solution of cane-sugar $C_{12}H_{22}O_{11}$ at 15° C (H = 1, C = 12, O = 16) (C H S C)

**5.** Give an account of the phenomena associated with semi-permeable membranes in connection with (*a*) gases, (*b*) solutions (Manchester, B Sc)

**6** What do you understand by the osmotic pressure of a solution ?
A certain weight of a substance when in the gaseous state occupied a volume of 10 litres at 97° C and 740 mm pressure The same weight of the substance when dissolved in 4 5 litres of water at 24° C gave an osmotic pressure of 770 mm of mercury What explanation can you give of these facts ? (O H S C)

**7.** What do you understand by the term "isotonic solutions" State the methods (direct and indirect) for comparing the osmotic pressure of solutions and describe in detail any one method (Manchester, B Sc)

**8.** Describe a method for the direct determination of the osmotic pressure of a solution How does the osmotic pressure vary with the temperature and with

the concentration of the solute? What conclusions can be drawn from the results for dilute solutions? (C W B H S C)

**9** Discuss the influence of van't Hoff's work on modern developments in chemistry (C H S C)

**10** What is meant by "osmotic pressure" and how may it be measured (*a*) directly, and (*b*) indirectly?

Calculate the osmotic pressure of a solution of cane-sugar ($C_{12}H_{22}O_{11}$) containing 150 grams per litre, at 0° C (J M B H S C)

**11** Explain carefully what is implied by the statement that substances in dilute solutions "obey the gas laws"? (O S)

## CHAPTER XXXVIII

**1** Show how the lowering of the vapour-pressure caused by dissolving a non-volatile solute in a solvent is related to the osmotic pressure of the solution

**2** Show theoretically that solutions of different substances in the same solvent must have identical vapour-pressures if their osmotic pressures possess the same value

At 20° C the vapour-pressure of ether is 442 mm of mercury When 6 1 grams of a substance was dissolved in 50 grams of ether, the vapour-pressure fell to 410 mm What is the molecular weight of this substance? (C S)

**3** How may the molecular weight of a substance be determined by the method of lowering of the vapour-pressure?

Calculate the molecular weight of a substance, a solution of which containing 7 08 grams, dissolved in 100 grams of water, has a vapour-pressure at 0° C of 4 557 mm, that of water being 4 620 mm What would be the osmotic pressure of the solution? (C S)

**4.** What is Raoult's law? Show that it forms the basis of methods for finding the molecular weights of substances in dilute solution Why must the solution be dilute?

0 511 gram of a substance dissolved in 40 grams of water causes an elevation of the boiling-point equal to 0 073° Calculate the molecular weight of the substance The molecular elevation constant for water (100 grams) is 5 2 How is the latter determined? (C W B H S C)

**5** Dry air was drawn in succession through a series of bulbs containing 4 257 grams of a substance *X* in 52 68 grams of ethyl alcohol and then through a similar series of bulbs containing pure alcohol The indrawn air and the two sets of bulbs were at the same constant temperature The loss of weight in the first series of bulbs was 1 292 grams and in the second series 0 0313 gram Calculate the molecular weight of *X* (C S)

**6** How may the molecular weight of a substance in solution be determined by the elevation of the boiling-point?

The boiling-point constant for water is 5 2 * A normal solution of a monobasic acid was found to give an elevation of 0 910° Calculate the degree of dissociation of the acid What would be its degree of dissociation in a hundredth normal solution? (C S)

**7** How may the molecular weight of a substance be determined by the method of elevation of the boiling-point?

The boiling-point of pure acetone is 56 38° at normal barometric pressure A solution of 0 707 gram of a compound in 10 grams of acetone boiled at 56 88° What is the molecular weight of the compound? (The molecular elevation constant for acetone is 16 7 *) (C S)

**8** Explain how the molecular weight of a substance may be determined from observations of the depression of the freezing-point If one gram of a substance

* For 100 grams of solvent

is dissolved in 15 grams of water the freezing-point is lowered 0 37° C What is the molecular weight of the dissolved substance? The "constant" for water is 19 * (C H S C)

**9** When 0 5 gram of sodium chloride was dissolved in 50 grams of water the freezing-point of the water was depressed 0 615° C The molecular depression for water is 18 5° * Calculate the apparent molecular weight of the dissolved salt and explain the result obtained

What other solvents are usually employed in determining molecular weights by this method? (L H S C)

**10** Describe the freezing-point method for determining molecular weights A solution of 34 2 grams of cane-sugar in 100 grams of water froze at −1 9°, a solution of 7 5 grams of potassium chloride in 100 grams of water froze at −3 36°, and a solution of 9 8 grams of an unknown substance in 100 grams of water froze at −3 82° The constant for water is 18 9° *

What conclusions do you draw from these data concerning the molecular condition of the first two substances in aqueous solution, and what is the molecular weight of the unknown substance (Bombay, B A)

**11** Describe shortly the methods available for the determination of the molecular weights of substances in solution Sketch and describe the apparatus which you consider gives the most accurate results, give reasons for your choice (C H S C)

**12** One per cent solutions of glucose ($C_6H_{12}O_6$), potassium chloride, and barium chloride freeze respectively at −0 103° C, −0 497° C, and −0 262° C How have these facts been explained? Say, giving reasons, whether you are satisfied with the explanation (O H S C)

**13** If you had discovered a new, anhydrous, non-volatile organic acid, how would you determine its molecular weight?

A certain organic acid was known to contain one molecule of water of crystallisation and to be tri-basic On heating 1 500 grams of the anhydrous calcium salt of this acid, 0 506 gram of calcium oxide was obtained What was the molecular weight of the original acid? (C H S C)

**14.** Write a brief essay on the properties of dilute solutions (C S)

## CHAPTER XXXIX

**1** Write notes on the following (*a*) degree of freedom, (*b*) phase, (*c*) eutectic point, (*d*) transition temperature

How would you measure the transition temperature for the two ordinary crystalline forms of sulphur?

**2** Write a short essay on *either* the phase rule or the ionic theory (C S)

**3.** Illustrate and explain the meaning of the following terms efflorescence, transition point, phase, fractionation (C S)

**4** Under what conditions is it possible to obtain from an aqueous solution of sodium sulphate (*a*) ice, (*b*) hydrated sodium sulphate, (*c*) anhydrous sodium sulphate? Give an explanation of the procedure necessary in each case (O & C H S C)

**5** Phenol and water are said to combine to form a hydrate How would you attempt to discover whether this is so, and determine its composition? (O S)

**6.** What is meant by the terms saturated and supersaturated as applied to solutions? Give an outline of any method of determining (and expressing) the solubility of a salt in water

The temperature-solubility relations of many salts are represented by discontinuous curves Sketch the simpler *types* of curve that are encountered and explain briefly their significance (C W B H S.C)

* For 100 grams of solvent

**7** Certain salts crystallise from aqueous solution in different forms under varying conditions of temperature Account for this behaviour

The solubility of a compound, $A$, at various temperatures is given below

| Grams of $A$ in 100 grams of solution | Temperature °C |
|---|---|
| 77 1 | − 15 |
| 78 5 | − 10 |
| 79 1 | − 8 |
| 79 5 | 0 |
| 80 7 | + 15 |
| 82 5 | + 25 |
| 84 1 | + 30 |
| 85 4 | + 35 |
| 85 5 | + 40 |
| 86 1 | + 68 |
| 86 6 | + 80 |
| 87 1 | + 100 |

At temperatures below − 8° C the saturated solution is in equilibrium with the hydrate $A$, $3H_2O$, above 32° C it is in equilibrium with the anhydrous salt Use the given data to determine the probable formula of the hydrate separating from a saturated solution between 32° C and − 8° C The molecular weight of $A$ is 205 (C H S C)

**8** Alloys of magnesium and zinc whose compositions are expressed as grams of magnesium per 100 grams of the mixture, freeze at the following temperatures

| Per cent Mg | Freezing-point | Per cent Mg | Freezing-point |
|---|---|---|---|
| 0 | 419° | 45 0 | 385° |
| 3 2 | 368° | 49 0 | 347° |
| 10 0 | 535° | 50 0 | 360° |
| 15 6 | 595° | 60 0 | 450° |
| 20 0 | 575° | 80 0 | 560° |
| 40 0 | 450° | 100 0 | 651° |

Plot these figures on graph paper and interpret the diagram (C W B H S C)

**9** Sulphuric acid is said to form solid hydrates of definite composition How would you proceed to test this statement and to ascertain the composition of the hydrates ? (L H S C)

**10** Show that (*a*) of two allotropic forms of a substance the one which has the lower vapour-pressure is the more stable, (*b*) two liquid phases in equilibrium with each other have the same vapour-pressure, (*c*) the vapour-pressure of a solution of a non-volatile substance cannot be greater than that of the pure solvent (O S)

## CHAPTER XL

**1** State and explain the law of Hess Indicate its use in determining the heat of formation of an organic compound

The heat of formation of water is 68,360 cal , and of carbon dioxide is 96,960 cal , both at 17° and constant pressure The heat of combustion of methane at 17° and constant pressure is 211,930 cal Calculate the heat of formation of methane at 17° C (*a*) at constant pressure, (*b*) at constant volume (Bombay, B A)

**2** Define the terms endothermic and exothermic as applied to compounds Illustrate your answer by reference to compounds of nitrogen

The heat of combustion of hydrogen is 65,000 cal per gram mol , of carbon 97,000 cal per gram atom , if the heat of combustion of ethylene is 340,000 cal per gram mol , what is its heat of formation ? (C S)

**3** How can it be determined experimentally whether heat is given out or absorbed in the synthesis of (*a*) ammonia, (*b*) nitric oxide ? What is the technical importance of these results ? (C S)

**4** Explain the importance of a knowledge of (*a*) heats of formation, (*b*) heats of combustion Suggest and explain a method by which the heat of formation of sodium hydroxide could be determined (C S)

**5.** From the following data, calculate the heat of formation of anhydrous aluminium chloride

$$2Al + 6HCl\ aq = Al_2Cl_6\ aq + 3H_2 + 239{,}760\ cal$$
$$H_2 + Cl_2 = 2HCl + 44{,}000\ cal$$
$$HCl + Aq = HCl\ aq + 17{,}315\ cal$$
$$Al_2Cl_6 + Aq = Al_2Cl_6\ Aq + 153{,}690\ cal$$

(Sheffield, Inter)

**6.** How is the heat of formation of a compound usually determined ? Given that

$$K + aq = KOH\ aq + \tfrac{1}{2}H_2 + 48{\cdot}1K,$$
$$H_2 + \tfrac{1}{2}O_2 = H_2O + 68{\cdot}4K,$$
$$KOH + aq = KOH\ aq + 13{\cdot}3K,$$

find the heat of formation of KOH from its elements (Bombay, B A)

**7.** When carbon monoxide, hydrogen and methyl alcohol are burnt completely in oxygen in closed vessels, the heats evolved per gram molecule are 67,700, 68,400 and 170,600 calories respectively Calculate the heat evolved in the reaction

$$CO + 2H_2 = CH_3OH$$

If the reaction is carried out at atmospheric pressure at 300° C , what work is done by the atmosphere on the system per gram molecule of methyl alcohol produced ? What effect will this have on the heat of reaction according as it occurs at constant volume or constant pressure ? (The gas constant $R$ is 2 calories per degree) (C S)

**8** From the heats of formation of carbon dioxide from carbon and from carbon monoxide .

$$C + O_2 = CO_2 + 97{,}650\ cal.,$$
$$CO + \tfrac{1}{2}O_2 = CO_2 + 68{,}000\ cal\ ,$$

calculate the heat of formation of carbon monoxide Does the result accord with your expectation ? How do you account for it ? (Sheffield, Inter)

**9.** What is meant by the heat of combustion and how is it determined ? 0 702 gram of benzoic acid, the heat of combustion of which is 6234 cal per gram, when burnt in compressed oxygen in a calorimeter, raised the temperature 1 263° 0 621 gram of fuel oil when similarly treated raised the temperature 1 682° What is the heat of combustion of the latter substance ? (Madras, B A)

**10.** State Hess's law of thermoneutrality Calculate the heat of formation of formic acid from the following data

Heat of combustion of carbon $(C,O_2)$ = 96,960 cal
,, ,, ,, ,, hydrogen $(H_2,O)$ = 68,360 ,,
,, ,, ,, ,, formic acid $(CH_2O_2,O)$ = 65,900 ,, (Punjab, B Sc)

**11** How would you determine approximately the heat of neutralisation of an acid ? The heats of neutralisation of one gram molecule of sodium hydroxide in aqueous solution by various acids are as follows HF, 16,300 cal , HCl, 13,700 cal , HBr, 13,700 cal , $HNO_3$, 13,700 cal , $CH_3COOH$, 13,200 cal , HCN, 2800 cal Discuss and explain these results (O & C H S C)

**12.** Define molecular heat of neutralisation When a dilute solution of a strong acid is neutralised by a solution of a strong base, the heat of neutralisation is found to be as nearly as possible the same in all cases How do you account for this ?

