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INORGANIC CHEMISTRY

BY

E. I. LEWIS, M.A. (CANTAB.), B.Sc. (LOND)., F.C.S.

HEAD MASTER OF THE METHODIST COLLEGE, BELFAST

PART I.

Cambridge

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PREFACE TO THE COMPLETE WORK.

THIS volume is the outcome of an attempt to provide a chemistry course for a class of boys of whom some had been promoted from a lower science set, and the rest had come over from the classical side. The course had therefore to be both a revision and an introduction.

In preparing the course an endeavour was made to follow the strictly logical method; hence no compound of unknown composition could be employed for chemical purposes except with the object of determining its composition. Acids, for instance, could not be used to supply hydrogen, nor potassium chlorate to supply oxygen. This imposed a somewhat unusual order and the introduction of some discussions not generally included in an elementary course. It demanded also the postponement of the convenient methods of preparing gases. Although at first sight these restrictions may appear fatal to efficiency, I found them in the event altogether advantageous. As soon as the student has obtained a little of a given substance and has recognised it by its properties, it is both quicker and less wasteful to supply him with sufficient for his experiments. Take, for instance, sulphur dioxide. As soon as he has obtained some of the gas by burning sulphur, the student can use a supply from a syphon for further experiments, and he may prepare it for himself by the usual method when he has sufficient knowledge to suggest the explanation

of the reaction. It is then not merely the 'Preparation of Sulphurous Oxide' but the 'Reduction of Sulphuric Acid.'

Nearly every lesson begins with the study of a simple reaction. This is followed by a discussion involving the suggestion of further experiments, as far as possible such as are suitable for the laboratory. Each lesson was carefully prepared beforehand, but the boys, in class, by their own reasoning, questioning, and suggestion, led me to alter radically the plans of many chapters. The changes were justified by the experience that other forms followed very much the same line of reasoning.

The notes of these discussions taken by the classes were not always sufficient for evening revision; for the more successful the lessons, the fewer were the notes taken, and, even after a few hours, the clearest impressions were likely to become obscured by subsequent work in other subjects. For this and other reasons it seemed desirable to incorporate the subject matter of the lessons in a logical order.

The encouragement I have received during the preparation of the book has led me to hope that it will supply a want felt by other teachers.

The book is meant to be used for the revision of lessons, chapter by chapter. A lasting impression of the important points of each lesson is most easily insured by setting a few problems each evening. These should be graduated. At the end of most chapters in Part I. some exercises and problems have been collected; these are supplementary to the text, and are more particularly suitable for a second revision; many of them are of scholarship standard.

The Atomic Theory has been offered later than usual, and is then studied thoroughly. There is perhaps no more insidious enemy to sound thinking than an undigested formula, and with the formulae the nomenclature based upon them must be postponed also. The experience of many teachers emphasises the advantage of this order of treatment.

I have endeavoured to avoid everything savouring of dogmatism. It is not always easy to recognise, and, but for Mr Neville's interest, many more instances would have survived.

In Part II. I have endeavoured to apply to senior forms a method which has promised well with junior boys. In this part there is a greater abundance of information; this is introduced not for committing to memory, but as material to support the arguments. The Arsenic family is not discussed systematically as it provides an excellent opportunity for the exercise of discretion in the use of reference books: it follows as an exercise on Chapter XXIII. As all the salts of importance are mentioned in the body of the book, there seems no advantage in devoting a special part to 'Metallic' Chemistry, especially as this branch can be learned most intelligently with the aid of reference books during the study of the Periodic Classification. Chapter XXVIII. is devoted mainly to the 'non-metallic' compounds of the elements concerned.

It will be noticed that greater prominence than usual has been given to 'out-of-doors' chemistry. More than any other, this part of chemistry secures the sympathetic interest of beginners.

In order to make the book more complete an Introductory Chapter has been added. This is mainly for reference. No experiments have been given in proof of the Gas Laws, or the other physical laws of almost equal importance. To treat these subjects adequately is possible in a physical text-book only; they are discussed briefly, but, I hope, sufficiently.

The examinations of the Oxford and Cambridge Joint Board (L. C., S. C., and H. C.), the University Local Examinations (senior and junior), and the London Matriculation Examination are fully covered. The Army Examination syllabus is sufficiently provided for by Part I.

I have to thank Messrs Longmans for the loan of Figures 44

and 105 from Mr Newth's text-book; the Cambridge University Press for Figures 101, 102, 103, and Lothar Meyer's Curve from Miss Freund's book, from which I have also derived the data for many of the problems; and Mr E. T. Bucknell and the Editors of the *School World* for Figure 52, and for permission to include the methods for obtaining the equivalent masses of sodium and of aluminium, &c. (pages 63 and 66).

Throughout the preparation of the book I have received unstinted help from my colleagues Mr H. O. Hale and Mr H. M. King; and Mr W. E. Cross of the Whitgift School has helped me with the proofs. I am greatly indebted to Dr H. O. Jones for much invaluable criticism in Part I., and to Mr F. H. Neville for both criticism and advice throughout the book. I have endeavoured to take full advantage of these. For the first part of Chapter XXXI. I have to thank Dr F. F. Blackman. I must also thank the University Press for the generous manner in which they have met my wishes.

E. I. L.

OUNDLE,
September, 1907.

The issue of the second edition of this book has enabled me to correct many oversights due to hasty reading of the proofs of the first edition. Advantage has been taken to bring it up to date (pp. 234 and 236). I should like to add that the diagrams are in most cases given to illustrate the more difficult experiments, and some few commercial processes. A large number of important experiments need no description. Many of these are only referred to in the text. Thus, although Chapter XIII. is entirely practical, the estimations alone are specially described.

E. I. L.

July, 1908.

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INTRODUCTORY CHAPTER.

It is expected that the student is already familiar with enough of Physics to understand gaseous pressure, the barometer, density of solids, liquids and gases, change of state, evaporation, boiling and vapour pressure, expansion of gases, Boyle's and Charles' Laws.

This introductory chapter discusses some of the above subjects but the student is recommended to revise them in his Physics book. For instance Glazebrook's *Hydrostatics*, Chapter VII, and *Heat*, Chapters VII, VIII, IX.

CHEMISTRY is that branch of natural science which deals with the intimate composition of bodies.

Every substance is distinguished from all others by definite physical properties. The study of these properties is the occupation of physicists and mineralogists. The physicist determines the density, specific heat, expansibility and other properties of water in its three phases, steam, liquid water and ice, and the change of energy which takes place when one phase changes to another. The mineralogist studies the forms assumed by water in its solid phase, ice. The chemist makes use of these properties to recognise water, but himself seeks to know, regardless of phase, what water is:—is it a body capable of yielding others or not? And to answer such a question he often employs heat energy and the energy of the electric current. Again the physicist determines the heat and light energy liberated when petroleum burns. The geologist studies the situations in which it is found and the conditions under which it was formed in the earth. The results of their investigations are valuable to the chemist, who for his part finds how the oil may still be formed, of what it consists, and what substances are formed by its combustion. The mathematician is interested in the flight and the kinetic energy of the bullet, but the chemist enquires what happens to the gunpowder during its explosion.

Water.

Of all bodies with which the chemist deals water is the most abundant in nature and is the most important both chemically and physically; the first step to its examination is to obtain it in a state of purity. Rain is the purest natural water, but even rain, as it descends, dissolves air and solids suspended in the air. In the soil new substances are dissolved and small undissolved particles may be held in suspension. To remove the latter from spring or tap water, the water is passed through filters. In the laboratory porous paper filters are used. Dissolved substances are not removed by filtration, and the water is freed from them by distillation, a process to be described later.

Water as a solvent of air.

We can prove, by heating it, that ordinary tap water contains dissolved air; the air is expelled because gases are less soluble in hot water than in cold. A flask is provided with a well-fitting cork through

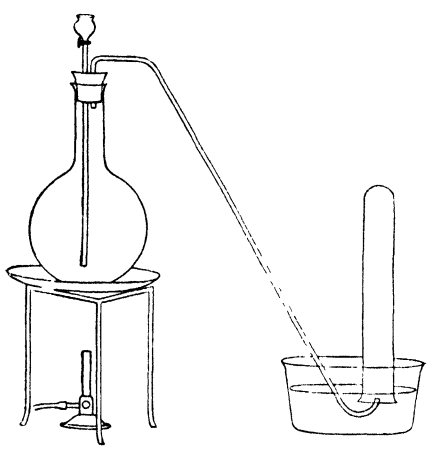


Fig. 1.

which pass a funnel, for the admission of water, reaching nearly to the bottom of the flask, and a delivery tube leading to a 'pneumatic' trough, the end of the delivery tube being submerged (Fig. 1). Water is introduced into the flask until all air has been displaced and the tap is turned off. A cylinder full of water is now inverted on a 'beehive' shelf over the upturned end of the delivery tube. The water in the flask is heated to boiling; air is expelled, which, passing

through the delivery tube and rising in the collecting cylinder, displaces the water therein. After boiling, any air which has stopped in the neck of the flask is displaced by more water. A considerable volume of air may be thus expelled, some of which will redissolve in the water over which it is confined. The boiled water aerates itself again on exposure to the air.

For some experiments described later in this book, the use of air-free water is essential. By a modification of the foregoing experiment a supply may be obtained and preserved. The delivery tube is bent downwards to dip under water in a beaker, the funnel is replaced by a short length of tubing which ends just inside the cork, and may be closed outside by rubber tubing and a clip (Fig. 2). Boiled water

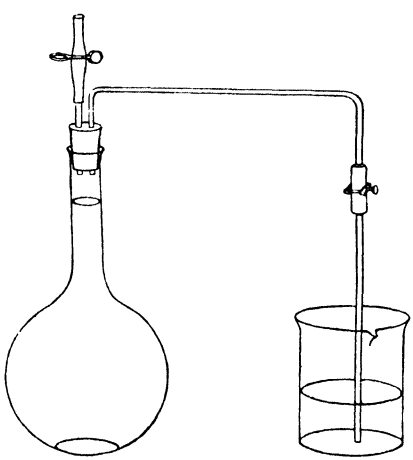


Fig. 2.

is placed in the flask and heated again with the short tube open and the delivery tube placed under water boiling in the beaker. When all the air in the flask has been expelled by steam the flame is removed and the open tube is clamped. As the flask cools boiling water is forced into it from the beaker, and finally the delivery tube is clamped.

The solubility of air in cold water may be roughly determined by the following method. A long graduated tube (Fig. 3) is filled with air-free cold water and inverted over a dish of the same. A few cubic centimetres of air are passed

to the top through flexible rubber tubing, which is then quickly withdrawn and the volume of air observed. The tube is stoppered by a cork through which passes a short glass tube, which can be closed by clamped rubber tubing. The air is thoroughly agitated with the water, the tube again inverted in the dish of water and the communicating tube unclamped. Water passes into the tube equal in volume to that of the dissolved air. The volume of undissolved air is observed, and the volume dissolved found by difference. It will be found that about 3 cubic centimetres of air dissolve per 100 cubic centimetres of water.

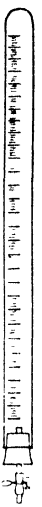


Fig. 3.

Water a solvent for liquids.

Water dissolves all gases to a greater or smaller extent. The solubility of liquids shows greater variation. Petroleum is practically insoluble in water, and when the two liquids are shaken together an emulsion of mixed droplets of water and petroleum is formed from which, on standing, the two substances separate in two layers, the upper and lighter consisting entirely of petroleum and the lower entirely of water. Ether is slightly soluble in water, and water is slightly soluble in ether; after agitation together, although two layers are formed, each layer contains both liquids, the lighter solution of water in ether floats on the heavier solution of ether in water.