How would you proceed in the laboratory to measure the heat of neutralisation of an acid ? (Madras, B A)

## CHAPTER XLI

1 State the law of mass action
When 1 mol of ethyl alcohol reacts with 1 mol of acetic acid until an equilibrium is obtained, then there is present in the solution 0 333 mol each of alcohol and acid, and 0 666 mol each of ester and water Determine the amount of ester present at equilibrium when (*a*) 3 mols of alcohol react with 1 mol of acid, (*b*) 1 mol of alcohol reacts with 1 mol of acid in the presence of 1 mol of water (C H S C)

2 What is meant by " the Law of Mass Action " ?
Illustrate the law by a concise description of *three* suitable reactions, and point out the factors affecting each reaction (J M B H S C)

3 Explain the meaning of the term *chemical equilibrium* as applied to the state of things existing in the vapour of ammonium chloride at a given temperature Point out clearly what would be the effect of (*a*) compressing the vapour, (*b*) vaporising the ammonium chloride in an atmosphere of hydrochloric acid gas (O H S C)

4 Distinguish between decomposition and dissociation, giving examples of each The vapour-density of phosphorus pentachloride was determined at 250° and was found to be 57 92 Calculate its degree of dissociation (P = 31, Cl = 35 5) (C S)

5 State Le Chatelier's law Discuss this law with respect to *either* (*a*) the union of nitrogen and hydrogen, or (*b*) the union of nitrogen and oxygen (C S)

6 Reversible reactions between gases may be divided into two types according as the number of molecules is unaltered by dissociation or increased Taking the reaction $2HI \rightleftharpoons I_2 + H_2$ as an example of the former type and the reaction $PCl_5 \rightleftharpoons PCl_3 + Cl_2$ as an example of the latter, point out how these two types differ as regards the effect of physical conditions on the equilibrium (C S)

7 In what respects does thermal dissociation (such as in the dissociation of iodine vapour $I_2 \rightleftharpoons 2I$) resemble and in what respects does it differ from the ionic dissociation of an electrolyte ?
One litre of iodine vapour at 1092° C and 760 mm was found to weigh 2 25 grams Calculate the proportion of monatomic molecules (I = 127) (O H S C)

8 Discuss the behaviour of nitrogen peroxide when heated from − 20° to 650° C The density of the gaseous peroxide at 80° is 25 6 ($H_2 = 1$), what inferences can you draw from this fact ? (O H S C)

9 In a series of six experiments with hydrogen iodide 0 96 gram of the latter in each experiment was entirely converted into vapour at the given temperatures and constant pressure and then quickly cooled The amount of iodine liberated in each experiment was determined by titration with 0 1N sodium thiosulphate, and the volumes of the latter for corresponding temperatures were as follows

| 250° | 290° | 330° | 360° | 400° | 420° |
|---|---|---|---|---|---|
| 13 25 c.c | 12 4 c c | 12 0 c c | 12 9 c c | 14 6 c c | 15 7 c c |

Calculate the percentage of hydrogen iodide dissociated at each temperature and express your results in form of a graph What conclusions do you draw from the form of the curve (J M B H S C)

10. Write a short essay on chemical equilibrium with special reference to (*a*) the meaning of the term, (*b*) the factors which determine the conditions of equilibrium Give examples (J M B H S.C)

11 Give an account of the factors which are of essential importance in the reversible changes represented by

(*a*) $CaCO_3 \rightleftharpoons CaO + CO_2$,

(*b*) $SbCl_3 + H_2O \rightleftharpoons SbOCl + 2HCl$ (J M B H S C.)

**12** Explain and illustrate the terms "active mass," "degree of dissociation," "equilibrium constant"

When pure ammonia is maintained at 480° C and a pressure of 1 atmosphere, it dissociates to give a gas containing 0 20% of ammonia by volume Determine (*a*) the degree of dissociation, (*b*) the equilibrium constant at this temperature (in terms of partial pressures), (*c*) the composition at the same temperature, but under a pressure of 5 atmospheres (C S)

**13** One litre of hydrogen iodide was maintained at atmospheric pressure at 300° C for some time, and then suddenly chilled to room temperature The contents of the flask, after solution in water, were found to oxidise 37 5 c c of N/10 sodium thiosulphate A similar experiment was performed at 500° C, when 50 c c of N/10 sodium thiosulphate solution were oxidised

Calculate (*a*) the degree of dissociation of hydrogen iodide at 300° and at 500° C, (*b*) the vapour densities of the gas at these temperatures Comment on your results (C S)

**14** State exactly what you understand by the expression

$$FeCl_3 + 3NH_4CNS \rightleftharpoons Fe(CNS)_3 + 3NH_4Cl$$

What is the effect of adding to the system (*a*) ammonium thiocyanate, (*b*) ammonium chloride Give your reasons (L H S C)

**15** What do you understand by the term "equilibrium-constant?" How would you investigate experimentally the equilibrium between ferric sulphate and potassium iodide in dilute sulphuric acid solution? (O S)

**16** How would you attempt to make a quantitative investigation of the reaction,

$$Fe^{+++} + Ag \text{ metal} \rightleftharpoons Fe^{++} + Ag^{+},$$

in dilute sulphuric acid solution in order to show that (*a*) it is reversible, (*b*) the position of the equilibrium depends on the concentration of the reagents? (O S)

**17** The equilibrium-constant for the reaction between acetic acid and alcohol, forming ethyl acetate and water, at 25° C is 4 Explain precisely what is meant by this statement If 5 gram-molecules of acetic acid react with 1 gram-molecule of alcohol at 25° C as completely as possible, what will be the composition of the equilibrium mixture? (O S)

**18** State the laws governing the distribution of a substance between two non-miscible solvents

A substance is twice as soluble in ether as it is in water, the molecular weight being the same in both solvents Compare the quantities extracted from *v* c c of aqueous solution, (*a*) by *v* c c of ether in a single operation, (*b*) by two successive applications of *v*/2 c c of ether (C S)

**19** What do you understand by the term "partition coefficient"?

100 grams of water containing 10 grams of succinic acid are shaken with 100 grams of ether In another experiment a similar quantity of succinic acid solution is shaken in succession with 10 quantities each of 10 grams of ether If the partition ratio ether/water for succinic acid is 5 1, what would be the amount of acid removed by ether from the aqueous solution in each case?

If the partition ratio of ethyl acetate between water and benzene be determined with rising concentrations of ethyl acetate, a point is reached when the whole system becomes uniform in composition How do you account for this fact? (C S)

**20** What laws describe the distribution of a solute between two immiscible solvents?

0 5 gram of acetic acid when dissolved in 20 grams of benzene depresses the freezing-point by 1 04° C From these data make what deductions you can concerning the constitution of acetic acid dissolved in benzene Describe an experiment by which you would confirm the correctness of your deductions

[The cryoscopic constant for 100 grams of benzene is 50] (C S)

## CHAPTER XLII

**1** Write a short account of the law of mass action Describe any experiments you have performed or seen which show the influence of concentration on *either* reaction velocity *or* equilibrium (O S)

**2.** How can the order of a chemical reaction be determined ? What conclusions can safely be drawn from the ascertained order of a reaction as to its mechanism (Manchester, B Sc)

**3** What is meant by the " order of a reaction " Describe in detail a method of determining the order of a reaction The data for the conversion of a compound *A* into its isomeride *B* are as follows

| Time $t$ = | 0 | 1 | 2 | 3 | 4 | 6 | 8 |
|---|---|---|---|---|---|---|---|
| Amount of $A$ $(a-x)$ = | 49 3 | 35 6 | 25 75 | 18 5 | 13 8 | 7 3 | 4 8 |

Show that the reaction is of the first order and deduce the formula that you employ (Bombay, B A)

**4** On what factors does the velocity of chemical change depend ?
It was found that a solution of cane-sugar in water was hydrolysed to the extent of 25% in 1 hour Calculate the time taken for 50% of the sugar to be hydrolysed, assuming that the reaction is unimolecular (C S)

**5** At 21° the following figures were found for the decomposition of nitrous acid in aqueous solution

| Time (min) - - | 0 | 90 | 135 | 195 |
|---|---|---|---|---|
| gm $HNO_2$ in 100 c c | 0 1468 | 0 1282 | 0 1247 | 0 1175 |

Show that the reaction is unimolecular and calculate the velocity coefficient

**6** From the following data show that the decomposition of $H_2O_2$ in aqueous solution is a monomolecular reaction

| Time in minutes - - | 0 | 10 | 20 |
|---|---|---|---|
| $N$ - - - - - | 22 8 | 13 8 | 8 25 c c |

where $N$ is the number of c c of $KMnO_4$ required to decompose a definite volume of the $H_2O_2$ solution (Punjab, B Sc Hons)

**7** What is understood by the rate of a chemical reaction ?
Give an account of the experiments which should be performed to determine the rate of a reaction (C H S C)

**8** Iodine is slowly liberated when solutions of potassium iodide and potassium persulphate are mixed Describe carefully how you would carry out measurements of the rate of this chemical change, and how you would plot and calculate the results
What effects would you expect changes of temperature and of concentration to have on the rate ? (O S)

## CHAPTER XLIII

**1** What criteria are applicable to catalysis ? Give an account of the intermediate-compound theory of catalysis, illustrating your answer by reference to reactions to which it has been applied (Sheffield, B Sc )

**2.** Mention the chief theories which have been advanced to explain catalysis and describe one of them in detail (Sheffield, Inter )

**3.** Write a short essay on the nature and uses of catalytic reactions (O H S C )

**4** What do you understand by the terms " positive catalysis," " negative catalysis," " autocatalysis " Give examples of each

**5.** Explain the meaning of the term *catalysis*, and illustrate your answer with reference to some well-known examples (C H S C )

## CHAPTER XLIV

**1** State Faraday's laws of electrolysis
Describe what happens when aqueous solutions of sodium chloride and sodium bisulphate are electrolysed under varying conditions (C H S C )

**2** Explain what takes place when an electric current is passed between two plates of copper immersed in copper sulphate solution, and indicate carefully the difference between the way in which the current is conducted by the solution and by a metal What is the relation between the quantity of metal deposited and the current passed ? How may equivalent weights be determined by an application of this relation ? (Madras, B A )

**3** What are the principal characteristics of electrolytic conduction ? How far do you consider they are to be explained by the hypothesis of ionic dissociation ? (O S )

**4** What observations have led to the view that salts are ionised in solution ? What is meant by the degree of dissociation of a weak electrolyte, and how is it measured ?

**5** A 1% solution of glucose, $C_6H_{12}O_6$, in water has a freezing-point of $-0.103°$ C A 1% solution of sodium chloride freezes at $-0.604°$ C and a 1% solution of potassium iodide at $-0.213°$ C Explain what conclusions can be drawn from these data (C = 12, O = 16, Na = 23, K = 39, Cl = 35 5, I = 127 ) (O S )

**6** State Faraday's laws of electrolysis and show how they may be experimentally verified
Explain on the basis of the ionic hypothesis the reactions which take place during the electrolysis of (i) dilute sulphuric acid, (ii) a hot solution of sodium chloride, (iii) a solution of potassium iodide (J M B H S C )

**7** An electric current is passed between platinum plates through solutions of copper sulphate, silver nitrate and dilute sulphuric acid, the solutions being placed in series Explain what happens in each case If 0 105 gram of copper is deposited in the first cell, calculate (*a*) the weight of silver separated from the second solution, (*b*) the volume of hydrogen, measured at 15° C and 740 mm , which is liberated from the third solution H = 1, Cu = 63 5, Ag = 108 (J M B H S C )

**8** The molecular conductivity of a 5% solution of chromium trioxide is not increased by further dilution , its freezing-point is $-1.34°$ C What conclusions can you draw as to the condition in which the oxide exists in solution (*K* for water = 19) (Bombay, B A )

**9** The theory of electrolytic dissociation has been described as " the wild Arrhenic speculation " State three clear and precise reasons why you consider this just or unjust (O S )

**10** Give a brief account of the " theory of ionisation " of strong electrolytes and of the evidence on which it is based

**11.** The conductances of the hydrogen ion and of the acetate ion are 315 and 35 mhos respectively If the specific conductivity of $N/1000$ acetic acid is $41 \times 10^{-6}$ mhos, calculate the degree of dissociation of the acid at this dilution

**12.** Explain what is meant by the molecular conductivity of a solution of an electrolyte and the ionic transport ratio

During the electrolysis of a solution of silver nitrate it was found that, after 0 1259 gram of silver had been deposited at the cathode, the solution had altered in concentration On precipitating with sodium chloride the silver contained in 20 c c of the cathode solution the following data were obtained weight of silver chloride (before electrolysis) 1 746 grams, weight of silver chloride (after electrolysis) 1 677 grams Determine the transport ratio of the silver and nitrate ions [Ag = 108, Cl = 35 5 ] (C S)

**13.** What is meant by the term " transport number " ?

In the electrolysis of a solution of hydrochloric acid between cadmium electrodes the following results were obtained, gain in chlorine round the anode and loss in chlorine round the cathode 0 00665 gram, silver deposited in a voltameter in series with the cell 0 1190 gram Find the transport numbers of the hydrogen and chlorine ions [Cl = 35 5, Ag = 108 ] (C S)

## CHAPTER XLV

**1.** How may the strength of an acid be determined, (*a*) when it is strong, (*b*) when it is weak ?

An aqueous solution of an acid so weak as to be practically un-ionised in the given solution boiled at 100 4° C, and 25 c c of the solution required 38 5 c c of normal soda for neutralisation The " boiling point " constant for water is 5 20 Determine the basicity of the acid (C S)

**2** What is meant by (*a*) the basicity, (*b*) the strength, and (*c*) the heat of neutralisation of an acid ?

Explain carefully (i) why the heat of neutralisation of strong acids is approximately constant, and (ii) how you could compare the strengths of acetic and sulphuric acids (J M B H C S)

**3** Give an account of the general properties of polybasic acids, illustrating your answer by a few examples How would you determine the basicity of a newly discovered acid ? (O S)

**4** What information with regard to the basicity of acids is obtainable from (*a*) their salts and esters, (*b*) their heats of neutralisation ? From these, or other considerations, discuss the basicity of weak acids such as hydrosulphuric and boric acids (C S)

**5** How can the relative strengths of acids and bases be determined ? Solutions of sodium carbonate and borax are alkaline to litmus whilst solutions of aluminium sulphate and zinc chloride are acid Give reasons for this behaviour and discuss the relative strengths of the acids and bases which are present in these salts (L H S C)

**6.** Explain what you understand by the terms *acid, base, salt* What evidence can you supply to show that solutions of acids contain hydrogen ions ? (C S)

**7.** If you were given a sample of a strong acid of unknown molecular weight, describe, with all essential details, how you would determine its basicity (C S)

**8.** An acid is a substance which in aqueous solution changes the colour of litmus from blue to red a base is a substance which effects the converse change

Criticise these statements as *definitions* of an acid and a base respectively (C S.)