Alcohol and water, or oil of vitriol and water, are soluble in each other in all proportions, and, once mixed, are very difficult to separate again. The mixing of either liquid with water is accompanied by contraction in volume. A 100 c.c. graduated flask is half filled with water and then carefully filled to the mark with alcohol. After shaking, the liquid will be found to fall short of the mark, and if water is run in from a burette, the contraction will be found equal to about 3 c.c.

Contraction usually accompanies solution and dilution, a fact it is very important to remember. Thus supposing a solution containing 10 grams of nitre in 100 c.c. of solution is to be made, that amount of the solid is placed in a graduated flask and water is added, little by little, with constant shaking,

until at last the mark is reached. If water is added to the mark before solution, then contraction will take place on shaking: this must be thorough or different parts of the solution will differ in concentration. If the solution is made by pouring 100 c.c. of water upon 10 grams of nitre there will be rather more than 100 c.c. of solution. Solutions of definite concentration should therefore be prepared by the first method.

Measuring vessels.

The vessels used for measuring liquids are the graduated cylinder, the burette, the marked (graduated) flask and the pipette. The graduated cylinder, having a large internal diameter, gives roughly approximate measure. The flask is used as described above; since it has a neck of comparatively small diameter, the percentage error need be only very slight. The pipette is used for delivering accurately (without shaking) definite small volumes of liquid, whilst a burette delivers within certain limits (up to 50 c.c.) any desired volume.

Water as a solvent for solids.

Solids differ widely in solubility. Thus sugar is very soluble, common salt is moderately soluble, whilst marble, sand and sulphur are practically insoluble. Some mixtures of a soluble and an insoluble substance are easily separated and their percentage compositions estimated. For the sake of illustrating a number of operations frequently carried out in the laboratory, we shall describe fully the quantitative examination of a mixture of very finely powdered sand and salt.

Quantitative estimation of a mixture of sand and salt.

A quantity of the mixture is weighed out and placed without loss in a beaker. This may be done in one of two ways.

Method I. By difference.

A quantity of the mixture is weighed in a stoppered tube, shaken out into the beaker, and the tube with any still adhering solid weighed again. The difference between the weighings is the amount of substance taken. This method is quite the best, and, if the same tube, whose weight is approximately known, is kept for all weighings, a suitable amount of solid to shake out can always be gauged.

Method II. The mixture is weighed in a watch-glass

which has previously been accurately weighed. In this case all that has been weighed out must be placed in the beaker. As much as possible is shaken in and the rest washed in by a stream of water from a wash bottle.

This method is convenient when an exact given weight of any solid is to be dissolved. If the solution is to be made in a flask, a glass funnel is placed in the neck and all the particles are swept by a stream of water into the flask.

The wash bottle is a flask fitted as in Fig. 4. Air is blown into it by the mouthpiece and a stream of water is discharged through the jet which is attached to the delivery tube by a short piece of rubber tubing, so that the fingers of the hand which holds the wash bottle may direct the current of water.

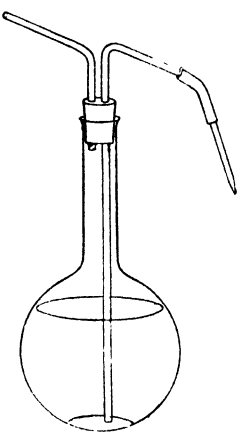


Fig. 4.

Pure water is now added to the mixture and the beaker and its contents are heated on a sand bath.

Glass vessels such as beakers should rarely be heated with a naked flame, and whenever such heating is necessary the flame should be brought gradually to the beaker and then kept in constant motion, but never allowed to touch the glass above the liquid. A better plan is to interpose a wire gauze which, by conduction, distributes the heat more evenly and does not readily allow the flame to pass through. The best practice is to place the beaker in a sand bath, that is upon dry sand contained in an iron tray: this ensures more gradual heating with good distribution of the heat; the cooling is also more gradual.

To hasten solution the liquid should be constantly stirred with a glass rod.

To avoid breaking the beaker the end of the rod is covered with a narrow band of rubber tubing.

When the salt appears to be dissolved the solution is 'decanted' (that is, poured from above the sediment) on to a filter paper and collected in a clean beaker.

In order that none of the solution may be lost, the outside rim of the beaker is lightly smeared with vaseline, and the liquid is guided to the apex of the filter paper by pouring it down the glass rod held against the rim of the beaker (Fig. 5).

When all the solution has been filtered, the undissolved sand is 'washed' by shaking it with pure water, and the

washings are likewise passed through the filter. The beaker is now held just over the funnel and the sand transferred to the filter paper with the aid of the glass rod. Finally every trace of sand is washed out of the beaker and down the rod by a well-directed stream of water from the wash bottle, the beaker in this case being held obliquely downwards. Any of the salt solution which may have remained in the pores of the paper is now washed through into the beaker, and the sand brought to the apex of the cone.

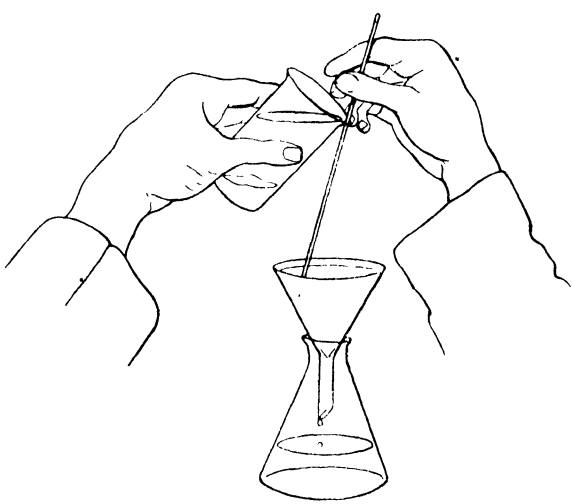


Fig. 5.

If coarse grained sand has been used the above operations with the filter may be omitted, and the solution and washings poured directly into an evaporating basin.

The salt solution is evaporated in a small weighed porcelain dish, more solution being added from time to time as water is driven off.

A beaker is less suitable for evaporation than the evaporating dish, for the latter is shallow and exposes a relatively large surface of liquid and, an additional advantage, it has no angles.

The heating is begun on a sand bath, and the boiling is not allowed to become too vigorous. When the solution has become so concentrated that there is danger of loss by spurting, the basin is raised above the sand on a clay triangle, or

it may be placed on the drying cone. In either case the desiccation is completed by convection currents of hot air. In the meantime the funnel with the filter paper has been placed in a drying cone standing on a sand bath (Fig. 6), the hot air ascending circulates around the funnel and effectually dries the paper and the sand.

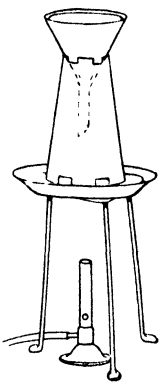


Fig. 6.

If the dry weight of the filter is known, or if a similarly dried filter paper of the same kind is used as a counterpoise, the weight of the sand may be found by difference: otherwise the sand is transferred to a weighed crucible as follows. The crucible and filter paper are placed on a piece of glazed paper and the sand dislodged from the filter by holding this in the fingers and gently working the sand into the crucible. The remainder of the sand is obtained by unfolding the filter and brushing it off with a small camel hair pencil. Any sand which misses the crucible is readily recovered from the glazed paper.

When fine powders are filtered it is impossible to dislodge all from the filter paper in this way, and the paper is burnt to ashes in the crucible by the method described in Chapter VII.

Saturation and super-saturation.

Most solids are more soluble at high than at low temperatures, and it is a matter of considerable importance to know the exact solubility of a substance at any given temperature. Before we show how this may be accomplished, the meaning of the term 'solubility' must be clearly understood. If some of the substance which photographers call 'hypo' is placed in a given quantity of water at ordinary temperatures and continually stirred, a condition will be reached such that no more of it will dissolve: the solution of 'hypo' and the undissolved solid 'hypo' are in equilibrium, the solution is said to be saturated, and the quantity of solid dissolved in that quantity of solution (or sometimes of solvent) is the solubility of 'hypo' at that temperature. If now the temperature is lowered some of the dissolved solid will be deposited—assuming again the solid state—until a new saturated solution is left, which at the new temperature can remain in equilibrium with the undis-

solved solid. If however the temperature is raised the new conditions are such that more solid dissolves to form saturated solutions of greater concentration.

When a hot saturated solution, *not* in contact with solid 'hypo' is left undisturbed to cool slowly, contrary to expectation, no solid is deposited during the cooling, and the solution may be kept unchanged for months provided no solid 'hypo' is allowed entrance; but, if a small crystal is added to the cold solution, solid 'hypo' is deposited until the solution is again at the concentration proper for a solution saturated at that temperature. The solution was evidently *not* in equilibrium with its own solid: it is said to be 'super-saturated.' The term 'solubility' is applied only to saturated, that is, to solutions which, in contact with their solids, neither dissolve more of the solid nor deposit any from solution.

Solubility curves.

In order to show at a glance the 'solubility' of any substance at different temperatures, the solubility is ascertained at a number of temperatures and a 'solubility curve' drawn connecting the plotted points, Solubilities at other temperatures may then be read from such a curve by interpolation. 'Hypo,' for reasons that will be mentioned in Part II, is an unsatisfactory substance for experiment, but common salt and saltpetre (nitre) answer the purpose very well. Water and an excess of salt (or nitre) are agitated together for some time in a small flask and the temperature of the solution is observed. Twenty cubic centimetres are carefully withdrawn by means of a pipette and run into a weighed evaporating dish. The quantity of salt dissolved is determined as before. Usually the solubility is expressed as so many grams of salt per 100 cubic centimetres of solution; when it is expressed otherwise the solution must be weighed before evaporation.

For the determination of solubility at higher temperatures a conical flask is heated in a water bath, that is, suspended in water which is being gradually heated. The solution must be vigorously stirred all the time, otherwise different parts will have different concentrations. At intervals, 20 c.c. of the solution are quickly withdrawn and evaporated.

As the pipette is probably colder than the solution, salt will crystallise out on the glass; it should be washed through into the dish. This pre-

caution introduces a slight error, for pipettes are graduated to deliver the required volume of liquid without washing.

In accurate work modified methods are employed which avoid errors, one simple precaution is to keep specially graduated pipettes in a tube immersed in the same water bath.

From results obtained by the above method the following curves were constructed (Fig. 7).

It will be noticed that the solubility of common salt increases slightly but regularly with increase of temperature, but that the solubility of nitre increases to a greater and

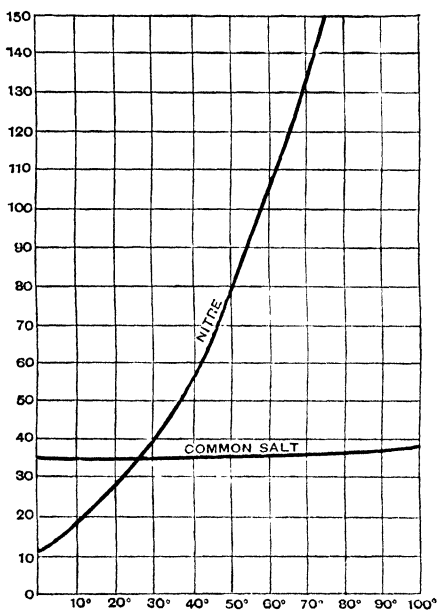


Fig 7.

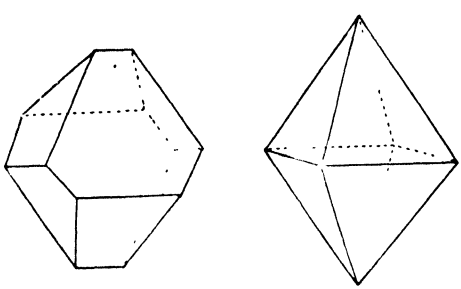
greater degree with the increase of temperature. At low temperatures nitre is the less soluble, at 25° C. both salts have the same solubility, but the curves diverge widely at higher temperatures.

By taking advantage of this difference, a mixture of salt and nitre may be separated more or less completely. The mixture is treated with successive small quantities of boiling water, which are decanted, and on cooling deposit nitre. The deposited solid is then treated as the original mixture. This method is called 'fractional crystallisation.' It is a most important operation in technical chemistry. The process varies considerably according

to the constituents of the mixtures and the relative quantities present, it therefore needs much experience to apply successfully. Some mixtures *cannot* be separated by fractional crystallisation, for a variety of reasons, some of which will appear later in the following chapters.

Crystallisation.

When a solution of alum saturated at a temperature a little above that of the laboratory is allowed to cool slowly, and then to evaporate spontaneously, the solid is deposited in crystals all of which are obviously of the same pattern (Fig. 8 a), and if the angles between the faces are measured the corresponding angle of different crystals will be found equal. These crystals grow as if the solution preferred to deposit the solid on the crystals already formed rather than to create new ones. If the cooling or the evaporation is rapid, there is less choice, and a larger number of smaller crystals are deposited. The smaller crystals are purer than the larger inasmuch as the larger are likely to



Figs. 8 a and b.

enclose vesicles of the solution; hence, to obtain a pure salt, a hot solution is rapidly cooled by a stream of cold water upon the containing vessel.

In making large crystals of alum slowly, it will be seen that the crystals are better formed where contact with the solution is not impeded by proximity to other crystals or to the sides of the vessel. When a small crystal is suspended by a thread in the middle of a saturated solution, and all other crystals are being constantly removed, it may be grown several inches from point to point, and, growth being equally favoured in all directions, it assumes the form of a perfect octohedron (Fig. 8 b). If we compare with it the tabular crystals formed on the bottom of the vessel in the ordinary

way, we shall recognise these as crystals whose perfect development has been hindered in certain directions. Whenever alum is grown under favourable conditions, it will crystallise in octohedra.

In a similar manner crystals of Borax, Blue Vitriol, Washing Soda, 'Hypo' and Saltpetre should be grown and their perfect crystals carefully drawn and studied. Common salt crystallises out as cubes. In salt deposits large cubes[1] of several inches edge are occasionally found.

Purification of water.

It is very important to have at command water which contains neither solids nor gases in solution. We have seen that the latter can be expelled by boiling; the solids remain, hence pure water is obtained

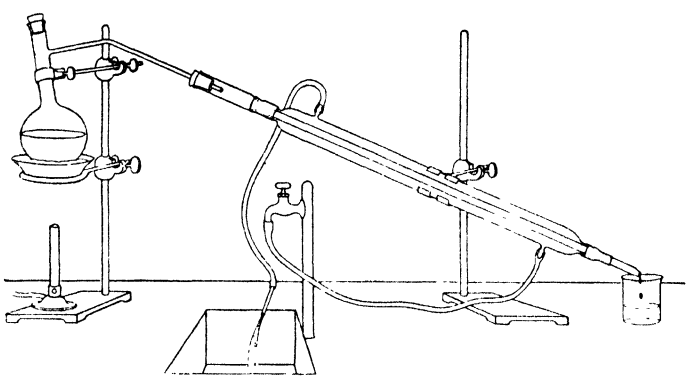


Fig. 9.

by the condensation of steam. This process is called 'distillation[2].' Distilled water may be obtained in small quantity by the simple process of boiling water in a retort whose neck leads into a flask which floats in water and is kept cold by a stream of water: the greater part of the steam condenses in the flask. A better apparatus is shown in Fig. 9. The water is boiled in a flask provided with a side tube and the steam is condensed in a Liebig's condenser. This consists of a tube surrounded by a jacket, through which passes an upward stream of cold water. The condensed

[1] 'Halite' from ἅλς = salt, and λίθος = stone.

[2] Distillare = to fall in drops.

water drips into the receiver. Only the middle portion is collected, for the expelled gases escape with the earliest and some solid substances may be vapourised with the last portions. For the production of distilled water on a large scale, stills are made of block tin and the condensers are worms of the same metal (or of silver) which is not acted on by water.

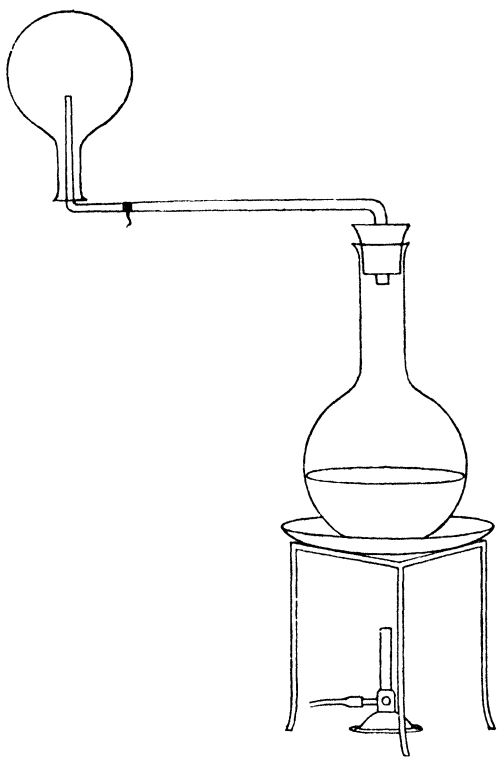


Fig. 10.

Glass is slightly dissolved by water, particularly by hot water: new vessels are especially likely to be attacked, and an earthy deposit is formed when even distilled water is boiled down in them. Hence vessels in which pure water or a solution of definite concentration is to be stored are first 'steamed'; Fig. 10 shows how this operation is performed.

Distinctive properties

As we have mentioned above, substances may be recognised and distinguished by their physical properties; as a rule more than one such

property is necessary. The most important physical properties for the purpose are colour, density, solubility, boiling and melting points, and crystalline form. Thus water is sufficiently distinguished by its melting and boiling points: other liquids are known which boil at about 100° C., and some solids are known which melt at about 0° C., but no other substance has both fixed points. It is usual therefore to begin the description of a substance with its physical properties. Water is a colourless, odourless, tasteless liquid and the most important of solvents. It is the standard substance for comparing densities of liquids and solids. The ratio of the density of any substance to that of water is called the relative density or specific gravity.

The metric system unit of mass—1 gram—is that of 1 cubic centimetre of water at its greatest density, + 4° C. Hence in metric units density and specific gravity are represented by the same number. The unit of heat is likewise derived from water. That quantity of heat which is absorbed by 1 gram of water in being raised from 0° C. to 1° C. is called the calorie[1]. Water is also the standard for comparing the 'specific heat' of bodies, that is, the quantity of heat required to raise 1 gram of the substance through 1 degree of temperature.

Solids.

Although colour is a useful property for the recognition of solids, too much significance may be attached to it, for certain substances are known whose colour varies with circumstances. The solubility is of great value provided one is dealing with a pure solvent. The melting point is easy to determine and is useful when a substance is pure. For bodies which fuse below 100° C., a water bath may be used. The powdered solid, sufficient easily to cover the bulb of a thermometer, is placed in a test tube which is immersed in water. The water is very slowly heated with constant stirring and the melting point observed. For higher temperatures—up to 200°—a bath of oil of vitriol is used.

As oil of vitriol gives dangerous wounds, great care must be exercised in using it.

For temperatures higher than 200° baths of other liquids are used, or some special method may be followed.

Crystalline form is a most important property, and the

[1] Calor = heat.

student is urged to obtain and draw as many as possible of the crystals of the important substances mentioned in this book, so that, whenever one is mentioned, its appearance comes unbidden to the mind.

For purposes of classification and recognition, mineralogists have arranged all crystalline forms in six systems. The classification is based upon the relative lengths of the chief axes of crystals, and their inclination to one another. These are directly related to the angles formed by the intersecting surfaces. Although the definitions of each system read simply, the complexity of forms included in any one system is so great as to render their exposition in an elementary book of little practical value. Suffice it to say that one system—the Regular System—has three axes of the same length, each being at right angles to both the others. The simplest forms in this system are the cube and the regular octohedron. As we have seen, alum separates from solution in octohedra. Common salt usually crystallises in cubes, it may however, in certain circumstances, crystallise in regular octohedra, or even in quite complex forms. Thus a drop of saturated brine placed on a glass slide and heated over a flame yielded microscopic crystals of the shape shown in Fig. 11.

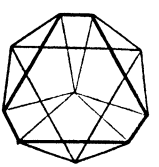


Fig. 11.

Hence, for the purpose of identification, it is important to produce crystals under ordinary conditions.

Inasmuch as the other systems are mentioned in the text, the following short descriptions are appended for reference:

I. **Asymmetric** (or triclinic) **System.** Three unequal oblique axes.
   Ex. Blue Vitriol.

II. **Monosymmetric** (or monoclinic) **System.** Three unequal axes, two of which intersect in an oblique angle, whilst the third is perpendicular to the other two.
   Exs. Gypsum, Felspar, Washing Soda.

III. **Rhombic** (or prismatic) **System.** Three unequal axes at right angles. (Rhombic in section.)
   Exs. Aragonite, Sulphur, Barytes, Nitre.

IV. **Quadratic** (or tetragonal) **System.** Three axes at right angles, of which two are equal.
   Ex. Cassiterite.

V. **Rhombohedral System.** Three equal axes, but not at right angles.
Exs. Calcite, Bismuth, Quartz.
Hexagonal System. Four axes, three of equal length.
Ex. Beryl.

Liquids.

Liquids are distinguished by colour, smell and density. As liquids have a fairly large coefficient of expansion the temperature of the determination of density must be given. The boiling point is most useful for the identification of pure liquids: the method of determination will be found in Glazebrook's *Heat.*

In this connection we may state that, with no exception, all gases have been liquefied, by cold or pressure, or both together.

It has been found, however, that for every gas there is a temperature above which the greatest obtainable pressure will not cause liquefaction. This temperature is called the **critical temperature,** and the pressure which just suffices to liquefy the gas at that temperature is called the critical pressure. These two points are constants of importance for each gas. The critical temperature must not be confused with the boiling point, which is much lower than the critical temperature.

The boiling point is that temperature at which the vapour pressure of the liquid is equal to 1 atmosphere (760 mm.); the temperature at which the liquid boils *under the ordinary atmospheric pressure.*

Liquids will evaporate below their boiling points, and will disappear entirely, provided their vapour is constantly removed.

Miscible liquids may, with more or less difficulty, be separated by the process of 'fractional distillation.' Thus, if a mixture of alcohol and water is heated, mainly alcohol is evolved at first, followed by fractions containing a greater and greater proportion of water. The fractions, collected in separate receivers, are again fractionally distilled. The operation is tedious, and special apparatus ('still heads') are used for shortening the process.

Advantage is taken of the fact that at lower pressures liquids boil at lower temperature for the separating of liquids (or for concentrating solutions), of which some of the constituents are injuriously affected by heat.

A flask (Fig. 12) is fitted into another similar flask and both are exhausted. The flask is then warmed to a safe temperature in a water bath. To avoid 'bumping' a fine stream of air bubbles is allowed to pass through the solution or mixture, through a finely drawn out tube. The pressure may be registered by the interposition of a gauge.

Gases.