**9** The molecular conductivity of acetic acid at infinite dilution is found to be 387 reciprocal ohms At the same temperature but at a dilution of 1 gm -mol in 1000 litres it is 55 reciprocal ohms What is the percentage dissociation of 0 1 *N* acetic acid? (C S)

**10.** Explain what is meant by the dissociation-constant of an acid and point out how it can be determined in the case of acetic acid

The electrolytic dissociation-constants of formic and acetic acids are $21 4 \times 10^{-5}$ and $1 8 \times 10^{-5}$ respectively What is the relative avidity (strength) of the two acids? (C S)

**11.** A weak monobasic acid is ionised to the extent of 2 per cent in decinormal solution Calculate approximately the degree of ionisation of this acid in *N*/50 solution at the same temperature (O & C H S C)

**12** The specific conductivity of a solution of acetic acid containing 1 gram equivalent in 13 6 litres is $44 8 \times 10^{-5}$ ohm$^{-1}$ Calculate the equivalent conductivity of a centinormal solution of acetic acid (C S)

**13** Explain what is meant by hydrolysis The following salts undergo hydrolysis in aqueous solution ferric chloride, potassium cyanide, sodium carbonate, and cupric sulphate Describe exactly how the existence of this phenomenon may be demonstrated in each case (C H S C)

**14.** Write short notes on three of the following (i) ionisation and electrolytes, (ii) solubility product, (iii) hydrolysis of salts, (iv) the neutralisation of an acid by a base Illustrate by examples (J M B H S C)

**15** Why is a solution of sodium carbonate alkaline? Why must phenol phthalein not be used as an indicator for titrations with sodium carbonate? (O S)

**16** What do you understand by the term hydrolysis? Exemplify your answer by reference to potassium cyanide and ammonium chloride Describe two methods by which the degree of hydrolysis of a salt in solution may be determined (C S)

**17.** What is meant by the terms "$p$H" and "buffer solution"?

Calculate the $p$H of (*a*) *N*/1000 hydrochloric acid, (*b*) *N*/1000 sodium hydroxide, assuming these solutions to be completely ionised ($K_w = 1 0 \times 10^{-14}$)

What are the hydrogen ion concentrations of solutions which have $p$H values of 2 25, 4 7 and 5 6 respectively? (C S)

**18** Calculate (*a*) the concentration of hydrogen ions and (*b*) the $p$H of solutions of *N*/10 and *N*/100 acetic acid on the assumption that the dissociation constant of the acid is $1 8 \times 10^{-5}$ for the given temperature (*c*) What would be the $p$H of the solution obtained by adding 25 c c of *N*/10 NaOH to 50 c c *N*/10 acetic acid, assuming that the sodium acetate is completely dissociated (J M B H S C)

**19** Write a brief essay on the theory and use of indicators in volumetric analysis

**20** What do you understand by the term "solubility product"? Discuss two examples of the application of the conception of solubility product Indicate briefly how you would determine the solubility product for lead chloride (O S)

**21.** How may the term solubility product be defined? Give three examples of the utility of this concept in qualitative analysis The solubility of barium sulphate is $2{\cdot}3 \times 10^{-4}$ grams in 100 c c of water What is the percentage error involved in washing a precipitate of 0 200 gram of barium sulphate with (*a*) a litre of water, (*b*) a litre of *N*/100 sulphuric acid? Ba = 137, S = 32, O = 16 (C S)

**22** An aqueous solution of ammonia is capable of precipitating certain metals as sparingly soluble hydroxides, but in the presence of ammonium chloride this precipitation is often prevented What explanation can be given of this phenomenon ? (C S)

**23.** Explain the following facts

(*a*) When hydrochloric acid is led into a saturated solution of sodium chloride, crystals of the salt are precipitated

(*b*) Many normal salts such as sodium carbonate and ferric chloride are alkaline or acid in solution

(*c*) Zinc sulphate is precipitated by hydrogen sulphide from a solution of zinc acetate, but not from a solution of zinc chloride (O H S C)

**24** Explain how the solubility of a sparingly soluble electrolyte may be increased or diminished by the presence of small quantities of other substances

One litre of a saturated solution of calcium sulphate at 18° contains 0 015 mol of the salt Calculate how much calcium sulphate should be precipitated by the addition of 0 025 mol of potassium sulphate to one litre of this saturated solution, both salts being regarded as practically completely ionised (C S)

**25** Explain the meaning of the term " solubility product," and give *two* examples of its importance in analysis

At 100° C , 100 c c of water dissolve 0 120 gram of silver cyanate (AgCNO) How much silver cyanate will be dissolved at this temperature by 100 c c of water containing 1 00 gram of silver nitrate ?

The silver salts may be regarded as completely ionised (C W B H S C)

## CHAPTER XLVI

**1** What are crystalloids and colloids ? Give instances Discuss some of the most important properties of a colloid Describe carefully a process by which a colloid can be obtained in a pure state (Bombay, B A)

**2.** Give two methods by which the sign of the electrical charge on a colloidal particle can be determined Discuss the part played by the charge in controlling the stability of the solution

**3** Give a brief account of *either* (*a*) the preparation and properties of colloidal solutions, *or* (*b*) the supposed analogy between gases and dilute solutions (J M B H S C)

**4** Gelatin, silicic acid, arsenious sulphide and ferric hydroxide can all be obtained in a colloidal state Which of these would you class as lyophobic and which as lyophilic colloids ? State the properties of the colloidal systems on which you base your classification

**5** Write a brief account of the preparation and properties of colloidal solutions In what respects do the physical properties of a colloidal solution of silicic acid differ from those of an aqueous solution of sodium chloride ? (J M B H S C)

**6** What is a colloidal solution ? Distinguish between colloidal solution and true solution

Describe how colloidal solutions of (*a*) any metal, (*b*) silica, may be prepared, and give a brief account of the properties of these solutions (C W B H S C)

**7** Give a short account of (*a*) dialysis, (*b*) gaseous diffusion Point out the analogy between these phenomena. (Camb 1st M B)

**8** How would you prepare colloidal solutions of (*a*) arsenic trisulphide, (*b*) platinum ? What are the distinctive properties of colloidal solutions ? (Camb 1st M B)

## Revision Problems on Physical Chemistry

**1.** 0 175 gm of a volatile substance displaced 19 0 c c of air collected over water at 15° and 740 mm pressure Calculate the molecular weight Vapour pressure of water at 15° is 12 7 mm (C H S C)

**2** A globe of 300 c c capacity was filled with a vapour and sealed at 250° C and 740 mm pressure As a result the globe increased in weight by 0 805 gm compared with its weight when full of air at 17° C and 740 mm pressure Calculate (*a*) the normal density, and (*b*) the relative density that the vapour would have if it were a gas at N T P

1 litre of hydrogen weighs 0 090 gm and 1 litre air weighs 1 29 gm at N T P

**3** A vessel of 250 c c capacity contains 0 500 gm iodine at 1200° C From the simple gas laws the pressure should be 720 mm if the iodine were in a state of $I_2$, but owing to dissociation according to the equation $I_2 \rightleftharpoons 2I$ the pressure is actually 1080 mm What fraction of the iodine is dissociated? (C W B H S C)

**4.** When two grams of phosphorus pentachloride were vaporised in a vessel of 750 c c capacity at 250° C the pressure produced was one atmosphere What is the degree of dissociation of the compound under these conditions?
[P = 31, Cl = 35 5] (O & C H S C)

**5** 127 c c of a certain gas diffused in the same time as 100 c c of chlorine under the same conditions Calculate the molecular weight of the gas [Cl = 35 5] (O & C H S C)

**6.** Calculate the weight of carbon dioxide which dissolves in 1 litre of water (*a*) when pure carbon dioxide at N T P is bubbled through water, (*b*) when a mixture of three volumes of carbon dioxide and one volume of hydrogen at N T P is bubbled through water
[Absorption coefficient of carbon dioxide at 0° C = 1 71]

**7** A mixture of equal volumes of chlorobenzene, $C_6H_5Cl$, and water are steam distilled under a pressure of 760 mm If the mixture boils at 91° C, calculate the percentage by weight of chlorobenzene in the distillate, given that the vapour pressure of water is 545 mm at 91° C [C = 12, Cl = 35 5]

**8** A solution contains 50 gm of glycerol ($C_3H_8O_3$) per litre Calculate its osmotic pressure in cm of mercury at 17° C (L H S C)

**9** A solution containing one gram molecule of magnesium chloride in 10 0 litres of water has an osmotic pressure of 6 10 atm at 0° C Calculate the apparent molecular weight of the dissolved salt and discuss its meaning (L H S C)

**10** If a car radiator has a capacity of two gallons, calculate the number of pints of glycerine, $C_3H_8O_3$, which will be required to make two gallons of anti-freeze mixture, the latter to withstand "twelve degrees of frost"
Depression-constant for water is 18 5 (centigrade scale) per 100 gm water, S G glycerine 1 3, assume that the volume of the anti-freeze solution is equal to the sum of the volumes of the water and glycerine before they are mixed, and that the ordinary depression of freezing-point equation is valid for the above solution

**11** 6 0 grams of a certain non-electrolyte were found to depress the freezing-point of 500 gm of water by 0 37° Calculate the molecular weight of the non-electrolyte What would be the osmotic pressure of the above solution at 15° C? [K = 18 5]

**12.** Calculate the heats of formation of hydrogen sulphide and of carbon disulphide from the following data

$$2H_2 + O_2 = 2H_2O + 136{,}000 \text{ cals}$$
$$S + O_2 = SO_2 + 71{,}080 \text{ cals}$$
$$2H_2S + 3O_2 = 2H_2O + 2SO_2 + 267{,}000 \text{ cals}$$
$$CS_2 + 3O_2 = CO_2 + 2SO_2 + 253{,}000 \text{ cals}$$
$$C + O_2 = CO_2 + 96{,}900 \text{ cals}$$

(London Medical)

**13.** At 390° the gas produced by the volatilisation of one gram molecule of nitrogen peroxide in a volume of one litre contains 30% of nitric oxide molecules Calculate the dissociation constant of nitrogen peroxide, ($NO_2$), under these conditions (C S)

**14** In a certain experiment at 356°, 1 20 millimols of hydrogen and 1 20 millimols of iodine was found to be in equilibrium with 9 60 millimols of hydrogen iodide If 6 00 millimols of hydrogen was heated in a bulb with 24 0 millimols of iodine at the same temperature, viz 356°, what would be the composition of the equilibrium mixture in terms of millimols? What would be the effect on this equilibrium of (*a*) doubling the pressure, (*b*) adding four millimols of argon to the bulb, (*c*) adding four millimols of hydrogen to the bulb?

**15** 25 c c of an $M/10$ solution of copper sulphate were mixed with 25 c c of $N$ ammonia, and the product, which contained an excess of ammonia, was then shaken with 75 c c of chloroform 50 c c of the chloroform were then removed and were found to neutralise 21 8 c c $N/40$ hydrochloric acid On the assumption that only the free ammonia can dissolve in the chloroform layer and that the partition coefficient, conc free ammonia in water conc free ammonia in chloroform, is 26 at the temperature of the experiment, calculate the formula of the complex cuprammonium ion

**16** Four experiments on the distribution of phenol between 50 c c of water and 50 c c of chloroform gave the following results weights of phenol added were 0 328 gm , 0 924 gm , 2 097 gm , 5 866 gm , and corresponding weights of phenol in chloroform layer were 0 254 gm , 0 761 gm , 1 85 gm , 5 43 gm What deductions can be made from these results? (C S , modified )

**17** A current of 0 02 amps was passed for 78 minutes between two platinum electrodes dipping into a solution of caustic soda Before electrolysis 50 00 gm of the cathode solution contained 0 1200 gm of caustic soda, and after electrolysis 0 1283 gm caustic soda Calculate the transport numbers of the sodium and the hydroxyl ions in this solution [One Faraday = 96,500 coulombs ]

**18** An $N/10$ solution of monochloracetic acid has a $p$H of 1 932 , calculate the dissociation constant of the acid

**19** If the dissociation-constant of a weak monobasic acid is $100 \times 10^{-6}$, calculate the concentration of the hydrogen of a solution containing 0 020 molecules of the acid and 0 20 molecules of its sodium salt per litre What is the $p$H of this solution?

**20** On the assumption that the following electrolytes are completely dissociated, calculate the $p$H of $M/1000$ solutions of (*a*) potassium hydroxide, (*b*) nitric acid, (*c*) sulphuric acid $K_w = 1 \times 10^{-14}$

**21** Calculate the solubility product of silver chromate, given that its solubility is $2\ 50 \times 10^{-2}$ gm per litre

The solubility product of silver chloride is $1\ 20 \times 10^{-10}$ Explain the bearing of the magnitude of these solubility products on the titration of sodium chloride by silver nitrate, using potassium chromate as indicator, and calculate what the concentration (in gram ions per litre) of the chromate ion should be for an accurate end-point [O = 16 , Cr = 52 , Ag = 108 ] (C S , modified )

**22** From 50 c c of a saturated aqueous solution of lead chloride at 15° C lead sulphide was completely precipitated by hydrogen sulphide and removed by filtration The filtrate and washings, from which hydrogen sulphide had been removed, required 32 9 c c $N/10$ sodium hydroxide when they were titrated Calculate in g -mol per litre the solubility of lead chloride in water at 15° C , and hence (on the assumption of complete dissociation) the solubility product [Cl = 35 45, Pb = 207 1 ] (O & C H S C )

## CHAPTER XLVII

**1** What are the chief uses, in the operations of organic chemistry, of the following substances sulphuric acid, nitrous acid, metallic sodium, phosphorus pentachloride, ammonia ? (O S)

**2** Give examples of the uses of phosphorus pentoxide, stannous chloride and metallic sodium as reagents in organic chemistry (C S)

**3** Illustrate the laboratory uses of potassium cyanide, aluminium chloride, concentrated sulphuric acid, and hydrocyanic acid (C S)

**4** Describe the more important uses of each of the following reagents in organic chemistry phosphorus pentachloride, alcoholic potassium hydroxide, acetyl chloride, metallic sodium (M B Cantab)

**5** Explain the principal applications in the laboratory of (*a*) sodium acetate, (*b*) sodium carbonate, (*c*) ammonium chloride (C S)

**6** What classes of organic substances are prepared by means of the chlorides of phosphorus, and how are they made ? Describe in detail the preparation of *one* such substance and give a full account of its properties (O H S C)

## CHAPTERS XLVIII-L

**1** How does methane occur naturally ? Describe *one* method for making it in the laboratory

If 10 c c of methane are exploded with 30 c c of oxygen in a eudiometer, what change in volumes takes place ? If a little potassium hydroxide solution is now introduced into the gas, what further change in volume takes place ? Assume that all measurements are made at normal temperature and pressure (J M B H S C)

**2** What different methods are available for the preparation of ethylene ? Give reasons for the structural formula you assign to it

How does ethylene react with (*a*) oxidising agents, (*b*) halogens, (*c*) concentrated sulphuric acid, (*d*) hydrogen ? State the conditions under which the reaction you mention takes place (O S)

**3** A quantity of ethylene was absorbed by shaking with an aqueous solution of hypochlorous acid The solution so produced was divided into two parts, the one was oxidised with chromic acid and yielded an acid, $C_2H_3O_2Cl$, the other was boiled and a volatile compound $C_2H_4O$ was liberated Elucidate these changes and compare them with those that take place with ethylene and sulphuric acid (C S)

**4** Give an account of the preparation and reactions of ethylene, and say why this compound is represented by the formula $C_2H_4$ (O & C H S C)

**5** Describe how (*a*) ethane, (*b*) ethylene, (*c*) acetylene can be prepared

Compare the reactions of these three compounds and show that the presence of an unsaturated linkage in the molecule causes greatly increased reactivity (C H S C)