The majority of gases are colourless and many are without smell. Some are both coloured and odorous. For gases colour, smell and taste are important distinguishing properties, and serve in some cases as the best indication of their presence, even when greatly diluted with air. All gases are soluble to some extent in water, air is amongst the least soluble, whilst ammonia—of which 1100 litres are dissolved by 1 litre of water at 0° C.—is the most soluble. Some gases on contact with water behave peculiarly, and cannot be said to have a solubility in water (Part II.).

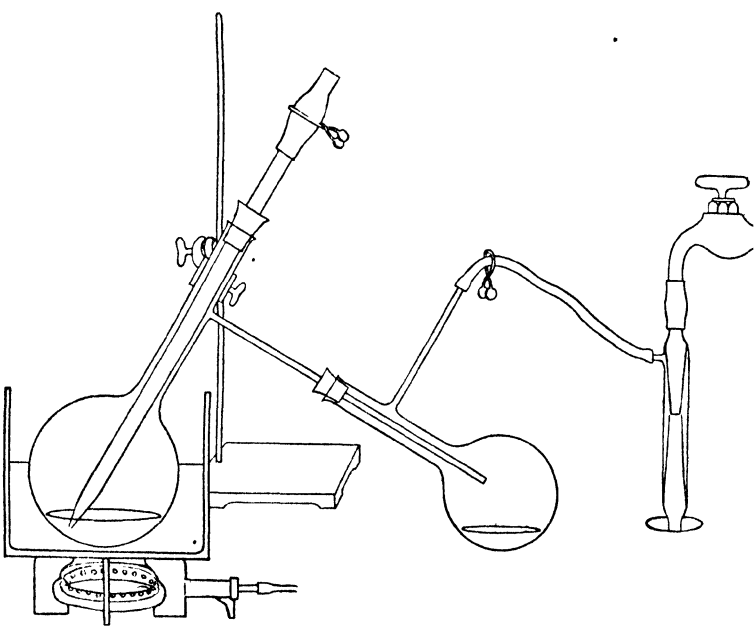


Fig. 12.

The density of gases, although a physical property, is of extreme importance in chemistry, and the student must have clear ideas concerning it. There are two laws which are true for all the common gases, namely, Boyle's Law and Charles' Law.

The first states that the volume of a given mass of gas varies inversely with the pressure, that is to say, the

density of a gas varies directly as the pressure. Hence it is necessary to compare the densities of gases at a standard pressure. This standard pressure is fixed at that exerted by a column of mercury 760 mm. high, the 'normal' atmospheric pressure at sea level: it is referred to shortly as 760 mm.

According to Charles' Law, all gases, when heated under constant pressure, increase in volume by the same relative increment for every degree rise in temperature, that is, all gases have the same coefficient of volume expansion. This is equal to $\frac{1}{273}$rd part of their volume at 0° C.

It follows that if the volume is kept constant the pressure must increase in the same proportion.

Hence, for the comparison of gaseous densities, a standard temperature must also be fixed: the melting point of ice 0° C. is chosen for this purpose.

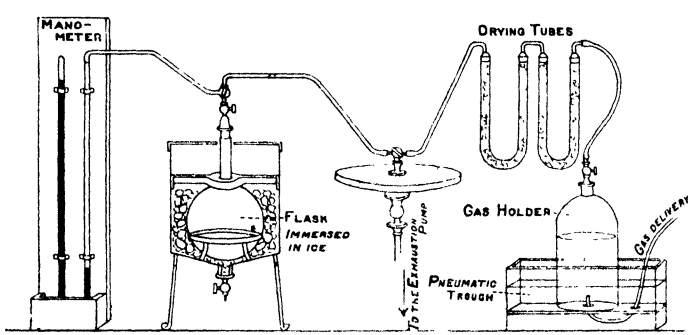


Fig. 13.

These two points—0° C. and 760 mm.—are called the standard temperature and pressure; hereinafter they will always be designated by the letters **S.T.P.** For comparing the densities of gases, air is commonly used, but in this book we shall usually employ for that purpose a gas which is very much lighter than air: this substance (hydrogen) is lighter, volume for volume, than any other gas, and therefore all gaseous specific gravities are represented as greater than unity. The specific gravity of air—of which 1 litre weighs 1·293 grams—referred to hydrogen is 14·45.

Regnault's method for determining the density of a gas

was to fill a globe of known capacity with the gas at S.T.P. and weigh it.

His apparatus and method are depicted in Fig. 13. He had two globes of the same mass and volume, one to hold the gas and the other (not included in the figure) to act as a counterpoise. He ascertained the capacity of the globe by weighing it first full of water at 4° C. and then vacuous. He surrounded it with melting ice, placed the space of manometer and globe in communication and exhausted both. The gas whose density was to be determined was very slowly admitted from the reservoir, through the drying tubes into the globe-manometer space. When the manometer registered a pressure of 760 mm., the globe was shut off, disconnected, dried thoroughly and weighed again.

It is not necessary to collect the gas at S.T.P., for, provided the actual temperature and pressure of the experiment are known, we can correct the experimental result by the two Gas Laws. Thus 300 c.c. of air collected at $t°$ C. and p mm. pressure would occupy at S.T.P. $300 \times \frac{p}{760} \times \frac{273}{273+t}$ cubic centimetres.

To take an example:—

Find the volume at S.T.P. of 1000 c.c. of air measured at 10° C. and 750 mm.

1000 c.c. at 750 mm. will occupy $1000 \times \frac{750}{760}$ c.c. at 760 mm. (Boyle's Law).

$(1000 \times \frac{750}{760})$ c.c. at 10° [273+10 absolute temperature] will occupy at 0° C. [A.T. = 273°] $(1000 \times \frac{750}{760}) \times \frac{273}{283}$ c.c. = 952 c.c.

The density of air may be found by the following experiment.

A round-bottomed flask of about 300 c.c. capacity is supplied with a well-fitting rubber stopper through which passes a short glass tube, which can be securely closed by clamped rubber tubing (Fig. 14). Its capacity is exactly determined by running water from a burette up to the mark reached by the stopper. About 20 to 30 c.c. of pure water are then left in the flask and the unclamped stopper inserted. The water is then boiled until the flask is filled with water and steam only. The rubber is clamped and the globe weighed cold. The flask is now unclamped

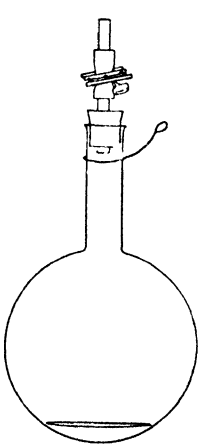


Fig. 14.

cautiously to prevent loss of vapour; air rushes in and the flask is weighed again. The volume of the air can be discovered by finding the volume of the water still remaining in the flask. The volume is corrected for temperature and pressure and a rough value for the density of air is obtained. One other correction must also be made because not all the water vapour condenses upon the cooling of the flask, hence the volume of the flask not occupied by liquid water is not wholly available for air. To obtain the true volume of the collected air we must deduct the volume of water vapour from the observed volume. The same result is achieved if we deduct from the barometric height the pressure exerted by this water vapour, that is to say, we correct for the pressure of the water vapour instead of its volume directly. This correction is easily made, because tables are constructed (Glazebrook's *Heat*, p. 130) showing the pressure exerted at all temperatures by water vapour in a space saturated with it. Thus, suppose the observed volume of the air was $300 - 10 = 290$ c.c. measured at 10° C. and 760 mm. At 10° C. the tables state that the aqueous vapour pressure is equal to that of 9·17 mm. mercury. Hence the air within the globe exerts a pressure of only $760 - 9{\cdot}17 = 750{\cdot}83$ mm. and the volume of the air at S.T.P. would be $\left(290 \times \frac{750{\cdot}83}{760} \times \frac{273}{283}\right)$ c.c.

The density of other gases may be compared with that of air by allowing them to displace air in a flask of known capacity, and by weighing the flask before and after the displacement.

The vapour density of substances which at ordinary temperatures are liquids may be determined, either by causing a known weight of the vapourised liquid to displace a measurable volume of air, or by filling a vessel of known capacity with the vapour at a known temperature, then sealing up the vessel and weighing it when cold (Chapter XII.). The volume and weight of the vapour being known and the temperature and pressure of the experiment being observed, the density under those conditions can be calculated. the specific gravity of the gas, referred to air, can be determined by finding the density of the air under the same conditions. It will be easily understood that, as the behaviour of all gases (at temperatures

far removed from the boiling point of their liquid phase) is represented by Boyle's and Charles' Laws, the same ratio is obtained by comparing with that of air at S.T.P. the density the vapour would have at S.T.P. if, instead of liquefying, it remained a gas on cooling. One litre of steam (if it did not condense at 100° C.) would at S.T.P. weigh ·8 gram. Its specific gravity is ·625 (air = 1) or 9 (hydrogen = 1).

The collection and storage of gases.

Gases which are only slightly soluble in water are usually collected by the displacement of water from inverted vessels. For this the 'pneumatic'[1] trough of Priestley is used. Gases which are moderately soluble in water may be collected, for immediate use, over hot water. Gases which are very soluble in water, or otherwise react with it, are collected by the displacement of air or in evacuated vessels. If the gas is lighter than air, it is collected by 'upward' displacement of air (Fig. 89). The gas is passed into an inverted jar by a delivery tube reaching to the top, as the vessel is filled the delivery tube is withdrawn, and finally the vessel closed either by a ground-glass disk or by a rubber stopper. Gases which are heavier than air are collected by 'downward' displacement, a method which differs from the last in the position of the receiver only (Fig. 47).

Gases must often be stored for future use. For this purpose the gasholder shown in Fig. 15 may be used. It is first filled with water and the taps above are closed; then it is placed in shallow water which covers completely the lowest tubulure.

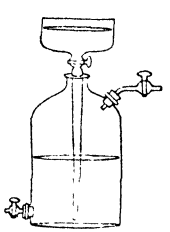


Fig. 15.

The stopper below is withdrawn, but the gasholder is still sealed by the water. Gas is now passed in through the tubulure, which also permits the escape of the displaced water. The stopper is replaced and the gasholder is ready for use. To obtain the gas, water is allowed to flow in from the funnel, expelling the gas through the side tube. A second jar may be used in place of the funnel (Fig. 16); water flows in at the bottom tubulure of the gasholder (or by a second tube passing through the

[1] πνεῦμα = air.

upper tubulure). With this latter apparatus the pressure may be nicely adjusted.

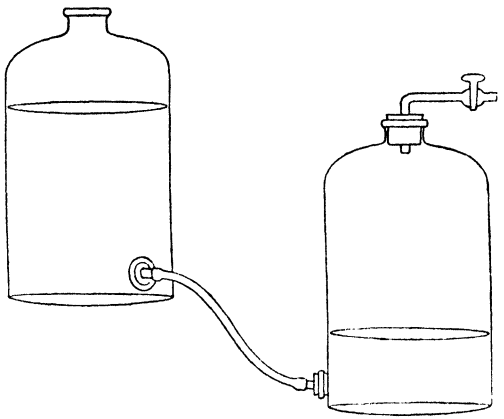


Fig. 16.

The apparatus of Fig. 17 is used when it is necessary to know the volume of gas evolved or displaced in any reaction.

This apparatus may be used to receive the air displaced by steam from a flask in determining the V.D. of steam.

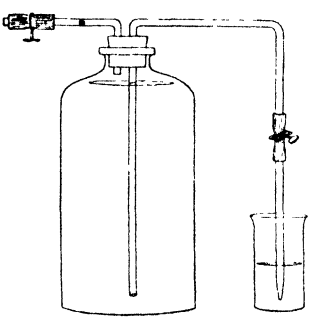


Fig. 17.