**6.** Write the structural formulae of methane and acetylene State the action of chlorine upon these two compounds, and show how expression is given to the reactions which take place by the constitutional formulae of the hydrocarbons (C H S C)

**7.** Describe the preparation and uses on a commercial scale of (*a*) hydrogen, (*b*) acetylene (C H S C)

**8** By what methods can acetylene be obtained in a pure condition ? How may the following substances be made from it (1) ethane, (2) benzene, (3) aldehyde, (4) ethyl alcohol ? (O S)

**9** Describe with experimental details the preparation of *two* of the following substances (*a*) ethane, (*b*) ethylene, (*c*) acetylene, (*d*) carbon monoxide
What products are formed, and under what conditions, when chlorine reacts with *each* of the four substances mentioned above ? (L H S C)

**10** What tests would you make to distinguish between ethane, ethylene and acetylene ? (O S)

## CHAPTER LI

**1** Give an account of the preparation and reactions of ethyl alcohol, and say why this compound is represented by the formula $C_2H_5OH$ (O & C H S C)

**2** How would you prepare from ethyl alcohol (*a*) ethyl bromide, (*b*) sodium ethylate ? What products would be formed by the reaction of these substances in molecular proportions, and how would you identify each of these products ? (O H S C)

**3** What chemical changes can take place, and under what conditions, between (*a*) ethyl alcohol and sulphuric acid, (*b*) ethyl alcohol, potassium bichromate, and sulphuric acid, (*c*) ethyl alcohol and atmospheric oxygen ? (O H S C)

**4** Draw the graphical formulae for the alcohols of molecular formula $C_3H_8O$
What products would be formed when each of these alcohols was (*a*) mildly oxidised, (*b*) vigorously oxidised ? (C H S C)

**5** How is ethyl alcohol obtained commercially ? How is it purified ? Explain carefully the evidence upon which the formula $CH_3CH_2OH$ is assigned to the molecule of this compound (J M B H S C)

**6** How are methyl and ethyl alcohols obtained ? How could you distinguish between them, and what is the action of sulphuric acid under different conditions on them ? (O S)

**7** Give a brief account of isomerism as shown in the butyl alcohols $C_4H_9OH$
How may the different types of alcohol be distinguished from one another ?
Mention another compound of different type which is isomeric with the butyl alcohols Compare the properties of this substance with those of the alcohols and show how the difference is expressed by structural formulae (C W B H S C)

## CHAPTER LII

**1** What is an aldehyde ? Describe the large-scale preparation of acetaldehyde How does this compound react with (*a*) a small quantity of concentrated sulphuric or hydrochloric acid, (*b*) dry ammonia gas, (*c*) caustic soda, (*d*) a saturated solution of sodium bisulphite, (*e*) oxidising agents ? (M B Camb)

**2** How is acetaldehyde usually obtained ? How could it be synthesised from its elements ? State the properties of this substance and indicate how they differ from those of formaldehyde (O S)

**3** By what general processes can the aliphatic ketones be prepared ? Select any ketone and describe its preparation and salient properties How would you distinguish between this ketone and its isomeric aldehyde ? (C W B H S C)

**4.** Given a supply of calcium formate and calcium acetate, what compounds could you obtain by heating them strongly (*a*) together, and (*b*) separately ?
Describe the principal properties of the organic compounds you mention (J M B H S C)

**5** What is the structural formula of acetone ?
Show that this formula is supported by the methods of formation and the chief reactions of acetone (O & C H S C)

**6** How is acetone prepared on the industrial scale ? Give the structural formula for this substance and outline the evidence on which it is based (L H S C)

**7** What is the constitutional formula for acetone, and on what grounds has it been assigned? How does this compound react with (*a*) phosphorus pentachloride, (*b*) bleaching powder and water, (*c*) hydroxylamine, (*d*) chromic acid mixture? (O S)

**8** Describe fully *one* method for the laboratory preparation of chloroform Explain the relationship between methane and chloroform What are the chief properties of chloroform? (J M B H S C)

## CHAPTERS LIII-LIV

**1** How can formic acid be prepared?
State fully how the constitutional formula for the acid can be established (C S)

**2** When formic acid vapour was passed through a long glass tube maintained at 300° C, complete decomposition occurred, and 21 6 c c of gases was collected which behaved in the following way on analysis
On treatment with potash solution the volume decreased to 15 2 c c 23 c c of oxygen were then added and the mixture exploded The volume after explosion was 24 2 c c, and this decreased to 15 4 c c on further treatment with potash
Discuss these results and give what explanation you can What further experiments would you make to test the correctness of your views? (C S)

**3.** How can acetic acid be prepared on a large scale, and what are its uses?
From acetic acid how may (*a*) acetic anhydride, (*b*) acetonitrile, (*c*) diethyl malonate be prepared? (C S)

**4** Describe how dilute acetic acid is manufactured and how it may be converted into glacial acetic acid
What is the action of acetic acid on (*a*) ethyl alcohol, (*b*) phosphorus trichloride, (*c*) chlorine? (J M B H S C)

**5** Describe in detail how, starting with sodium acetate, you would prepare (*a*) methane, (*b*) acetic anhydride, (*c*) monochloracetic acid? (O S)

**6** How would you proceed in order to substitute one of the non-acid hydrogen atoms in the molecule of acetic acid, by (*a*) a hydroxyl group, (*b*) a cyanogen group, (*c*) a carboxyl group, (*d*) an amino group? (M B Camb)

**7** State and explain what you consider to be the simplest reactions by which acetic acid could be converted into (*a*) acetamide, (*b*) acetone, (*c*) ethane, (*d*) ethyl acetate (O S)

**8** How may the following substances be prepared (*a*) acetyl chloride from acetic acid, (*b*) acetic anhydride? What classes of compounds yield acetyl derivatives? (C H S C)

**9** How many acids of the formula $C_4H_9CO_2H$ should be capable of existence? Outline a scheme for the synthetical production of each

**10.** Describe with essential practical details how you would prepare dry ether from absolute alcohol How may the constitution of ether be demonstrated? (J M B H S C)

**11** Distinguish between an ether and an ester Describe how you would prepare one example of each of these classes of compounds from ethyl alcohol (C S)

**12** What is an ester? Give *three* methods for the preparation of esters
On boiling 0 277 gm of an ester with 50 c c of decinormal sodium hydroxide until the reaction was complete, the resulting liquid required 18 5 c c of decinormal hydrochloric acid for neutralisation If the ester were derived from a monobasic acid and monohydric alcohol, what would be its molecular weight? (J M B H S C)

**13** Describe a laboratory method for the preparation of ethyl iodide Explain briefly how, starting from ethyl iodide, you could obtain specimens of (*a*) diethyl ether, (*b*) ethylene, (*c*) ethyl alcohol, and (*d*) ethane (J M B H S C)

**14.** Give an account of the preparation and properties of the monohalogen derivatives of the paraffins

**15** Discuss the preparation and synthetic uses of (*a*) acetoacetic ester, (*b*) malonic ester

## CHAPTERS LV-LVI

**1** Give the names and structural formulae of the oxidation products of glycol Describe the preparation, from any source you may select, and the properties of any one of them (M B Camb)

**2** Among *polyhydric alcohols* glycerol is of special importance, and is distinguished by the facility with which it is convertible by dehydration into the *unsaturated aldehyde* acrolein
Explain as fully as you can the four words italicised in the above passage (O S)

**3** Describe how glycerine is obtained from fats Give an account of the properties of glycerine Why is it considered to be a tri-hydroxy compound ? (M B Camb)

**4** To what class of compounds do the fats belong ? Write the structural formula of a compound of this kind Describe the preparation of a derivative of a fat (M B Camb)

**5** Compare the behaviour of glucose and fructose towards (*a*) oxidising agents, (*b*) acetylating agents, (*c*) phenyl hydrazine (M B Camb)

**6** Explain how lactic acid can be obtained from ethyl alcohol, and malonic acid from acetic acid (C S)

**7** Describe the preparation and the resolution of *either* the lactic acids, *or* the tartaric acids (C S)

**8** Give an account of the isomerism of the varieties of (*a*) tartaric acid, and (*b*) lactic acid (M B Camb)

**9** How many isomeric carboxylic acids of the molecular formula $C_3H_6O_3$ are known ? Explain how you account for the existence of these isomers, and give some account of their chemical and physical behaviour (O & C H S C)

**10** How can urea be synthesised ? Give an account of the properties of this substance How can it be estimated in solution ?

**11** How may aminoacetic acid and urea be synthesised ? State the more important characteristics and reactions of these substances (C H S C)

**12** Give some account of the occurrence in nature, the preparation, and the main properties, of oxalic acid How may this substance be converted into (*a*) formic acid, (*b*) methyl oxalate, and (*c*) oxamide ? (C W B H S C)

## CHAPTERS LVII-LVIII

**1** By what methods can primary amines be synthesised in the laboratory ? Mention the characteristic properties of primary amines, and explain how they may be distinguished from secondary and tertiary amines

**2** Explain how an atom of hydrogen in ammonia may be replaced by (*a*) the ethyl group, (*b*) the acetyl group
Compare and contrast the properties of the resulting compounds (C S)

**3** How may acetamide be prepared ? Describe the properties of this compound and indicate the steps necessary to convert it into a methyl-amine (M B Camb)

**4.** When ethyl iodide is treated with potassium cyanide a substance is obtained which is different from that obtained when silver cyanide is used Compare the

reactions of these two ethyl compounds and deduce their structural formulae What conclusions about the structural formula of hydrocyanic acid can be drawn from these facts ? (O H S C)

**5** How may nitriles be prepared ? Give examples of the uses of nitriles in the synthesis of (*a*) carboxylic acids and (*b*) amines Discuss the evidence upon which the structural formula of the nitrile grouping is based (M B Camb)

**6** Distinguish between nitro-compounds, nitrates and nitrites How would you establish the structural formulae of ethyl nitrite and nitroethane ? (O S)

**7** Give an account of the isomerism of (*a*) maleic and fumaric acids (*b*) ethyl nitrite and nitroethane, and explain how the respective constitutional formulae are established (C S)

## CHAPTERS LIX-LXI

**1** Give reasons for assigning a " closed ring " formula to benzene Show how the isomerism of the benzene derivatives supports this structure (J B H C)

**2.** Why is benzene represented with a symmetrical formula ? By what reagents can benzene be attacked and what are the products in each case (O S)

**3.** What are the characteristics and properties of (*a*) paraffins, (*b*) aromatic hydrocarbons ?
Illustrate your answer by reference to the properties and reactions of methane, benzene, and toluene (O H S C)

**4** A certain homologue of benzene has the formula $C_8H_{10}$ Write the possible structural formulae for this compound and give the systematic name for each formula What experiments could you make in order to determine whether the substance is a mono- or a di-substituted benzene ? (M B Camb)

**5** When toluene is treated with chlorine, what conditions determine whether substitution in the nucleus or in the side-chain takes place ? Contrast the properties of the resulting products (M B Camb)

**6** Write a short account of the preparation and properties of nitrobenzene. What is the evidence upon which the constitutional formula $C_6H_5NO_2$ is based ? (O S)

**7** How would you prepare benzaldehyde from toluene ? Compare the properties of acetaldehyde and benzaldehyde, drawing attention to any marked differences of behaviour (J M B H S C)

**8** How may benzaldehyde be prepared ? Give an account of the reactions of this substance with (*a*) potassium cyanide, (*b*) hydrogen cyanide, (*c*) aqueous sodium hydroxide, and (*d*) phenylhydrazine (M B Camb)

**9** Describe *two* methods of making phenol from benzene Discuss, by comparing the properties and structure of phenol with those of the aliphatic alcohols, whether phenol should be classed as an alcohol (O H S C)

**10** Give a full account of the way in which you would prepare and isolate a specimen of phenol *either* from a specimen of aniline hydrochloride *or* from one of potassium benzene sulphonate, explaining as clearly as you can the chemical reactions and the physical principles involved in the process which you choose (O H S C)

**11** How is phenol obtained commercially ?
Describe its chief physical and chemical properties, pointing out in what respects it (*a*) resembles, and (*b*) differs from an alcohol
By what tests would you recognise phenol ? (J M B H S C)

**12.** Trace the steps by which benzene is converted into salicylic acid How does salicylic acid react with (*a*) acetic anhydride, (*b*) methyl alcohol in presence of sulphuric acid , (*c*) soda-lime ?

**13** Write equations to express the action of (*a*) phosphorus pentachloride, (*b*) sodium hydroxide, (*c*) metallic sodium, on (i) benzoic acid, (ii) phenol, and (iii) benzyl alcohol Describe the action of water on the various products obtained in the above reactions (C W B H S C)

**14.** What experiments would you actually perform to illustrate the characteristic differences between (*a*) phenol and ethyl alcohol, (*b*) aniline and ethylamine ? (O S)

**15** Starting from benzene, by what methods would you prepare aniline, benzoic acid, toluene, and iodobenzene ? (C W B H S C)

**16** Describe in detail the preparation of aniline from nitrobenzene Indicate the steps necessary for the conversion of aniline into (*a*) phenol, (*b*) phenyl iodide, and (*c*) acetanilide (M B Camb)

**17** A substance is described as a primary aromatic amine How could you test the accuracy of this description ? How might it react with sulphuric acid under different conditions ? (O S)

**18** Discuss the preparation and general reactions of diazonium salts (C S)

**19** What is meant by the diazotisation of aniline ? Describe exactly how the reaction is carried out Why is this reaction of such importance ? Give examples (O H S C)

**20** Give in outline the extraction of benzene from its chief source How may the following groups be introduced into the benzene nucleus (*a*) $-NH_2$, (*b*) $-SO_3H$, (*c*) —OH, (*d*) —Cl ? (J M B H S C)

**21** How may the following changes be effected (*a*) benzoic acid to benzene, (*b*) aniline to phenylhydrazine, (*c*) benzene to phenol, and (*d*) benzene to benzoic acid (H = 1, C = 12, O = 16, Br = 80) (M B Camb)

## General Questions on Chapters XLVII-LXI

**1** Explain, by means of examples, what information about an organic compound can be conveyed by its structural formula (C S)

**2** Explain and illustrate the importance of structural formulae in the study of organic chemistry, describing the main types of atomic linkage occurring in carbon compounds

Show how the structural formula of any one organic substance may be inferred both from methods of synthesis and from its chemical reactions (O S)

**3** Distinguish between "empirical formula," "molecular formula," and "graphical formula"

How may the formulae assigned to *two* of the following be established oxalic acid, acetone, normal propyl alcohol, ethylene ? (C S)

**4** Show, by means of examples, what you understand by (*a*) structural isomerism, (*b*) homologous series, and (*c*) polymerism (O S)

**5** Why is it sometimes necessary to consider the arrangement of atoms in three dimensions in order to account for the isomerism of certain carbon compounds ? (O H S C)

**6** Write a brief account of the development of the modern theory of valency with especial reference to the compounds of carbon (C W B H S C)

**7.** Give an account of some chemical reactions in which the linkage between two carbon atoms is broken (C S)

**8** What is meant by "unsaturation" in organic chemistry ? Explain why (*a*) ethylene, (*b*) benzene, (*c*) acetaldehyde, (*d*) acetone are considered to be unsaturated compounds (C W B H S C)

**9** Reactive carbon compounds are generally those in whose formulae some unsaturation is indicated Exemplify and discuss this statement (C S)

**10** Give an account of the properties of the hydroxyl (—OH) group in organic compounds, and show how the character of this group is influenced by the nature of the other atoms or groups present in the molecule (C W B H S C)

**11** What properties are associated with substances containing the group —COOH ? Starting with one such compound, how may *three* derivatives of it be formed ? (O & C H S C)

**12** How may the following acids be obtained (1) oxalic, (2) formic, (3) benzoic ? State briefly the more important properties of these acids How do their metallic salts behave on heating ? (O S)

**13** Give an account of the general properties of the $—NH_2$ group, indicating how these properties vary with the nature of the grouping to which it is attached (C S)

**14** Describe the distinctive reactions of (*a*) primary, secondary and tertiary alcohols, and (*b*) primary, secondary and tertiary amines (M B Camb)

**15** Give examples of the various types of compounds containing the —OH group or the $—NH_2$ group Show how the properties of these substances are related to the type of radical to which these groups are joined (C S)

**16** A certain solid organic compound is either an amine, an amide, or a nitrile How would you make a quantitative estimation of the nitrogen it contains, and what experiments would you carry out in order to assign the compound to its class ? (C H S C)

**17** Explain fully the reactions upon which the formulae of four of the following substances rest methyl cyanide, methyl nitrite, urea, oxalic acid, ethylene (C S)

**18** Explain fully the reactions which justify the formulae of *four* of the following acetyl chloride, monochloracetic acid, normal propyl alcohol, acetone, ethyl hydrogen sulphate (C S)

**19** Compare and contrast in methods of preparation and reactions the following substances acetyl chloride, ethylidine dichloride, chloroacetic acid, and chlorobenzene (C S)

**20** In what respects do (*a*) amines, (*b*) hydroxy compounds, (*c*) aldehydes of the aromatic series differ from those of the aliphatic series ? (O S)

**21** Discuss the action of chlorine on three of the following (*a*) ethyl alcohol (*b*) toluene, (*c*) phenol, (*d*) an alkaline solution of urea (O S)

**22** Give an account of the action of nitrous acid upon (*a*) amides, (*b*) aliphatic amines, (*c*) aromatic amines, (*d*) amino acids (M B Camb)

**23** How may the presence of sulphur in an organic compound be recognised, and by what methods may the proportion of this element be estimated ? Give the names and structural formulae of *two* organic compounds of different type which contain sulphur (C W B H S C)

**24** How may salicylic acid be prepared on the technical scale ? How is it possible to prepare a derivative of this acid in which (*a*) the hydroxyl group, and (*b*) the carboxyl group, alone is involved ? (M B Camb)

**25** " Distillation is one of the most valuable methods at the disposal of the organic chemist " Discuss this statement with respect to fractional distillation and distillation in steam Explain the principles underlying these processes, and describe in detail apparatus necessary for efficiency (J M B H S C)

**26.** Describe, with necessary practical details, how you would separate the constituents of the following pairs of substances and obtain each in a reasonably pure state (*a*) methyl alcohol and acetone, (*b*) nitrobenzene and aniline, (*c*) benzene and toluene (O.H.S.C.)

**27** Tabulate the steps you would take to decide if a given organic substance (*a*) was a simple compound or a mixture, (*b*) contained nitrogen, (*c*) contained a hydroxyl group, (*d*) belonged to the aliphatic or aromatic series of compounds (O S)

**28.** Describe carefully the preparation of (*a*) a pure sample of the silver salt of an organic acid, and (*b*) the acetyl derivative of a compound containing one or more hydroxyl groups

Explain fully the importance of these preparations (C S)

## Problems in Organic Chemistry

**1** A compound, containing carbon, hydrogen, and oxygen only, gave the following results on analysis 0 1460 gm gave 0 3740 gm $CO_2$ and 0 1540 gm $H_2O$

A vapour density determination of the compound gave a value of 42 (H = 1)

The compound gives a crystalline product on shaking with a saturated solution of sodium bisulphite It also reacts with hydroxylamine and phenyl hydrazine, but not with acetyl chloride On oxidation it yields acetic acid and propionic acid as main products Determine the molecular and structural formulae of the compound (C W B H S C)

**2** An organic compound containing 58 5% of carbon, 7 3% of hydrogen, and 34 2% of nitrogen when boiled with hydrochloric acid was converted into a monobasic acid, the ethyl ester of which had a vapour density of 44 What is the constitutional formula of the original compound ? Describe briefly the chief reactions of the class of compounds to which it belongs (O & C H S C)

**3** On analysis 0 2354 grm of an organic substance yielded 0 4705 grm of carbon dioxide and 0 1930 grm of water 0 5180 grm of the substance dissolved in 23 8 grm of benzene ($k = 26$ 1) caused an elevation of 0 65° in the boiling-point Suggest constitutional formulae for compounds which would satisfy these data (C H S C.)

**4** 15 c c of a mixture of carbon monoxide and methane were mixed with 30 c c of oxygen and sparked After cooling to room temperature, and treatment with a strong solution of potassium hydroxide, 7 5 c c of gas remained This volume was completely absorbed by an alkaline solution of pyrogallol Calculate the volume of methane present in the original mixture (C H S C)

**5** An organic liquid has the composition C = 49 31, H = 6 85, O = 43 84% Its vapour density (O = 16) is 73 On treatment with ammonia it gives a white precipitate of empirical formula $CONH_2$ This precipitate, when boiled with sodium hydroxide solution, gives off ammonia and leaves a residue which, on evaporation and treatment with hot concentrated sulphuric acid, gives off a mixture of carbon monoxide and carbon dioxide

What is the liquid ? Give the equations for the above reactions (O & C H S C)

**6** An organic acid on analysis gave the following percentage numbers C = 57 70, H = 3 71, O = 38 59%

The silver salt of the acid gave 56 8% of silver on ignition and the vapour density of the ethyl ester was found to be 111 (H = 1)

What are the molecular formula and the basicity of the acid ? (C W B H S C)

**7.** A compound of carbon, hydrogen and oxygen which gave on analysis C = 59 9%, H = 13 45% was treated with hydrobromic acid, and the isolated product whose vapour density was 61 5 gave the following analytical results (*a*) on combustion, C = 29 25%, H = 5 74%, (*b*) by the Carius method, 0 25 gram gave 0 382 gram silver bromide

Write down an equation or equations which are in accordance with these data (J M B H S C)

**8** 0 2316 gram of an organic substance containing carbon, hydrogen and nitrogen, but no other element, yielded 0 5584 gram carbon dioxide and 0 3141

gram water on combustion Its vapour density was found to lie between 35 and 40 Calculate the empirical formula of the substance
What isomers having this formula should exist ? (J M B H S C)

**9** An acid on ultimate analysis yielded the following data 0 3754 gm gave 0 5599 gm of $CO_2$ and 0 1718 gm of $H_2O$ The acid was esterified in a solution of ethyl alcohol, and it was found that 0 2746 gm of the ester dissolved in 25 67 gm of ethylene dibromide depressed the freezing-point of this solvent 0 763° C Determine the molecular weight of the acid and suggest a possible formula for it (K = 118° for 100 grams solvent) (C H S C)

**10** Explain briefly, with a diagram of the apparatus employed, the method of determining the percentages of carbon and hydrogen in an organic compound
0 185 gram of an organic compound gave on combustion 0 440 gram of carbon dioxide and 0 225 gram of water, the vapour density of the compound is 37 What is the molecular formula of the compound, and what structural formulae are possible for it ? (O & C H S C)

**11** On combustion 0 27 gram of an organic substance gave 0 4023 gram of $CO_2$ and 0 2061 gram of $H_2O$ In a nitrogen determination 0 24 gram gave 45 6 c c of dry nitrogen at N T P Find the empirical formula
On heating the substance with phosphorus pentoxide an alkyl cyanide was formed, while hydrolysis of the substance gave an ammonium salt Identify the substance and explain the reactions (C W B H S C)

**12** A crystalline solid soluble in water to an acid solution, proved on analysis to have the percentage composition carbon 32, hydrogen 4, and oxygen 64
It was found that 25 c c of a solution which contained 9 grams of this solid per litre required for neutralisation (with phenol phthalein as indicator) 30 c c of $\frac{N}{10}$ caustic soda solution What conclusions can you draw as to the formula of the substance, and what further experiments would you make to determine its molecular formula ? (O H S C)

**13** The hydrochloride of a monacid organic base contains 37 2% of chlorine The quaternary ammonium iodide obtained by treating the base with methyl iodide contains 59 1% of iodine What is the constitution of the base ?

(C = 12, N = 14, Cl = 35 5, I = 127) (C S)

**14** Discuss the structural formulae which are possible for an organic acid with the percentage composition C = 40, H = 6 7, O = 53 3, and a molecular weight not greater than 100 (O S)

**15** A crystalline organic substance containing only carbon, hydrogen, nitrogen, and perhaps oxygen gave the following results on analysis C 40 68%, H 8 48%, N 23 73% Calculate its empirical formula Boiled with a mixture of alcohol and sulphuric acid it gave an ester of vapour density 44 (H = 1) and ammonium sulphate was left in the reaction mixture Follow out these reactions and say what the original substance is Indicate briefly how you would prepare it (O H S C)

**16.** Some ammonium acetate was heated in a sealed tube and a white crystalline substance (*A*) was obtained On treatment with bromine and caustic potash solution *A* produced a colourless gas (*B*) with a fishy, ammoniacal smell On dissolving *B* in water and adding nitrous acid, nitrogen was given off, and on fractional distillation the residual liquid gave a colourless volatile inflammable liquid (*C*) On passing the vapour of *C*, mixed with air, over a heated copper spiral a pungent gas (*D*) was formed which reduced Fehling's solution and ammoniacal silver nitrate Identify *A*, *B*, *C* and *D*, write their formulae and give equations for the changes in which they were formed For what purposes are *C* and *D* used in everyday life ? (J M B H S C)

## PROBLEMS IN ORGANIC CHEMISTRY WITH SOLUTIONS

**1** When one volume of gas containing carbon and hydrogen only was exploded with excess of air a contraction of $2\frac{1}{2}$ volumes followed, and there was a further contraction of 2 volumes on treatment with potash What conclusion would you draw from these data ? What suggestions can you make with respect to the gas, and how would you test these experimentally ? (Cambridge Schols , 1926 )

The gas is a hydrocarbon, which yields twice its volume of carbon dioxide Its formula is therefore $C_2H_{2x}$, since the number of hydrogens must be even On explosion

$$\underset{1\text{ vol}}{C_2H_{2x}} + \underset{(2+x/2)\text{ vols}}{(2+x/2)\,O_2} = \underset{2\text{ vols}}{2CO_2} + xH_2O$$

The contraction $1+2+x/2-2=2\frac{1}{2}$ vols

$$x/2=3/2 \quad \text{and} \quad x=3$$

The formula of the gas is therefore $C_2H_6$ and its combustion in oxygen may be represented by the equation

$$\underset{1\text{ vol}}{C_2H_6} + \underset{3\frac{1}{2}\text{ vols}}{3\tfrac{1}{2}O_2} = \underset{2\text{ vols}}{2CO_2} + \underset{\substack{\text{Contraction}\\ 2\frac{1}{2}\text{ vols}}}{3H_2O}$$

The gas could be brought into contact with bromine, or it could be shaken with concentrated sulphuric acid, when unsaturated hydrocarbons would be absorbed The fact that the gas was not absorbed would show that it was a *saturated hydrocarbon* A determination of its vapour density (about 15) would then show that the gas was the second member of the paraffin series, $C_2H_6$, with a molecular weight of 30 Finally, if suitable apparatus was available, the gas could be condensed to a liquid and its freezing-point and boiling-points measured

**2** After explosion of 10 c c of a gaseous compound with excess of air and restoration to the original temperature and pressure there was a contraction of 20 2 c c and a further contraction of 19 9 c c when the resulting gases were treated with potassium hydroxide The products of combustion were carbon dioxide and water only and the weight of 1 litre of the gas at N T P was 2 05 grams What was the molecular formula of the gas ? How can its molecular structure be established ? (Cambridge Schols , 1928 )

The compound gives twice its volume of carbon dioxide, and is therefore of the $C_2$ series Since it is oxidised to water and carbon dioxide only, we may represent the explosion by the equation

$$\underset{1\text{ vol}}{C_2H_{2x}O_y} + \underset{2\text{ vols}+\frac{1}{2}(x-y)\text{ vols}}{2O_2+\tfrac{1}{2}(x-y)O_2} = \underset{2\text{ vols}}{2CO_2} + \underset{\text{Contraction 2 vols}}{2xH_2O}$$

The contraction $1+2+\frac{1}{2}(x-y)-2=2$ vols

$$\tfrac{1}{2}(x-y)=1 \quad \text{or} \quad x-y=2$$

The molecular weight of the gas is $2\times\dfrac{2\ 05}{0\ 0896}=46$

Let $y=0$, then $x=2$ and the compound is $C_2H_4$, mol wt 28
$y=1$, ,, $x=3$ ,, ,, ,, ,, $C_2H_6O$, mol wt 46

This is evidently the correct formula, but since the original compound was gaseous it cannot be ethyl alcohol and must therefore be methyl ether, $CH_3\,O\,CH_3$ Its molecular structure could be established by preparing it, (i) from methyl alcohol, or (ii) from methyl iodide and sodium methoxide

**3.** A liquid compound of the formula $C_3H_8O$, when heated with an excess of concentrated sulphuric acid, gives a gas of the formula $C_3H_6$, which is dissolved on shaking with cold sulphuric acid On diluting and boiling the solution so formed, a liquid is recovered, but is isomeric with the original liquid What explanation can you suggest of the course of the reactions?