The whole apparatus must be perfectly *air-tight.* The gas enters by the short tube and expels its own volume of water through the long tube. The expelled water is collected in a beaker or a measuring cylinder. The delivery tube must reach below the surface of the expelled water. When the temperature is constant, raise the beaker until the water is at the same level in both vessels. Close the clip and remove the beaker. Correct for temperature and pressure.

Aspirators.

When a current of air is to be passed through any apparatus, it may either be forced through from a gasholder or 'drawn through' by an aspirator.

The air is really forced through by its own pressure to a region of lower pressure.

The form of aspirator differs with the experiment. The simplest form is a vacuous globe (Fig. 38), the volume of the air drawn in is identical with the capacity of the globe. The aspirator may also take the form of a large jar containing water, with the 'intake' tube reaching just below the stopper.

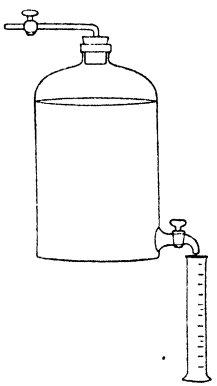


Fig. 18.

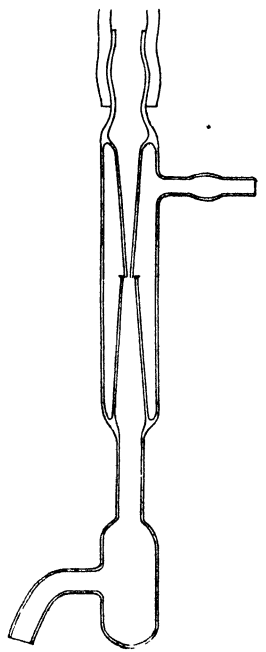


Fig. 19.

The water may be drawn off either by a siphon or by a tap near the bottom (Fig. 18). The volume of air which replaces the water is ascertained by measuring the volume of water which flows out. If it is not desired to collect the air drawn through, and if a rapid current must be aspirated, the water suction pump is very convenient. This pump (Fig. 19) acts by the principle of Sprengel's mercury pump (Glazebrook's *Hydrostatics*, p. 193).

Drying of gases.

The relative quantity of water vapour in the air can be determined by aspirating air through a series of weighed U-tubes containing reagents which

are hygroscopic[1], that is, will absorb water vapour (for the experiment see Glazebrook's *Heat*, p. 147). Such substances are constantly used for drying gases in chemical experiments. Amongst them are quicklime, oil of vitriol, and a white substance called fused calcium chloride: their chemical nature will be explained later; at present we are only concerned with their powerful hygroscopic properties. Fused calcium chloride is a light substance, and therefore very convenient for weighing. It is placed in U-tubes of thin glass, two such tubes are efficient to dehydrate a slow current of air.

When not in use the contents of the U-tubes are protected from moist air by means of caps made of a short piece of glass rod and a piece of junction tubing.

Oil of vitriol is a more efficient dehydrating agent than fused calcium chloride, but it is a heavy liquid (S.G. 1·84) and not so suitable for weighing; it is generally placed in a

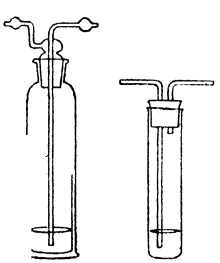


Fig. 20.

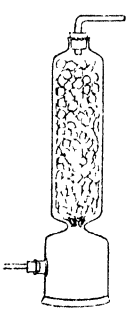


Fig. 21.

Dreschel tower (Fig. 20)—or some simple modification of this apparatus—and the gas to be dried is slowly bubbled through it; or pieces of broken glass or pumice-stone contained in U or straight tubes may be wetted by it and the gas passed through the tubes. Quicklime may sometimes be employed in cases where there are objections to the use of oil of vitriol and fused calcium chloride; it is packed in small pieces in a tube, or, better, in a vertical tower (Fig. 21).

When gases are to be stored **dry**, they may, with some exceptions, be collected over mercury.

[1] ὑγρός = damp, and σκοπῶ to examine.

Measurements of gases.

When a volume of gas is measured, it is obviously necessary to state the conditions under which the measurement is made, or to express the volume as so many cubic centimetres measured at S.T.P. Hence, in observing the volume of gas over mercury or water, the levels of the liquid within and without the measuring vessel must be equal, or else the difference in height must be estimated and the necessary deduction made from the height of the barometer (13·6 mm. water balances 1 mm. of mercury). But when gases are measured over water, the correction for aqueous vapour (p. 20) must always be made, for the vapour exerts a definite pressure and correspondingly depresses the column of water. When gases are collected over mercury, no such correction is necessary, as the pressure of mercury vapour at ordinary temperatures is negligible.

Heating and drying of solids.

It has been mentioned above that whenever a naked flame is used, it should be brought to glass vessels gradually and with a swaying motion, and should never be allowed to heat the vessel above the region of its contents, unless the material is specially resistent.

Porcelain vessels may be heated to any temperature, but at the beginning the heating, and at the end the cooling, should be gradual.

Besides the use of gauze, sand bath and drying cone, other methods are frequently adopted. The water bath is merely heated water, the temperature of which can be controlled. For a temperature of 100° C. a steam bath is used, and the vessel is then supported above the water, generally on porcelain rings (Fig. 22). For higher constant temperatures oil baths are in use, or air chambers. The heating in the drying cone can be, and should be, regulated by attention to the height of the flame. When a substance, which has been dried by any of the above methods, is to be weighed, it is generally placed in a 'desiccator'[1] to cool. A desiccator (Fig. 23) is a vessel made in two parts which fit together air-tight: it

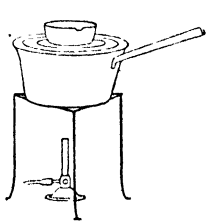


Fig. 22.

[1] Desicco = to dry.

contains a highly hygroscopic substance to attract water vapour. Many substances which are injuriously affected by heating are entirely dried in the desiccator. In this case the desiccator is exhausted frequently to hasten the evaporation of the moisture. Substances which are to be left open to the air, but protected from moisture, are sometimes placed in flasks whose stoppers carry a tube containing fused calcium chloride.

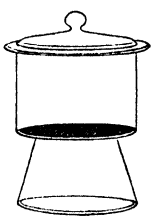


Fig. 23.

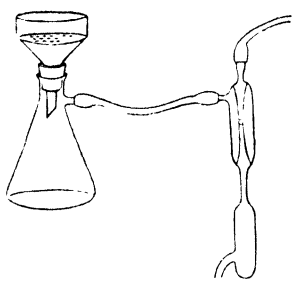


Fig. 24.

Much preliminary drying can be effected by the use of the Buchner filter funnel and a suction pump. This funnel has a flat perforated base on which the filter paper is placed. The filtrate is delivered into a special flask as shown in Fig. 24.

A simple form of this funnel can be made by passing an ordinary funnel and a short length of tubing through a cork which fits well into a boiling tube. To the short tube a piece of rubber tubing is attached, and air may be sucked through by the mouth. To prevent the rupture of the filter paper, the latter is strengthened by folding with it—outside—a circle of fine linen.

General Remarks.

Apparatus should be air-tight unless there is a special reason to the contrary.

Corks must be carefully bored. When they are fitted to glass tubing the latter must be held at the near end; severe cuts are given by the broken glass when this precaution is neglected, and valuable time is wasted.

Glass tubes should always be rounded at the ends, and delivery tubes, unless for special reasons, end flush with the

cork. An unnecessary length of tubing mars the appearance of the apparatus and may interfere with the experiment.

When rubber tubing is used for joining two pieces of glass tubing the latter should touch, unless a clip is to be used, or free play is needed.

All reagent bottles must be replaced directly the substance has been taken.

The golden rule for the majority of experiments is: use small quantities of reagents. As soon as you have acquired some knowledge use it to estimate beforehand convenient quantities of chemicals for the experiments. Try to become intelligently independent of detailed instructions.

Benches should be kept clean and dry, and no litter of any kind should be tolerated.

A balance is a delicate instrument and can only be kept serviceable by careful and intelligent use: on no account should reagents be allowed to come in contact with the scale pans.

All glass and porcelain vessels should be kept scrupulously clean.

To dry narrow tubing and flasks, a current of hot air is passed through them. The air may be blown from a hand or foot bellows along a glass tube, portions of which are heated in a flame.

Records of experiments must be made at the time, and so neatly that a fair copy is superfluous. Scrupulous cleanliness is necessary for this. All notes that admit of tabulation should be so recorded. No data that are necessary for the proper working out of results should be omitted. From the full notes the essential data can be abstracted when necessary. Diagrams of the apparatus used should always be included and all the precautions observed should be explained: these may be written in a margin in order not to interfere with the description. The description of the experiments should be concise; nothing of interest or importance should be omitted. Unexpected phenomena may find an explanation at a later date, and when they are the outcome of carelessness their records will act as warnings.

Your wits should be even more active in the laboratory

than in the class-room: unintelligent practical work means waste of material as well as of time.

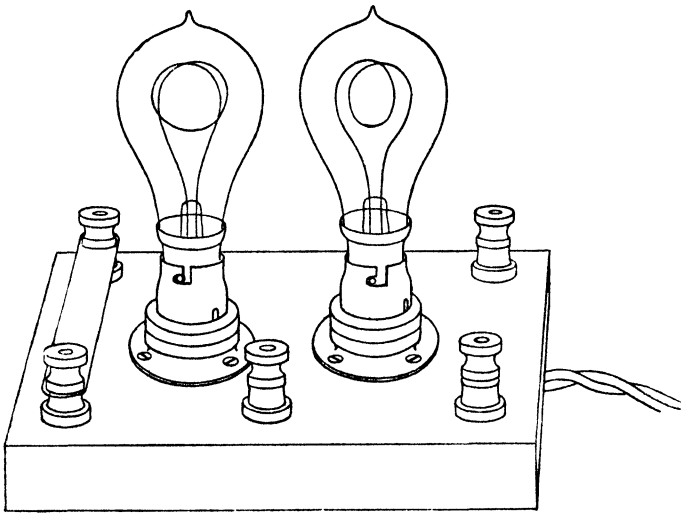


Fig. 25

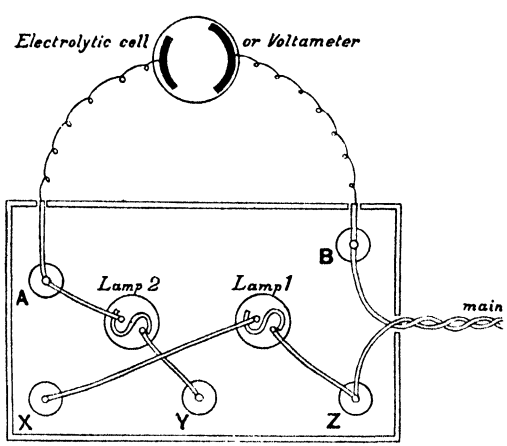


Fig. 26.

Plan of Resistance (from above).

Bar connections.

X to Y diverts current through both lamps *in series.*
X to A „ „ Lamp 1.
Y to Z „ „ Lamp 2.
X to A and Y to Z throws in both lamps in parallel.
B and Z must never be connected, otherwise there will be a short circuit.

Note. Electric current.

Many important experiments require a current of electricity and, if the main current used for lighting is continuous, this may be employed, unless an alternating current is required. The following apparatus is useful as a resistance (Fig. 25). It consists of two lamp sockets fixed into a board and the wiring is such that the current may be made to pass through one or both lamps by the interposition of metal bars between the terminals (Fig. 26).

When the current (from a 100 volt main) is passed through two 5-candle power lamps and then through a copper voltameter, a firmly adhering deposit of copper is obtained. For other experiments one or two 10- or 16-candle power lamps may be used. The resistance is very cheaply made and a whole class can be occupied at one time without any of the discomforts of a number of cells.