(Cambridge Schols, 1925)

The liquid is converted into a gas according to the equation

$$C_3H_8O - H_2O = C_3H_6$$

The gas is an olefine of the series $C_nH_{2n}$, the liquid is evidently an alcohol derived from it Only one formula is possible for the olefine, namely, that of propylene, $CH_3CH{=}CH_2$, but the addition of sulphuric acid might take place in two ways as follows

$$CH_3CH_2CH_2O\,SO_2OH \leftarrow CH_3CH{=}CH_2 \rightarrow CH_3CH(O\,SO_2OH)CH_3$$

The right-hand product is formed in accordance with Markownikoff's rule for the formation of addition compounds from olefines and must therefore be assumed to be the main product of the action On hydrolysis with water *iso*propyl alcohol will be produced

$$CH_3CH(O\,SO\,OH)CH_3 + H_2O = CH_3CH(OH)CH_3$$

The original liquid must therefore have been *normal* propyl alcohol

These conclusions could be verified by oxidising the isomeric alcohols with chromic acid, when propyl alcohol yields propionaldehyde, $CH_3CH_2CHO$, whilst the isomeric *iso*propyl alcohol yields acetone, $CH_3COCH_3$.

**4** A colourless crystalline substance, with a vapour density of 41 6, was warmed with aqueous sodium hydroxide, when a heavy liquid insoluble in water was produced The aqueous portion, neutralised and divided into three parts, gave (*a*) a positive test for chloride, (*b*) a deep red colour with ferric chloride, changing to a red precipitate on boiling, (*c*) the last portion reduced dilute potassium permanganate Discuss these data, and suggest a formula for the original compound (C = 12, Cl = 35 5, O = 16) (Cambridge Schols, 1929)

This is a difficult problem, which can only be solved by giving strict attention to the exact wording of the text

(i) A vapour density of 41 6 corresponds with a molecular weight of 83 If this is correct, the molecules of the conclusion compound can only contain *one* or *two* atoms of chlorine, XCl or $XCl_2$, where X = 48 or Y = 12 The latter is impossible in an organic compound, since $CCl_2$ represents a radical and not a molecule, and there is no room left even for two atoms of hydrogen if the vapour density and molecular weight are exact Moreover, there is no crystalline monochloride of molecular weight 83, which yields an oil with caustic soda The vapour density is therefore set aside provisionally as misleading, and we wonder if it is a misprint

(ii) We find a key to the solution of the problem in the fact that the aqueous solution gives a "positive test" for chlorine This evidently refers to a mere trace of silver chloride, and not to a substantial precipitate We therefore conclude that the original substance contains chlorine, but that most of it remains in the insoluble liquid produced by the action of caustic soda

(iii) At this stage we guess that the liquid must be chloroform and that the crystalline substance from which it is prepared must be chloral hydrate To check this, we add up the molecular weight of chloral hydrate and find it to be 165 5, and are confirmed in our guesswork by noting that this is just four times the given vapour density The vapour density is therefore not a misprint, but is correct for chloral hydrate when dissociated into chloral and water, and we are now certain that the problem has been solved correctly

(iv) The other product of the hydrolysis of chloral hydrate is sodium formate This is a reducing agent and would account for the reduction of dilute potassium permanganate, we also guess that the familiar red colour which acetates give with ferric chloride may also be given by formates, although we did not know this previously, and therefore see no reason to doubt the correctness of our solution.

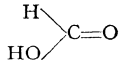
**5.** When sodium is dissolved in methyl alcohol and the solution is heated with chloroform a liquid compound is formed containing 45 3% of carbon and 9 4% of hydrogen, the rest being oxygen Heated with dilute sulphuric acid this liquid yields formic acid What information concerning the constitution of formic acid can be obtained from these facts ? (Cambridge Schols , 1926 )

The liquid compound has the empirical formula $C_4H_{10}O_2$ It is prepared by the action of sodium methoxide, $CH_3ONa$, on chloroform, $CHCl_3$, by a process in which the chlorine and sodium are eliminated, presumably in the form of sodium chloride This suggests the equation

$$CHCl_3 + 3NaOCH_3 = 3NaCl + CH(OCH_3)_3$$

The product, which has the right formula, is trimethoxymethane or methyl orthoformate. Hydrolysis would be expected to yield methyl alcohol and a compound of the $C_1$ series as follows

$$CH(OCH_3)_3 + 3H_2O = CH(OH)_3 + 3CH_3OH$$

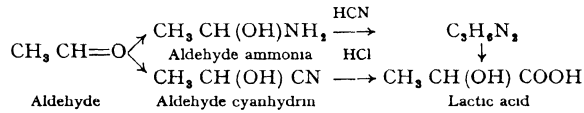
The formula of formic acid, however, is not $CH_4O_2$ but $CH_2O_2$, *i e* a molecule of water has been lost Since the removal of one of the hydroxyl radicals with the CH hydrogen would leave two free valencies, $>C(OH)_2$, we conclude that water has been lost by loss of a molecule of water from *two hydroxyl groups attached to the same carbon atom* Ample precedents for this exist, *e g* the hydrolysis of ethylidene dibromide, $CH_3CHBr_2$, yields acetaldehyde, $CH_3CHO$ We therefore infer (i) that formic acid contains a CH group, (ii) that it contains one unchanged hydroxyl group, (iii) that the two other hydroxyl groups have given rise to a carbonyl group by loss of water $>C(OH_2) \rightarrow >C{=}O + H_2O$ The formula for formic acid is therefore confirmed as 

**6.** When aldehyde-ammonia, $CH_3CH(OH)(NH_2)$, is treated with hydrocyanic acid a compound $C_3H_6N_2$ is formed This, when boiled with hydrochloric acid, yields ammonium chloride and a substance which is converted by nitrous acid into lactic acid

$$CH_3CH(OH)CO_2H$$

Explain how you would interpret these changes, writing structural formulae for the intermediate products (Cambridge Schols , 1927 )

We begin by writing down the well-known formulae of aldehyde, aldehyde ammonia, aldehyde cyanhydrin and lactic acid




By comparing the formula $C_3H_6N_2$ of the unknown compound with the formula $C_2H_7NO$ of aldehyde ammonia, it is seen that, by the action of hydrogen cyanide, an atom of oxygen and an atom of hydrogen are replaced by an atom of carbon and an atom of nitrogen This is presumably a simple esterification, as represented by the equation

$$CH_3CH(OH)NH_2 + HCN = CH_3CH(CN)NH_2 + H_2O$$

Now a cyano-group is usually hydrolysed by the action of boiling hydrochloric acid to ammonium chloride and a carboxyl group, *e g*

$$CH_3CN + HCl + 2H_2O = CH_3CO\,OH + NH_4Cl$$

On hydrolysis, therefore, a compound of the above type should yield ammonium chloride and an acid, viz $CH_3CH(NH_2)CO\,OH$, exactly as described in the question

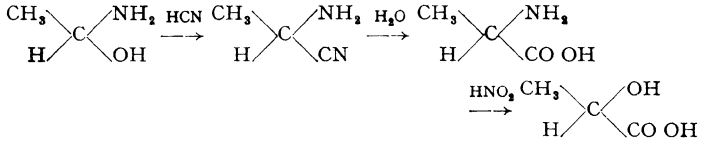
Nitrous acid is known to convert aliphatic amino-groups into hydroxyl groups, *e g*

$$\underset{\text{Glycine}}{NH_2\,CH_2\,CO\,OH} + HNO_2 = \underset{\text{Glycollic acid}}{HO\,CH_2\,CO\,OH} + N_2 + H_2O$$

We may therefore suppose that the acid, $CH_3\,CH(NH_2)\,CO\,OH$, which is a homologue of glycine, will behave similarly and yield lactic acid

$$NH_2\,CH_2\,CO\,OH + HO\,NO = HO\,CH_2\,CO\,OH + N_2 + H_2O$$

The sequence of changes recorded in the question may therefore be represented by the scheme




**7.** A neutral compound containing 60% of carbon, 5% of hydrogen and 35% of nitrogen, on being treated with boiling concentrated hydrochloric acid, was converted into a substance of acidic properties containing 40 7% of carbon and 5 1% of hydrogen, but no nitrogen It was found that 0 59 gram of this substance neutralised 10 c c of normal sodium hydroxide solution, and when boiled with a solution of hydrogen chloride in absolute ethyl alcohol it was converted into a neutral liquid of vapour density 87 Draw what conclusions you can as to the constitution of the substances referred to (Cambridge Schols , 1913 )

$$(C = 12,\ N = 14,\ O = 16,\ Na = 23)$$

The empirical formula of the original compound is $C_2H_2N$, which must be doubled in order to give an even total of valencies, $C_4H_4N_2$ The empirical formula of the acid is $C_2H_3O_2$, which must be doubled for the same reason, $C_4H_6O_4$ The equivalent of the acid is 59, and that of its ester is therefore $59 + 28 = 87$ , but the vapour density of the ester is 87 and its molecular weight 174 The molecular weight of the acid is therefore $2 \times 59 = 118$, in agreement with the formula, $C_4H_6O_4$, and the acid is dibasic since its equivalent is only 59 Allowing for two carboxyl groups, we can write the acid as $C_2H_4(CO_2H)_2$ It is therefore either

$$\begin{matrix} CH_2\,CO\,OH \\ | \\ CH_2\,CO\,OH \end{matrix}$$
Succinic acid

or

$$CH_3\,CH\begin{matrix} CO\,OH \\ CO\,OH \end{matrix}$$
Methylmalonic acid

and the ester is

$$\begin{matrix} CH_2\,CO\,OEt \\ | \\ CH_2\,CO\,OEt \end{matrix}$$
Ethyl succinate

or

$$CH_3\,CH\begin{matrix} CO\,OEt \\ CO\,OEt \end{matrix}$$
Ethyl methylmalonate

The parent compound would then be ethylene cyanide, $CN\,CH_2\,CH_2\,CN$, or ethylidene cyanide, $CH_3\,CH(CN)_2$, probably the former, since it is easy to prepare by the action of potassium cyanide on ethylene bromide

**8.** A neutral compound containing 25 5% of nitrogen after being heated with hydrochloric acid gave an acid substance containing 48 7% of carbon and 8 1% of hydrogen, but no nitrogen

0 2 gram of this acid required for neutralisation 27 0 c c of decinormal sodium hydroxide solution , the vapour density of the ethyl ester was 51 Draw what conclusions you can as to the nature of the original nitrogenous substance

(Cambridge Schols , 1919 )

The equivalent weight of the acid formed by hydrolysis is

$$0\,2 \times 10 \times 1000 \div 27 = 74\ 1.$$

The molecular weight of its ethyl ester is $2 \times 51 = 102$ The difference of 28 corresponds with the replacement of $H = 1$ by $C_2H_5 = 29$ The acid is therefore monobasic, with a molecular weight of 74 The numbers of atoms of carbon, hydrogen and oxygen in the molecule are

$$C = 74 \times \frac{48.7}{100} \div 12 = 3, \quad H = 74 \times \frac{8.1}{100} \div 1 = 6, \quad O = 74 \times \frac{43.2}{100} \div 16 = 2.$$

The acid is therefore propionic acid, $C_2H_5 CO OH$, and the original substance is ethyl cyanide, $C_2H_5 CN$, which contains 25 5% N, as stated in the question The hydrolysis can be represented by the equation

$$C_2H_5 CN + HCl + 2H_2O = C_2H_5 CO OH + NH_4Cl$$

**9** The formula of a substance is $C_4H_8O_4$ It has many of the properties of an aldehyde or ketone On oxidation it gives a tartaric acid When fully acetylated it gives an acetyl-derivative the molecular weight of which is about 250 Show that these conditions are satisfied by each of four substances, that two of these are optical isomers of the other two, and that the tartaric acids obtained from one pair of isomers are optically active while the other pair give meso-tartaric acid

(Cambridge Schols , 1930 )

The compound in question contains two atoms of hydrogen less than the alcohol I, and might therefore be the aldehyde II, of the ketone III

I $CH_2OH$ — $CHOH$ — $CHOH$ — $CH_2OH$

II $CHO$ — $CHOH$ — $CHOH$ — $CH_2OH$

III $CH_2OH$ — $CO$ — $CHOH$ — $CH_2OH$

I and II could be oxidised to tartaric acid, but III would yield an acid of the $C_3$, $C_2$ or $C_1$ series (probably glyceric acid and carbon dioxide) and can therefore be eliminated The triacetyl-derivative $C_4H_5O_4(CO\,CH_3)_3 = C_{10}H_{14}O$ of II would have a molecular weight of 246, in agreement with observation

The aldehyde II contains two asymmetric carbon atoms, like tartaric acid , it could therefore exist in a *d* and *l* form, corresponding to *d* and *l* tartaric acids It could also exist in a form corresponding with *meso*-tartaric acid , but, since the " end-groups " are not identical, " internal compensation " would not be complete The incompletely compensated acid could then exist in *d* and *l* forms, but both would yield inactive *meso*-tartaric acid on oxidation

# ANSWERS TO QUESTIONS

## CHAPTERS I-VIII

**11.** Eq wt 29.5 Chloride bromide 2 1

**20.** $X_3O_4$, $XO_2$ At wt 207 2 $X_3O_4 + 4HNO_3 = 2X(NO_3)_2 + XO_2 + 2H_2O$

**22.** At. wt 30 91 $M_4$, $MCl_3$, $MOCl_3$ **24.** $MCl_3$ At wt 74·9

**26.** Eq wt 30 62 At wt 183 7 $MO_3$ **27.** $MO_2$ $M_2O_3$

**39.** 41 4% **40** (*a*) 2 50 gm (*b*) 3 38 gm (*c*) 3 10 gm

**41.** 29 8 **42** 8 93

**43.** Eq wts 10 3 and 6 17, valency 3 and 5, at wt 30·9, the figures are in accordance with the law of multiple proportions

**44.** 40% NO, 40% $N_2O$, 20% $N_2$ **45** 50 c c $H_2$, 25 c c CO, 25 c c $CO_2$ **46.** $XH_3$

**47.** 200 6, 200 6, 1 67 **48** 26 7 **49** 133 **50.** Mg = 24 40, C = 12 00

**51.** Ag = 107 88, Cl = 35 44, Li = 6 95 **52** Ag = 107 93, S = 32 05

**53** M = 39 17 **54** 107 95, 12 03 **55** 9 10

**56.** $MO_3$, $12(NH_4)_3PO_4$ **57.** 14 9 gm

**58.** Eq wt 29 7, at wt 118 8, m wt 260 8, $MCl_4$

## CHAPTERS IX-X

**7.** 1,248,000 grams **18** 144 c c **19.** 6 8 grams.

## CHAPTERS XI-XII

**7** $Na_2CO_3 = 46$ 1%, NaCl = 53 9%

## CHAPTERS XIV-XV

**4** CO = 18 c c, $H_2$ = 16 c c, $CO_2$ = 16 c c **14** CO

## CHAPTER XVI

**21.** 66 1% **26.** 94 0% Too high % of nitrogen

**37.** $N_2O$, $NH_2OH$

## CHAPTERS XIX-XX

**4.** Expansion of 18 c c **21.** 40% S, 60% O

**30.** $Na_2SO_4$, $10H_2O \xrightarrow{\text{heat}} Na_2SO_4 + 10H_2O$

## CHAPTER XXI

**14.** $ClO_2$, equation, p 284

## CHAPTERS XXII-XXIV

**4** Mercurous compound

## CHAPTERS I-XXVII

**29** (*a*) Eq wt = 28, 71 4% of metal (*b*) $Na_2S_2O_4$ **37** 54 7%

## CHAPTERS XXVIII-XXXII

**13** 30 0% $NH_4Cl$ **14** 0 184N

**16** (*a*) The element is oxidised from the bivalent state to the tervalent state by iodine, and to the quadrivalent state by ferric iron.