NOTE ON THE SOLUBILITY OF GASES.

The meaning of the term 'solubility,' as applied to gases, should be grasped surely. It is a common experience that a bottle, containing a solution of ammonia which has been saturated with the gas under the ordinary laboratory conditions of temperature and pressure, must even under the same conditions be opened with caution. Ammonia escapes, and will continue to escape until the concentration of the solution has decreased considerably. The original solution is not said to be supersaturated since it was in equilibrium with gaseous ammonia. When however the bottle is opened, and some gaseous ammonia diffuses into the air, the conditions are changed. The original solution is not in equilibrium with the gas under the new conditions, nor will a stable equilibrium be reached until, by preventing further diffusion of ammonia, the conditions may again become constant.

The following two 'laws' represent the behaviour of some gases.

Henry's Law (1803). The *mass* of a gas dissolved by a definite quantity of liquid is directly proportional to the pressure of the gas. Or,—with Boyle's Law,—the *volume* of a gas absorbed by a definite volume of liquid is independent of the pressure exerted by the gas.

Dalton's Law of Partial pressures. The mass of a gas dissolved from a mixture of gases is proportional to the pressure which that gas exerts, not to the total gaseous pressure. Or, the solubility of a gas is independent of the presence of other gases.

PROBLEMS. I.

1 gram of air occupies 773·3 c.c. at S.T.P.
1 litre of air weighs 1·2932 grams (approx. 1·3) at S.T.P.
1 litre of hydrogen weighs 0·089894 gram (approx. ·09) at S.T.P.

1. Describe the gasholder used in gasworks. Explain its action.

2. Draw a solubility curve for borax from the following data: 100 parts of water dissolve 2·83 parts of borax at 0° C., 4·65 parts at 10°, 7·88 parts at 20°, 11·9 at 30°, 17·9 at 40°, 27·41 at 50°, 40·43 at 60°, 57·85 at 70°, 76·19 at 80°, 116·66 at 90°, 201·43 at 100°.

3. Measure the angles and draw crystals of some of the following: Iceland Spar, Quartz, Fluor Spar, Galena, Pyrites, Felspar, Tourmaline, Apatite, Hornblende, Blende, Selenite and Carborundum.

4. 97·3 c.c. of air are collected over mercury at 754 mm. pressure and 15° C. What is its weight?

5. If the same volume of air is collected over water, find its true volume under the same and standard conditions. What is its weight?

6. What volume at 8° C. and 765 mm. will 5 grams of air occupy?

7. What volume under standard conditions will 1 gram of hydrogen occupy?

8. One gram of a certain gas was found to occupy 521·6 c.c. at 5° C. and 750 mm. What is its density relative to air and to hydrogen?

9. 0·147 gram of a certain gas collected in a tube over water occupied 108·2 c.c. at 10° and 760 mm. Excess height of water in tube 20·5 mm. What is its density relative to hydrogen? (Aq. v.p. at 10° C. = 9·2 mm.)

10. A laboratory specimen of oil of vitriol s.g. 1 84 contained 4% by weight of water. What volume must be taken in order to make up 250 c.c. of solution containing 49 grams of the pure substance per litre.

11. Describe the structure and action of the Berkefeld and Pasteur-Chamberland filters for drinking water.

12. Draw the solubility curve for Green Vitriol.

100 parts of water dissolve

at 10°	15°	33°	60°	90°	100° C.
61	70	151	263	370	333 parts of vitriol.

Comment on the solubility of the substance.

What is the solubility at 0° C.; at 17° C.; at 45° C.; at 110° C.?

Do you think your answers are equally trustworthy?

Commit to memory:

Log 760 = 2·8808, Log 273 = 2·4362,
Log ·08989 = $\bar{2}$·9537, Log 11·13 = 1·0464.

CHAPTER I.

WATER AND ITS CONSTITUENTS.

Electrolysis.

THE Electric Current produces different effects according to the nature of the substances that allow its passage.

When an electric current flows along a metal wire, no alteration occurs in the metal, although heat and magnetic effects may be produced. If the wire is cut the current does not cease to flow, provided the cut ends are in contact, and should they be drawn a short distance apart the circuit may still be found to be complete, a series of sparks passing between the terminals as an electric arc light. Increase the distance between the cut ends of the wire: the circuit is

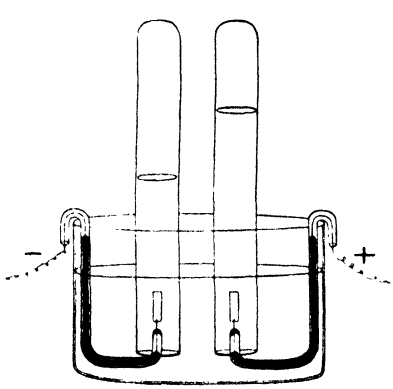


Fig. 27.

broken. The current will not cease if the ends still in contact are placed under absolutely pure water, but separate the ends by a short distance and a series of sparks may again

be observed. Increase the distance: the circuit is again broken. From this it appears that pure water is, like air, a bad conductor, whilst the metal wire is a good conductor of electricity.

If a little oil of vitriol is added to the water, currents of electricity easily pass; at the same time bubbles of colourless gas appear upon the ends of the metal wire and, disengaging themselves, rise to the surface. They may conveniently be collected under inverted tubes filled with water, as shown in Fig. 27. The terminals should be of platinum foil, and are called **electrodes**[1]; that at which the current is said to enter the water is distinguished as the positive electrode, or **anode**, that at which the current is said to leave the water as the negative electrode, or **kathode**[2].

A lecture bench apparatus shown in Fig. 28 is called a Voltameter, after Volta the Italian electrician. [Draw the apparatus, and describe its action.]

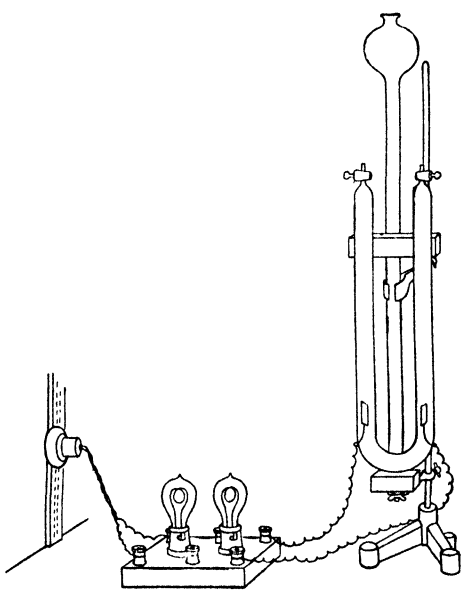


Fig. 28.

The current may be taken directly from the electric mains with the apparatus shown in Fig. 25 for a resistance.

[1] ἤλεκτρον, ὁδός = a way.
[2] κατά = downwards; ἀνά = upwards.

It will be observed that rather more than twice as much gas rises from the kathode as from the anode, and should the direction of the current be reversed, gas rises twice as fast from the new kathode as from the new anode.

These gases differ entirely in their properties. When inverted burettes filled with the gases are slowly depressed with the stopcocks open, a lighted match inflames the issuing kathode gas, whilst the anode gas is not inflamed, but will cause the match to burn more brightly. If a burning taper is thrust up into a jar of the kathode gas, it lights the gas but is itself extinguished. On the other hand, the anode gas cannot be ignited, but will cause the taper to burn more vigorously than in air. Hence we can easily distinguish these gases.

The selective faculty they showed in appearing at different electrodes foreshadowed inherent differences in their properties, and since unlike charges of electricity are known to attract one another, the gas which is evolved at the positive anode is called an **electro-negative** substance, whilst that which appears at the negative kathode is called an **electro-positive** substance. Substances which undergo decomposition when allowing the electric current to pass are called **electrolytes**[1].

In the electrolysis of water the anode gas is 16 times as heavy as the kathode gas. Being lighter than any known gas $\left(\frac{1}{14{\cdot}4}\text{ times as heavy as air}\right)$, the latter is generally used instead of air as the standard substance in determining specific gravities of gases. One litre of the kathode gas weighs ·09 gram at S.T.P.

Both gases are very slightly soluble in cold water: 100 c.c. of water, at 0° C., dissolves about 4 c.c. of the anode gas and about half the quantity of the kathode gas.

Both gases have recently been liquefied at very low temperatures by Sir James Dewar. The liquid of the kathode gas is colourless and under atmospheric pressure boils at 20·5° absolute temperature (−252·5° C.); the liquid of the anode gas is pale blue and boils 70° higher (−182·5° C.).

If we compare all the above properties with those of steam

[1] ἤλεκτρον, λύειν = to loose.

(gaseous water), we find none which would lead us to associate these gases with water; nevertheless it has been proved that during the electrolysis, only the water diminishes in quantity, which implies that the gases are set free by decomposition of the water, and this view is confirmed by the reproduction of pure water from them.

Combination.

For this purpose the electrolytic gases are collected together over mercury in a graduated glass tube called a eudiometer (Fig. 29). Platinum wires pierce its walls on opposite sides near the closed end and almost meet within. The passing of an electric spark causes explosion and the inside walls of the eudiometer are dimmed with moisture. At the time of the explosion the tube is pressed tightly on to a rubber pad to prevent expulsion of the mercury, and when the pressure is released, mercury enters and fills the whole tube save for the trace of water formed. By repeatedly introducing and exploding fresh quantities of the mixture, a supply of liquid is obtained having all the properties of pure water.



Fig. 29.

This experiment was first performed quantitatively by Cavendish in 1781.

Both gases were known before their relation to water was discovered. The kathode gas which had, up to that time, been called inflammable or combustible air, was renamed **Hydrogen**[1] from ὕδωρ = water, γεννᾶν = to produce. The anode gas had a year or two before been called **Oxygen**, an unfortunate choice, as we shall learn later on.

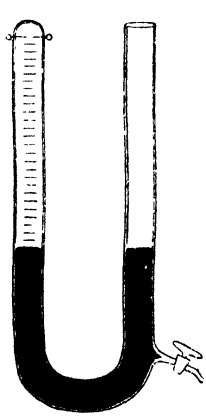


Fig. 30.

In the experiment just described the gases were exploded in exactly the proportion in which they are liberated by electrolysis, but the experiment may be varied by exploding them in other proportions. A eudiometer bent to the form of a U (Fig. 30) is more convenient than

[1] German Wasserstoff.

the straight tube. Hydrogen is first admitted and its volume determined, the mercury in both arms being brought to the same level with the aid of a stopcock. Oxygen is then let in and the new volume observed with the same precaution. The open end of the tube is now closed by the thumb and the gases submitted to the spark. The mercury is again brought to the same level in both limbs by pouring mercury in. If the volume of the hydrogen is twice that of the oxygen, the whole of the gas combines; but any excess of either hydrogen or oxygen remains uncombined.

The liquid water produced in the foregoing experiments occupies very little space, but if the conditions of the experiment are altered, so as to keep the product of the explosion in the gaseous state, its volume will be considerable; and it is obviously of interest to determine this volume. Water is gaseous above 100° C., therefore the closed limb of the eudiometer must be surrounded with the vapour of a substance which boils at a temperature well above 100° C. Such a substance is found in amyl alcohol which boils at 130° C.

A convenient apparatus is shown in Fig. 31. After the introduction of hydrogen the vapour of amyl alcohol must be passed through the jacketing tube until the thermometer inside it registers a constant temperature. The volume of the hydrogen is then read and the oxygen introduced. As soon as the thermometer returns to the same temperature as before, the volume of the mixed gases is noted, the volume of the oxygen being given by difference. The spark is then passed and the volume of residual gas is observed when the thermometer again registers the original temperature. If twice as much hydrogen as oxygen is introduced the volume of the steam will be found equal to that of the hydrogen alone. That is, two volumes of hydrogen combining with one volume of oxygen yield two volumes of steam. The density of the steam must therefore be $\frac{2}{3}$ times as great as that of the mixture of gases.

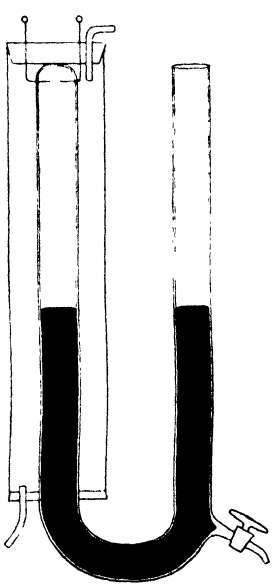


Fig. 31.

We might have anticipated this result from our knowledge of the specific gravities of the gases concerned.

1 litre of hydrogen = ·09 gram at S.T.P.;
∴ 2 litres „ „ = ·09 × 2 „ „ „
and 1 litre „ oxygen = ·09 × 16 „ „ „
∴ 3 litres „ mixture = ·09 × 18 „ „ „
∴ 1 litre „ „ = ·09 × 6 „ „ „
whilst 1 „ „ steam = ·09 × 9 reduced to S.T.P. (see Introduction),
and $\frac{\cdot 09 \times 9}{\cdot 09 \times 6} = \frac{3}{2}$.

From the above numbers it follows that in every 9 grams of water 1 gram of hydrogen has combined with 8 grams of oxygen, and that the percentage composition is 88·88 of oxygen and 11·11 of hydrogen.

Elements.

The question follows naturally whether the gases obtained by the electrolysis of water can undergo any further decomposition. The most effective resolving agents at our command are heat and electricity, but neither by exposing hydrogen to a very high temperature nor by submitting it to powerful electric discharges can we make it yield anything differing from itself. For this reason it is called an **element.**

The case of oxygen is at first sight different. Under a prolonged electric discharge at ordinary temperatures it decreases in volume and acquires a characteristic smell. After such treatment the gas has been cooled rigorously, with the result that a dark blue liquid separated out before the liquefying point of oxygen was reached. Is this a new element obtained by the resolution of oxygen? No: for it has been shown that the gas of this blue liquid, which has the odour very strongly marked, after heating to 200° C. became pure odourless oxygen. It is to be regarded as oxygen in a modified condition. Oxygen like hydrogen is an element, it has, however, a modified form (allotrope[1]), which on account of its smell was named ozone[2].

The formation of a small quantity of ozone accompanies the electrolysis of water; on opening the stopcock of the voltameter the smell can be distinguished.

[1] ἄλλος = another, τρόπος = manner.
[2] ὄζω = I smell.

The partial conversion of oxygen into ozone is easily accomplished as follows (Fig. 32) A glass tube closed at one end is fitted into a tube of larger diameter, so as to leave an annular space into which oxygen can be admitted by an inlet near the top. The outer tube is drawn out and fused on to one of narrow bore bent upwards and again bent at a right angle at the level of the inlet tube. Diluted oil of vitriol is placed in the inner tube and the whole apparatus is immersed in the same liquid. If the wires from an induction coil are now placed one in each liquid, the surfaces of these liquids in contact with the glass tubes become terminals of large area, and when the coil is working, a discharge will take place through two thicknesses of glass and the oxygen in the annular space. Such a discharge taking place without sparking is called a **silent discharge**. A slow stream of oxygen passing through the annular space will be exposed to the silent discharge and will be partially converted into ozone, the characteristic smell of which will be noticeable at the exit tube. If the apparatus is modified (Fig. 104) so that the oxygen space may be closed by stopcocks and any change of pressure within it indicated by means of a manometer, it can be shown that during the discharge a lowering of pressure takes place in the annular space. This implies that the conversion of oxygen into ozone is accompanied by a contraction in the volume of the gas. The apparatus may be heated cautiously, and when the gas regains its ordinary temperature the pressure becomes normal again. The alternate contraction and expansion may be repeated as often as desired. The manometer contains pure oil of vitriol.

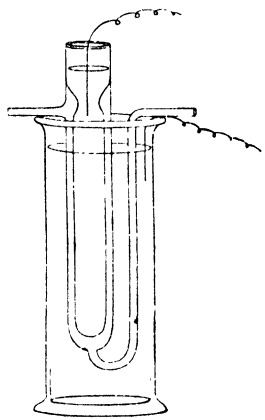


Fig. 32.

Compounds and mixtures.

The properties of water differ so widely from those of its components that they give no indication of its composition. Water is not produced by the simple act of mixing oxygen and hydrogen in the right proportion. In such a mixture each element retains its properties unmodified by the presence of the other: this is the chief distinguishing feature between a mixture and a chemical compound.

The components of a mixture may often be partially or completely separated by mechanical means, whereas no such methods will separate the hydrogen and oxygen united in water. Such mechanical methods of separation depend on differences in density and solubility, in boiling points, &c.

In 1831 Graham discovered that gases will escape through

small pores at rates which are inversely proportional to the square roots of their densities; hence hydrogen having one-sixteenth ($\frac{1}{16}$) the density of oxygen will diffuse (or escape) through a porous partition four times as fast.

The velocity of diffusion of hydrogen may be contrasted with that of air, which has nearly the density of oxygen, in the following experiment.

The mouth of a thistle funnel is efficiently stopped with a layer of plaster of Paris, a substance which on hardening becomes porous. The stem of the funnel is placed in coloured water, and a beaker inverted over the bowl of the funnel (Fig. 33). Air will diffuse through the plaster diaphragm in both directions at the same rate, and therefore the heights of water within and without the stem will be practically equal. Hydrogen is now passed up into the beaker. This gas diffuses through the partition so much more quickly than the air within can diffuse out, that the gaseous pressure within the funnel is augmented and gas escapes in bubbles from the stem. On removing the beaker, the hydrogen diffuses out so much faster than the air can pass in, that water ascends in the stem.



Fig. 33.

When two volumes of hydrogen and one of oxygen are mixed and well shaken up with water the two gases do not dissolve in the proportions in which they are found in the mixture. The dissolved gases may be recovered by boiling the water and collecting the gases evolved over mercury. The percentage of oxygen by weight is now 94·1 instead of 88·8, its percentage in the original mixture.

Since oxygen boils at $-182°$ C. and hydrogen at about $-250°$ C., it is evident that the former will succumb first to gradual cooling. Thus a mixture of hydrogen and oxygen may be partially separated into its constituents in three distinct ways, but neither by diffusion, by solution, nor by liquefaction can the composition of water be altered.

Heat effect.

In addition to the increase in density and the change in chemical properties, another phenomenon of great importance is observed when a mixture of hydrogen and oxygen becomes steam: much heat is evolved. By exploding a mixture of known composition in a specially constructed calorimeter, the exact quantity of energy lost in the form of heat by this reaction may be determined. It is found that 29,345 calories are always set free

when 9 grams of steam are formed, and if the steam condenses to water the total evolution is 34,200 calories. This great evolution of heat accounts for the high temperature of the oxy-hydrogen flame, in which hydrogen is burning in an atmosphere of oxygen.

If the energy set free during the formation of water is restored to the system it should be possible to resolve the water into its components. In confirmation of this it is found that if a rapid current of steam, produced by boiling water, is passed over a spiral of platinum wire maintained at white heat by a powerful electric current, part of the water is decomposed into its elements, and these are swept away and separated by the excess of steam before they have opportunity to recombine at a lower temperature (Fig. 34).

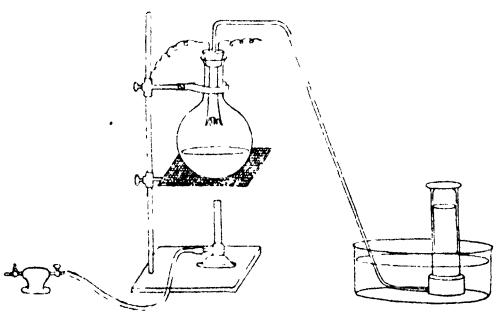


Fig. 34.

It is important to realise that a local high temperature alone is necessary to explode hydrogen and oxygen, a large quantity of heat is not required. The actual quantity of heat supplied by the electric spark is small, but it will start the combination of very large volumes of the mixed gases. Reaction begins in the immediate neighbourhood of the spark and is accompanied by an evolution of heat. This heat causes combination of the next layer of gas, and thus an explosion wave is developed which proceeds in all directions with a great, but measurable velocity. The influence of temperature upon the reaction has been carefully studied. A mixture of the pure gases in the proper proportions kept for many months at 155° C. gave no indication of combination; at 448° C. slow but complete combination took place; explosion

occurred at 606° C. Whether combination takes place rapidly or slowly 34,200 calories of heat are liberated when 9 grams of water are produced. Reactions which are accompanied by the liberation of heat are termed **Exothermic.**

We may now recapitulate the most important lessons.

We have found that water may be split up into Hydrogen and Oxygen, and by the reverse action water may be reformed by their combination. To these reactions the general terms ANALYSIS[1] and SYNTHESIS[2] are applied respectively and both operations testify to the compound nature of water. The hydrogen and oxygen differ entirely from water. They combine in fixed proportion by weight and by volume, and their combination is marked by a development of heat likewise definite in amount.

We have met in oxygen and hydrogen two substances that so far have never been resolved further. Such bodies are called **Elements.** They can only be changed by additive processes. Up to the present time some seventy different elements have been discovered. Many of these like hydrogen are known in only one form, others like oxygen are known in more than one form.

Amongst the best known elements are:—Silver, Gold, Copper, Carbon, Iron, Tin, Lead, Zinc, Aluminium, Mercury (Quicksilver), Sulphur, and less known are Magnesium, Bismuth, Antimony, Cadmium. Most of the above will be mentioned in the next two or three chapters and should be handled and described if possible.

[1] ἀναλύειν = to unloose.

[2] σύνθεσις = putting together, composition.

PROBLEMS. II.

1. Suggest reasons why the volumes of the electrode gases are not exactly in the same proportion as that in which they combine.

2. Make a full comparative table of the physical and chemical properties of hydrogen, of oxygen, of a 2 : 1 by volume mixture of the gases, and of steam.

3. 24 c.c. of hydrogen and 15 c.c. of oxygen are exploded at 130° C. What volume of gas remains and what is its composition?

4. 5·8 c.c. of oxygen were let into a straight eudiometer over mercury, the gas having previously been found to contain only 85% pure oxygen by volume. The height of the column of mercury in the eudiometer was then 232 mm. Pure hydrogen was then admitted until the volume of mixed gases was 26·3 c.c. The height of the mercury in the eudiometer was then 23 mm. After explosion the volume of residual gas was 17·8 c.c. Time was given for the gas to return to the temperature of the laboratory: the height of the mercury in the instrument was now 120·4 mm. The atmospheric pressure was 753·4. Calculate the proportion by volume in which hydrogen and oxygen combine. What important corrections, if any, were omitted?

5. Describe carefully the physical and chemical changes which would occur if, starting with ice at −4° C. the temperature is raised gradually to 2000° C., the pressure remaining constant.

6. If ·2 gram of hydrogen is burnt in a calorimeter (water equivalent = 2) immersed in 698 grams of water at 0° C., what will be the final temperature?

7. After the silent discharge in an ozone contraction tube, the vitriol rose 2 cm. in the near limb of the manometer. Turpentine, which absorbs ozone but not oxygen, was then liberated by the breaking of a tube which had been kept in the oxygen space. The vitriol of the manometer now rose a further 4 cm. Compare the densities of oxygen and ozone. What is the specific gravity of ozone compared with hydrogen?