(*b*) The reducing metal is converted into a bivalent salt by ferric sulphate and into a tervalent salt by permanganate

**19** 14 28% **20** 21 9%

**25** (*a*) 21 6 c c *N*/10 NaOH and 28 8 c c *N*/10 $KMnO_4$
(*b*) 134 8 c c *N*/10 $K_2Cr_2O_7$

## CHAPTER XXXIII

**2.** No, because $P/T$ is not a constant **5.** 25 2

**7** 39,350 cm /sec at 0°, 84,950 cm /sec at 1000°, $5\ 49 \times 10^{-14}$ ergs at 0°, $2\ 56 \times 10^{-13}$ ergs at 1000°

**12.** 226

## CHAPTER XXXIV

**4** $CH_3CH=CH_2$

## CHAPTER XXXVI

**3.** $p_{CO_2} = 130\ 5$ mm, $p_{CO} = 610\ 3$ mm **6** $Cl_2$

**7.** 49 6 mm **8** 27 4% **9** 80 5%, $C_2H_4Br_2$

## CHAPTER XXXVII

**2.** 3·46 atm **3** 2 04 atm **4** 6 91 atm **10** 9 83 atm

## CHAPTER XXXVIII

**2** 116. **3.** 92 2, 17 2 atm **4** 91 **5** 153

**6** 75% dissociated Since the acid is strong, dissociation will be practically complete at *N*/100

**7.** 236 **8.** 342 **9** 30 1

**10.** M = 341, normal, M = 42 2, $i = 1\ 77$, dissociated into ions, M = 48 5 **13.** 210

## CHAPTER XL

**1.** (*a*) 21,750 cal, (*b*) 21,170 cal **2.** − 16,000 cal

**5.** 321,960 cal **6.** 1032K

**7** 33,900 cal, 2,292 cal Heat of reaction at constant pressure will be 2292 cal greater than that at constant volume

**8.** 29,650 cal **9.** 9385 cal per gram **10.** 99,420 cal

## CHAPTER XLI

**1.** (*a*) 0 903 (*b*) 0 543 **4** 80 0% **7** 3 15% **8.** 79 7%

**9.** 17 7%, 16 5%, 16 0%, 17 2%, 19 5%, 20 9% Degree of dissociation shows a minimum about 320° Below this temperature dissociation is exothermic, above it, endothermic

**12** (*a*) 99 6% (*b*) $2\ 62 \times 10^4$ (*c*) 1% $NH_3$

**13** (*a*) 17 6%, 31 7%, (*b*) 30 5, 22 6 The increase in the dissociation of hydrogen iodide shows that it is an endothermic decomposition for the given temperature range The fall in the vapour density with temperature is solely due to the expansion of the gases, since the number of molecules is not altered by dissociation

**17.** 0 9449 mol ester and water, 0 0551 mol alcohol, 4 0551 mols acid

**18** (*a*) $\frac{2}{3}$ of total is extracted, (*b*) $\frac{3}{4}$ of total is extracted

**19** (*a*) 8 33 grams, (*b*) 9 83 grams

**20** The apparent molecular weight is 120, therefore acetic acid is almost entirely in the form of " double " molecules $(CH_3\ CO\ OH)_2$ in the benzene

## CHAPTER XLII

**3.** $k_{mono} = 0\ 141, 0\ 141, 0\ 142, 0\ 138, 0\ 138, 0\ 119$

**4.** 2 41 hours

**5** $k_{mono} \times 10^4 = 6\ 55, 5\ 26, 4\ 91$, mean 5 57

**6** $k_{mono} \times 10^2 = 2\ 18, 2\ 21$

## CHAPTER XLIV

**5.** From glucose expt the molecular depression of the freezing-point = 1 854°, NaCl, $M_{obs} = 30\ 7$, $M_{calc} = 58\ 5$, KI, $M_{obs} = 87\ 1$, $M_{calc} = 166$, hence the halides are highly dissociated

**7** (*a*) 0 357 gram silver, 40 1 c c hydrogen

**8** $M_{obs} = 70\ 9$, $CrO_3 = 100$ (calc) If present as $H_2Cr_2O_7$ completely dissociated into 3 ions, M should be $100 \times \frac{2}{3} = 66\ 7$

**12** Transport number for $Ag^+ = 0\ 588$, for $NO_3^- = 0\ 412$ Value is too high for $Ag^+$, because an insufficient volume of the cathode solution was analysed

**13** Transport number for $H^+ = 0\ 83$, for $Cl^- = 0\ 17$

## CHAPTER XLV

**1.** Dibasic **9.** 1 53% **10** 3 45 1 **11.** 4·5%.

**12** 16 5 $ohms^{-1}$

**17** (*a*) pH = 3, (*b*) pH = 11, $5\ 62 \times 10^{-3}$, $2\ 0 \times 10^{-5}$, $2\ 5 \times 10^{-6}$.

**18.** (*a*) $1\ 34 \times 10^{-3}$, $4\ 15 \times 10^{-4}$, (*b*) 2 87, 3 38, (*c*) 4 78

**21** (*a*) 1 15%, (*b*) 0 00227% **24.** 1 084 gm $CaSO_4$

**25.** 0 0159 gram

## REVISION PROBLEMS IN PHYSICAL CHEMISTRY

**1.** 226 **2.** 7 61 gm, 84 6 **3.** 50% **4.** 82 3%

**5.** 44 0 **6.** 3 36 gm, 2 52 gm **7.** 71 1% **8.** 982 cm.

**9.** 35 **10.** $3\frac{1}{4}$ pints **11.** 60, 4 7 atm

**12** 5,580 cals., 13,940 cals.

**13** If concentrations are expressed in partial pressures, $K = 3.52$, but if in g.-mols per litre, $K = 0.0446$

**14** 0.12 millimols $H_2$, 18.1 millimols iodine, 11.8 millimols hydrogen iodide, (*a*) none, (*b*) none (*c*) new equilibrium is 0.30 millimols $H_2$, 14.4 millimols iodine, 10.2 millimols hydrogen iodide

**15** $Cu(NH_3)_4^{++}$

**16** The phenol in the chloroform layer has twice the molecular weight of that in the aqueous layer for the higher concentrations, but in dilute solution (first set of figs.) the dissociation of the molecules in the chloroform layer is appreciable

**17** $Na = 0.215$, $OH = 0.785$ **18** $1.55 \times 10^{-3}$

**19** $10^{-7}$, 7 **20** 11, 3, 2.70 **21** $1.71 \times 10^{-12}$, $1.42 \times 10^{-2}$

**22** 0.0329 g.-mols, $3.56 \times 10^{-5}$

## CHAPTERS XLVIII-L

**1** Contraction on explosion = 20 c.c., further contraction = 10 c.c.

## CHAPTERS LIII-LIV

**12** 88

## PROBLEMS IN ORGANIC CHEMISTRY Pp. 849-850

**1** $C_5H_{10}O$, $CH_3CO.CH_2.CH_3$ **2** $CH_3C{\equiv}N$

**3** $CH_3CH_2CH_2COOH$ $(CH_3)_2CHCOOH$, $C_2H_5COOCH_3$, $CH_3COOC_2H_5$ $HCOOCH_2CH_2CH_3$ $HCOOCH(CH_3)_2$ also hydroxyaldehydes and ketones *e.g.* $HOCH_2CH_2CHO$, acetoin $CH_3CH(OH)CO.CH_3$, etc., and dioxan, $O\langle\begin{smallmatrix}CH_2.CH_2\\CH_2.CH_2\end{smallmatrix}\rangle O$

**4** 10 c.c.

**5** Ethyl oxalate $(COOC_2H_5)_2$

$(COOC_2H_5)_2 + 2NH_3 = (CO.NH_2)_2 + C_2H_5OH$,

$(CO.NH_2)_2 + 2NaOH = (CO.ONa)_2 + 2H$

$(COONa)_2 + H_2SO_4 = Na_2SO_4 + CO + CO_2 + H_2O$

**6** $C_8H_6O_4$, basicity = 2

**7** $C_3H_7OH + HBr = C_3H_7Br + H_2O$

**8** $C_4H_{11}N$, $CH_3CH_2CH_2CH_2NH_2$ $\begin{smallmatrix}CH_3\\CH_3\end{smallmatrix}\rangle CHCH_2NH_2$, $\begin{smallmatrix}C_2H_5\\CH_3\end{smallmatrix}\rangle CHNH_2$ (*d* and *l*) $(CH_3)_3CNH_2$ $CH_3CH_2CH_2NHCH_3$, $(CH_3)_2CHNHCH_3$, $CH_3CH_2NHCH_2CH_3$, $(CH_3)_2NCH_2CH_3$

**9** $M = 165.5$, $C_4H_6O_4$

**10** $C_4H_{10}O$, $CH_3CH_2CH_2CH_2OH$, $(CH_3)_2CHCH_2OH$, $\begin{smallmatrix}C_2H_5\\CH_3\end{smallmatrix}\rangle CHOH$, $(CH_3)_3COH$, $CH_3CH_2OCH_2CH_3$, $CH_3OCH_2CH_2CH_3$, $CH_3OCH(CH_3)_2$

**11** Acetamide $CH_3CO.NH_2$

**12** Empirical formula $C_2H_3O_3$, probably tartaric acid of molecular formula, $C_4H_6O_6$

**13** $CH_3CH_2CH_2NH_2$, or $(CH_3)_2CHNH_2$

**14** $CH_3CO.OH$, $HOCH_2CH_2CO.OH$, $CH_3CH(OH)CO.OH$

**15** Acetamide, $CH_3CO.NH_2$

**16** $A = CH_3CO.NH_2$, $B = CH_3NH_2$ $C = CH_3OH$, $D = H_2CO$

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# LOGARITHMS

| | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 1 2 3 | 4 5 6 | 7 8 9 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **10** | 0000 | 0043 | 0086 | 0128 | 0170 | 0212 | 0253 | 0294 | 0334 | 0374 | 5 9 13<br>4 8 12 | 17 21 26<br>16 20 24 | 30 34 38<br>28 32 36 |
| **11** | 0414 | 0453 | 0492 | 0531 | 0569 | 0607 | 0645 | 0682 | 0719 | 0755 | 4 8 12<br>4 7 11 | 16 20 23<br>15 18 22 | 27 31 35<br>26 29 33 |
| **12** | 0792 | 0828 | 0864 | 0899 | 0934 | 0969 | 1004 | 1038 | 1072 | 1106 | 3 7 11<br>3 7 10 | 14 18 21<br>14 17 20 | 25 28 32<br>24 27 31 |
| **13** | 1139 | 1173 | 1206 | 1239 | 1271 | 1303 | 1335 | 1367 | 1399 | 1430 | 3 6 10<br>3 7 10 | 13 16 19<br>13 16 19 | 23 26 29<br>22 25 29 |
| **14** | 1461 | 1492 | 1523 | 1553 | 1584 | 1614 | 1644 | 1673 | 1703 | 1732 | 3 6 9<br>3 6 9 | 12 15 19<br>12 14 17 | 22 25 28<br>20 23 26 |
| **15** | 1761 | 1790 | 1818 | 1847 | 1875 | 1903 | 1931 | 1959 | 1987 | 2014 | 3 6 9<br>3 6 8 | 11 14 17<br>11 14 17 | 20 23 26<br>19 22 25 |
| **16** | 2041 | 2068 | 2095 | 2122 | 2148 | 2175 | 2201 | 2227 | 2253 | 2279 | 3 6 8<br>3 5 8 | 11 14 16<br>10 13 16 | 19 22 24<br>18 21 23 |
| **17** | 2304 | 2330 | 2355 | 2380 | 2405 | 2430 | 2455 | 2480 | 2504 | 2529 | 3 5 8<br>3 5 8 | 10 13 15<br>10 12 15 | 18 20 23<br>17 20 22 |
| **18** | 2553 | 2577 | 2601 | 2625 | 2648 | 2672 | 2695 | 2718 | 2742 | 2765 | 2 5 7<br>2 4 7 | 9 12 14<br>9 11 14 | 17 19 21<br>16 18 21 |
| **19** | 2788 | 2810 | 2833 | 2856 | 2878 | 2900 | 2923 | 2945 | 2967 | 2989 | 2 4 7<br>2 4 6 | 9 11 13<br>8 11 13 | 16 18 20<br>15 17 19 |
| **20** | 3010 | 3032 | 3054 | 3075 | 3096 | 3118 | 3139 | 3160 | 3181 | 3201 | 2 4 6 | 8 11 13 | 15 17 19 |
| **21** | 3222 | 3243 | 3263 | 3284 | 3304 | 3324 | 3345 | 3365 | 3385 | 3404 | 2 4 6 | 8 10 12 | 14 16 18 |
| **22** | 3424 | 3444 | 3464 | 3483 | 3502 | 3522 | 3541 | 3560 | 3579 | 3598 | 2 4 6 | 8 10 12 | 14 15 17 |
| **23** | 3617 | 3636 | 3655 | 3674 | 3692 | 3711 | 3729 | 3747 | 3766 | 3784 | 2 4 6 | 7 9 11 | 13 15 17 |
| **24** | 3802 | 3820 | 3838 | 3856 | 3874 | 3892 | 3909 | 3927 | 3945 | 3962 | 2 4 5 | 7 9 11 | 12 14 16 |
| **25** | 3979 | 3997 | 4014 | 4031 | 4048 | 4065 | 4082 | 4099 | 4116 | 4133 | 2 3 5 | 7 9 10 | 12 14 15 |
| **26** | 4150 | 4166 | 4183 | 4200 | 4216 | 4232 | 4249 | 4265 | 4281 | 4298 | 2 3 5 | 7 8 10 | 11 13 15 |
| **27** | 4314 | 4330 | 4346 | 4362 | 4378 | 4393 | 4409 | 4425 | 4440 | 4456 | 2 3 5 | 6 8 9 | 11 13 14 |
| **28** | 4472 | 4487 | 4502 | 4518 | 4533 | 4548 | 4564 | 4579 | 4594 | 4609 | 2 3 5 | 6 8 9 | 11 12 14 |
| **29** | 4624 | 4639 | 4654 | 4669 | 4683 | 4698 | 4713 | 4728 | 4742 | 4757 | 1 3 4 | 6 7 9 | 10 12 13 |
| **30** | 4771 | 4786 | 4800 | 4814 | 4829 | 4843 | 4857 | 4871 | 4886 | 4900 | 1 3 4 | 6 7 9 | 10 11 13 |
| **31** | 4914 | 4928 | 4942 | 4955 | 4969 | 4983 | 4997 | 5011 | 5024 | 5038 | 1 3 4 | 6 7 8 | 10 11 12 |
| **32** | 5051 | 5065 | 5079 | 5092 | 5105 | 5119 | 5132 | 5145 | 5159 | 5172 | 1 3 4 | 5 7 8 | 9 11 12 |
| **33** | 5185 | 5198 | 5211 | 5224 | 5237 | 5250 | 5263 | 5276 | 5289 | 5302 | 1 3 4 | 5 6 8 | 9 10 12 |
| **34** | 5315 | 5328 | 5340 | 5353 | 5366 | 5378 | 5391 | 5403 | 5416 | 5428 | 1 3 4 | 5 6 8 | 9 10 11 |
| **35** | 5441 | 5453 | 5465 | 5478 | 5490 | 5502 | 5514 | 5527 | 5539 | 5551 | 1 2 4 | 5 6 7 | 9 10 11 |
| **36** | 5563 | 5575 | 5587 | 5599 | 5611 | 5623 | 5635 | 5647 | 5658 | 5670 | 1 2 4 | 5 6 7 | 8 10 11 |
| **37** | 5682 | 5694 | 5705 | 5717 | 5729 | 5740 | 5752 | 5763 | 5775 | 5786 | 1 2 3 | 5 6 7 | 8 9 10 |
| **38** | 5798 | 5809 | 5821 | 5832 | 5843 | 5855 | 5866 | 5877 | 5888 | 5899 | 1 2 3 | 5 6 7 | 8 9 10 |
| **39** | 5911 | 5922 | 5933 | 5944 | 5955 | 5966 | 5977 | 5988 | 5999 | 6010 | 1 2 3 | 4 5 7 | 8 9 10 |
| **40** | 6021 | 6031 | 6042 | 6053 | 6064 | 6075 | 6085 | 6096 | 6107 | 6117 | 1 2 3 | 4 5 6 | 8 9 10 |
| **41** | 6128 | 6138 | 6149 | 6160 | 6170 | 6180 | 6191 | 6201 | 6212 | 6222 | 1 2 3 | 4 5 6 | 7 8 9 |
| **42** | 6232 | 6243 | 6253 | 6263 | 6274 | 6284 | 6294 | 6304 | 6314 | 6325 | 1 2 3 | 4 5 6 | 7 8 9 |
| **43** | 6335 | 6345 | 6355 | 6365 | 6375 | 6385 | 6395 | 6405 | 6415 | 6425 | 1 2 3 | 4 5 6 | 7 8 9 |
| **44** | 6435 | 6444 | 6454 | 6464 | 6474 | 6484 | 6493 | 6503 | 6513 | 6522 | 1 2 3 | 4 5 6 | 7 8 9 |
| **45** | 6532 | 6542 | 6551 | 6561 | 6571 | 6580 | 6590 | 6599 | 6609 | 6618 | 1 2 3 | 4 5 6 | 7 8 9 |
| **46** | 6628 | 6637 | 6646 | 6656 | 6665 | 6675 | 6684 | 6693 | 6702 | 6712 | 1 2 3 | 4 5 6 | 7 7 8 |
| **47** | 6721 | 6730 | 6739 | 6749 | 6758 | 6767 | 6776 | 6785 | 6794 | 6803 | 1 2 3 | 4 5 5 | 6 7 8 |
| **48** | 6812 | 6821 | 6830 | 6839 | 6848 | 6857 | 6866 | 6875 | 6884 | 6893 | 1 2 3 | 4 4 5 | 6 7 8 |
| **49** | 6902 | 6911 | 6920 | 6928 | 6937 | 6946 | 6955 | 6964 | 6972 | 6981 | 1 2 3 | 4 4 5 | 6 7 8 |

| | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 1 2 3 | 4 5 6 | 7 8 9 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **50** | 6990 | 6998 | 7007 | 7016 | 7024 | 7033 | 7042 | 7050 | 7059 | 7067 | 1 2 3 | 3 4 5 | 6 7 8 |
| **51** | 7076 | 7084 | 7093 | 7101 | 7110 | 7118 | 7126 | 7135 | 7143 | 7152 | 1 2 3 | 3 4 5 | 6 7 8 |
| **52** | 7160 | 7168 | 7177 | 7185 | 7193 | 7202 | 7210 | 7218 | 7226 | 7235 | 1 2 2 | 3 4 5 | 6 7 7 |
| **53** | 7243 | 7251 | 7259 | 7267 | 7275 | 7284 | 7292 | 7300 | 7308 | 7316 | 1 2 2 | 3 4 5 | 6 6 7 |
| **54** | 7324 | 7332 | 7340 | 7348 | 7356 | 7364 | 7372 | 7380 | 7388 | 7396 | 1 2 2 | 3 4 5 | 6 6 7 |
| **55** | 7404 | 7412 | 7419 | 7427 | 7435 | 7443 | 7451 | 7459 | 7466 | 7474 | 1 2 2 | 3 4 5 | 5 6 7 |
| **56** | 7482 | 7490 | 7497 | 7505 | 7513 | 7520 | 7528 | 7536 | 7543 | 7551 | 1 2 2 | 3 4 5 | 5 6 7 |
| **57** | 7559 | 7566 | 7574 | 7582 | 7589 | 7597 | 7604 | 7612 | 7619 | 7627 | 1 2 2 | 3 4 5 | 5 6 7 |
| **58** | 7634 | 7642 | 7649 | 7657 | 7664 | 7672 | 7679 | 7686 | 7694 | 7701 | 1 1 2 | 3 4 4 | 5 6 7 |
| **59** | 7709 | 7716 | 7723 | 7731 | 7738 | 7745 | 7752 | 7760 | 7767 | 7774 | 1 1 2 | 3 4 4 | 5 6 7 |
| **60** | 7782 | 7789 | 7796 | 7803 | 7810 | 7818 | 7825 | 7832 | 7839 | 7846 | 1 1 2 | 3 4 4 | 5 6 6 |
| **61** | 7853 | 7860 | 7868 | 7875 | 7882 | 7889 | 7896 | 7903 | 7910 | 7917 | 1 1 2 | 3 4 4 | 5 6 6 |
| **62** | 7924 | 7931 | 7938 | 7945 | 7952 | 7959 | 7966 | 7973 | 7980 | 7987 | 1 1 2 | 3 3 4 | 5 6 6 |
| **63** | 7993 | 8000 | 8007 | 8014 | 8021 | 8028 | 8035 | 8041 | 8048 | 8055 | 1 1 2 | 3 3 4 | 5 5 6 |
| **64** | 8062 | 8069 | 8075 | 8082 | 8089 | 8096 | 8102 | 8109 | 8116 | 8122 | 1 1 2 | 3 3 4 | 5 5 6 |
| **65** | 8129 | 8136 | 8142 | 8149 | 8156 | 8162 | 8169 | 8176 | 8182 | 8189 | 1 1 2 | 3 3 4 | 5 5 6 |
| **66** | 8195 | 8202 | 8209 | 8215 | 8222 | 8228 | 8235 | 8241 | 8248 | 8254 | 1 1 2 | 3 3 4 | 5 5 6 |
| **67** | 8261 | 8267 | 8274 | 8280 | 8287 | 8293 | 8299 | 8306 | 8312 | 8319 | 1 1 2 | 3 3 4 | 5 5 6 |
| **68** | 8325 | 8331 | 8338 | 8344 | 8351 | 8357 | 8363 | 8370 | 8376 | 8382 | 1 1 2 | 3 3 4 | 4 5 6 |
| **69** | 8388 | 8395 | 8401 | 8407 | 8414 | 8420 | 8426 | 8432 | 8439 | 8445 | 1 1 2 | 2 3 4 | 4 5 6 |
| **70** | 8451 | 8457 | 8463 | 8470 | 8476 | 8482 | 8488 | 8494 | 8500 | 8506 | 1 1 2 | 2 3 4 | 4 5 6 |
| **71** | 8513 | 8519 | 8525 | 8531 | 8537 | 8543 | 8549 | 8555 | 8561 | 8567 | 1 1 2 | 2 3 4 | 4 5 5 |
| **72** | 8573 | 8579 | 8585 | 8591 | 8597 | 8603 | 8609 | 8615 | 8621 | 8627 | 1 1 2 | 2 3 4 | 4 5 5 |
| **73** | 8633 | 8639 | 8645 | 8651 | 8657 | 8663 | 8669 | 8675 | 8681 | 8686 | 1 1 2 | 2 3 4 | 4 5 5 |
| **74** | 8692 | 8698 | 8704 | 8710 | 8716 | 8722 | 8727 | 8733 | 8739 | 8745 | 1 1 2 | 2 3 4 | 4 5 5 |
| **75** | 8751 | 8756 | 8762 | 8768 | 8774 | 8779 | 8785 | 8791 | 8797 | 8802 | 1 1 2 | 2 3 3 | 4 5 5 |
| **76** | 8808 | 8814 | 8820 | 8825 | 8831 | 8837 | 8842 | 8848 | 8854 | 8859 | 1 1 2 | 2 3 3 | 4 5 5 |
| **77** | 8865 | 8871 | 8876 | 8882 | 8887 | 8893 | 8899 | 8904 | 8910 | 8915 | 1 1 2 | 2 3 3 | 4 4 5 |
| **78** | 8921 | 8927 | 8932 | 8938 | 8943 | 8949 | 8954 | 8960 | 8965 | 8971 | 1 1 2 | 2 3 3 | 4 4 5 |
| **79** | 8976 | 8982 | 8987 | 8993 | 8998 | 9004 | 9009 | 9015 | 9020 | 9025 | 1 1 2 | 2 3 3 | 4 4 5 |
| **80** | 9031 | 9036 | 9042 | 9047 | 9053 | 9058 | 9063 | 9069 | 9074 | 9079 | 1 1 2 | 2 3 3 | 4 4 5 |
| **81** | 9085 | 9090 | 9096 | 9101 | 9106 | 9112 | 9117 | 9122 | 9128 | 9133 | 1 1 2 | 2 3 3 | 4 4 5 |
| **82** | 9138 | 9143 | 9149 | 9154 | 9159 | 9165 | 9170 | 9175 | 9180 | 9186 | 1 1 2 | 2 3 3 | 4 4 5 |
| **83** | 9191 | 9196 | 9201 | 9206 | 9212 | 9217 | 9222 | 9227 | 9232 | 9238 | 1 1 2 | 2 3 3 | 4 4 5 |
| **84** | 9243 | 9248 | 9253 | 9258 | 9263 | 9269 | 9274 | 9279 | 9284 | 9289 | 1 1 2 | 2 3 3 | 4 4 5 |
| **85** | 9294 | 9299 | 9304 | 9309 | 9315 | 9320 | 9325 | 9330 | 9335 | 9340 | 1 1 2 | 2 3 3 | 4 4 5 |
| **86** | 9345 | 9350 | 9355 | 9360 | 9365 | 9370 | 9375 | 9380 | 9385 | 9390 | 1 1 2 | 2 3 3 | 4 4 5 |
| **87** | 9395 | 9400 | 9405 | 9410 | 9415 | 9420 | 9425 | 9430 | 9435 | 9440 | 0 1 1 | 2 2 3 | 3 4 4 |
| **88** | 9445 | 9450 | 9455 | 9460 | 9465 | 9469 | 9474 | 9479 | 9484 | 9489 | 0 1 1 | 2 2 3 | 3 4 4 |
| **89** | 9494 | 9499 | 9504 | 9509 | 9513 | 9518 | 9523 | 9528 | 9533 | 9538 | 0 1 1 | 2 2 3 | 3 4 4 |
| **90** | 9542 | 9547 | 9552 | 9557 | 9562 | 9566 | 9571 | 9576 | 9581 | 9586 | 0 1 1 | 2 2 3 | 3 4 4 |
| **91** | 9590 | 9595 | 9600 | 9605 | 9609 | 9614 | 9619 | 9624 | 9628 | 9633 | 0 1 1 | 2 2 3 | 3 4 4 |
| **92** | 9638 | 9643 | 9647 | 9652 | 9657 | 9661 | 9666 | 9671 | 9675 | 9680 | 0 1 1 | 2 2 3 | 3 4 4 |
| **93** | 9685 | 9689 | 9694 | 9699 | 9703 | 9708 | 9713 | 9717 | 9722 | 9727 | 0 1 1 | 2 2 3 | 3 4 4 |
| **94** | 9731 | 9736 | 9741 | 9745 | 9750 | 9754 | 9759 | 9763 | 9768 | 9773 | 0 1 1 | 2 2 3 | 3 4 4 |
| **95** | 9777 | 9782 | 9786 | 9791 | 9795 | 9800 | 9805 | 9809 | 9814 | 9818 | 0 1 1 | 2 2 3 | 3 4 4 |
| **96** | 9823 | 9827 | 9832 | 9836 | 9841 | 9845 | 9850 | 9854 | 9859 | 9863 | 0 1 1 | 2 2 3 | 3 4 4 |
| **97** | 9868 | 9872 | 9877 | 9881 | 9886 | 9890 | 9894 | 9899 | 9903 | 9908 | 0 1 1 | 2 2 3 | 3 4 4 |
| **98** | 9912 | 9917 | 9921 | 9926 | 9930 | 9934 | 9939 | 9943 | 9948 | 9952 | 0 1 1 | 2 2 3 | 3 4 4 |
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