8. Is the composition of water altered by dissolving oxygen in it?

CHAPTER II

THE ELEMENTS OF THE AIR.

The First Law of Chemical Combination.

Oxidation.

When a substance combines with oxygen it is said to be **oxidised:** when a compound is deprived of oxygen it is said to be **reduced.** When hydrogen is oxidised, water is formed. Water is produced whether hydrogen burns in oxygen or in air, therefore oxygen either free or combined must occur in air. The process of oxidation is less violent in air.

To prove that water is produced by the combustion of hydrogen in air, the hydrogen is burnt at a jet. The flame is partly surrounded by a bell jar (Fig. 35) supporting a flask through which a constant current of cold water circulates. The steam produced condenses on the flask and the inside of the bell jar, and water drops into a beaker. The jar may be dispensed with. For success in this experiment an abundant supply of hydrogen is necessary. A simple method of preparing hydrogen will be described in Chapter IV.

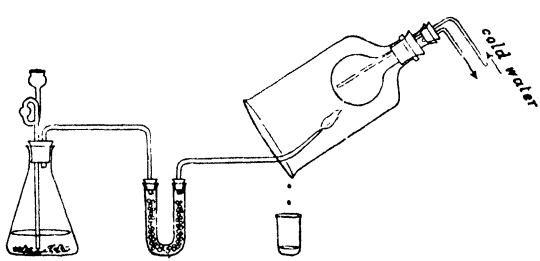


Fig. 35.

In all cases when hydrogen is passed through apparatus, the latter must not be heated, nor the issuing gas ignited, until it is certain that all the air has been displaced. Bad accidents may happen if the precaution is ignored. Of course the apparatus must be air tight.

When hydrogen is exploded with air in a eudiometer there is a diminution in volume. The greatest proportional contraction occurs when dry air is mixed with $\frac{2}{3}$ of its volume of hydrogen. The hydrogen and $\frac{1}{5}$ of the air (oxygen) combine to form water which condenses; the remaining $\frac{4}{5}$ of the original air will neither burn nor support combustion, nor may life be sustained in an atmosphere of it.

Therefore the French call it Azote[1] and the Germans call it Stickstoff, that is choke matter, but its English name is **Nitrogen.** It is 14 times as heavy as hydrogen and its liquid boils at $-193°$ C.

When iron filings are allowed to rust in any volume of air enclosed over water, $\frac{1}{5}$ of it is used up, and the residual air is identical with that of the last experiment.

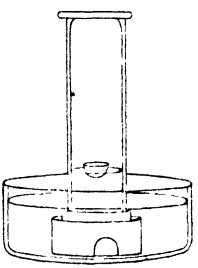


Fig. 36.

Moistened iron filings are placed in a small porcelain basin which is floated on water, and a jar of air inverted over it (Fig. 36). The water rises gradually about $\frac{1}{5}$ of the way up the cylinder, and then stops. The residual air can be used for experiment.

Air a mixture.

An artificial air, identical with pure atmospheric air, may be made by mixing together nitrogen and oxygen in the proportion of 4 to 1 by volume. Since no change of volume occurs, the density of air may be calculated from those of its components.

Nitrogen is only half as soluble as oxygen in water, therefore partial separation of the gases in air can be accomplished by first shaking air with water and then boiling the solution (Introduction). The gas expelled is richer in oxygen. If the process is repeated with each richer sample, nearly pure oxygen is eventually obtained. When air is liquefied and the temperature allowed to rise slowly, a large proportion of the nitrogen evaporates first, leaving the liquid richer in oxygen.

For the above reasons amongst others, air is regarded as a mixture of, and not as a compound of oxygen and nitrogen.

Several undoubted compounds of nitrogen and oxygen do exist but they are totally unlike air. Strong evidence in favour of the view that air is a mixture and not a compound

[1] ἀ privative, ζωτικός = life.

would be afforded if the gases could be separated by the purely mechanical operation of diffusion, but if it is remembered that the densities of oxygen and nitrogen are in the ratio of 16 : 14—and therefore their rates of diffusion are approximately as 15 : 16 ($\sqrt{14} : \sqrt{16}$)—the tedium of such a process will be appreciated. In the oxidation experiments air may often be substituted for oxygen with advantage, for it costs nothing, and moreover the presence of nitrogen serves to diminish the violence of the reaction.

The greater violence of oxidation in pure oxygen may be illustrated by the use of fine steel springs such as are used in watches or small clocks. A straightened spring passed through a brass disc is made red hot in a bunsen burner, and although it soon becomes non-luminous if left in the air, when the red hot steel is quickly plunged into pure oxygen, oxidation proceeds with such violence that the incandescent molten oxide—which is black—is shed in all directions. If the spring is too thick, or not clean, it may be necessary to start the combustion. Some thread is tied on the end and dipped in molten sulphur, and this is ignited before plunging in oxygen.

Simple oxidations may be carried out either in the air or by passing oxygen over the heated metal contained in suitable boat-shaped porcelain vessels placed in a combustion tube.

Treated in this way mercury acquires a red covering, lead a yellow, copper a black, magnesium a white, and cadmium a brown. In all cases the boat with its contents increases in weight, owing to the absorption of oxygen: an oxide of the metal is said to be formed.

Composition of oxides.

The percentage composition of certain oxides may be found by choosing methods which ensure the complete oxidation of the metal and the retention of all the oxide produced. Magnesium is one of the most convenient metals to employ; it burns readily, but care must be taken, for its oxide is so voluminous that it is easily carried away in the air currents produced by the burning. It is usual to place a weighed quantity (about 2 grams) of well-scraped magnesium ribbon in a weighed crucible, and alternately to heat the crucible with the lid on, and to cool with the lid raised, until no further increase of weight is observed. We may obtain consistent results, by substituting for the crucible a gold-assay cup covered with the pierced lid of a Rose's crucible, and by passing through the flanged

tube, (Fig. 37) quite slowly, dry air, or better oxygen, from a cylinder or reservoir. The heating may be continuous and

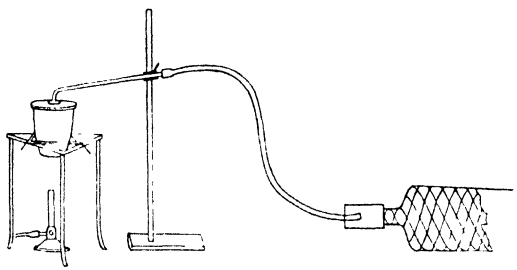


Fig. 37.

the lid untouched, scarcely any oxide will be found on the side of the cup and none will reach a quarter of an inch above the metal.

It must be remembered that a very slight error in weighing to the third place of decimals, (the 'rider' weighings) introduces a considerable percentage error.

An example of the results obtained by the above method is appended. Too little metal was used.

Oxidation of Magnesium.

Weight of crucible (without a lid) .....22·2300 grams
" " " " + metal ...22·3100 "
" " " " + oxide ...22·3615 "
Weight of metal .....0·0800 gram
" " oxide .....0·1315 "
" " oxygen ...0·0515 by difference
Percentage composition.....60·8 magnesium
" " .....39·2 oxygen

Other metals are usually more difficult to oxidise successfully. Upon copper wire for instance an almost impenetrable covering of oxide is formed, which protects the metal within; even the copper threads of 'flexible wire' still retain an unoxidised core after hours of heating in oxygen. Precipitated copper, washed in air-free water and dried with alcohol and ether (Chapter IX.), gives better results.

A weighed quantity is placed in a weighed boat and heated for some time in a current of dry air or oxygen, and weighed again.

Composition of air.

The composition of the air by weight is ascertained by causing the oxygen of a current of air to oxidise copper. Air is drawn slowly through purifying and drying agents, over an excess of heated copper, into a vacuous and weighed balloon of known capacity (Fig. 38).

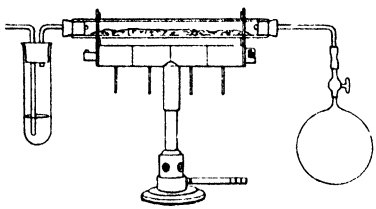


Fig. 38.

The whole of the oxygen is retained by the copper and only atmospheric nitrogen enters the balloon. The increase in weight of the copper gives the weight of oxygen absorbed, and the increase in weight of the globe together with the weight of nitrogen remaining in the combustion tube gives the weight of the nitrogen.

The percentage composition of air is:

	By volume.	By weight.
Oxygen	21	23
Nitrogen	79	77

The numbers are so nearly alike because the densities of the gases are so nearly equal.

This method is used to prepare atmospheric nitrogen, or the air may be forced over the copper and the nitrogen collected over water.

Oxidation by steam

Iron is not only readily oxidised by the free oxygen of air, but it is almost as easily oxidised by the oxygen combined in steam, and in this action a large volume of hydrogen is liberated. An iron tube containing

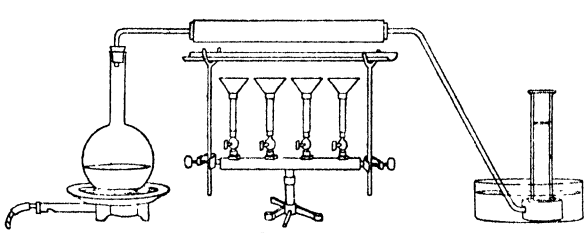


Fig. 39.

iron turnings is heated in a furnace and steam passed through (Fig. 39). A black oxide will accumulate in the tube, the hydrogen will pass on and may be collected over water. The purity of the hydrogen depends upon the purity of the iron.

When magnesium and a glass tube are substituted for iron, the magnesium bursts into flame and the escaping hydrogen may be lit at a jet. This method is more striking, but the tube usually cracks.

Reduction by hydrogen.

The reverse action occurs when hydrogen is passed over heated iron oxide; steam is produced and the iron oxide is reduced to the metal. Such reversible reactions are very common in Chemistry. The oxide of copper is more suitable than that of iron and consequently is employed in an important series of experiments in which this action plays a part. For instance, by passing hydrogen over a weighed quantity of strongly heated black copper oxide and weighing the metal produced, the oxide may be analysed with fair accuracy even by beginners.

In practice, instead of hydrogen for reducing oxides, one often uses coal gas, because of its convenience. Only about 50 % of it is hydrogen and the other constituents also assist in the reduction.

Black copper oxide occurs as a mineral called Melaconite and it may also be prepared artificially by at least four different methods, but no matter how it is prepared, it is found always to have the same percentage composition as the native black oxide.

One cannot expect the analyses performed by the elementary methods pursued in schools to be in exact agreement, yet, in spite of the neglect of details, the agreement is striking.

The analyses of the yellow oxides of lead and of bismuth yield similar results.

Red oxide of mercury may be analysed by heating alone.



Fig. 40.

A weighed quantity of red oxide is placed in a weighed hard glass bulb tube with a long stem (Fig. 40). Cautious heating decomposes the oxide, mercury which collects about the middle of the tube is tapped back into the bulb, and the tube weighed again.

The first Law of chemical composition.

Every oxide will be found to have a definite composition: this is true for all undoubted chemical compounds. This truth is generalised in the 'Law of Constancy of Composition' (or Law of Definite Proportion) which states that **every true compound, no matter how it is formed, contains its elements combined together in definite fixed ratios by weight** (Proust 1800).

It has been discovered that air varies slightly in composition, an additional reason for believing it to be a mixture.

By modifying the apparatus for reducing copper oxide and by using pure dry hydrogen, the gravimetric composition of water may be determined. As we shall learn later on, the exact ratio of the masses of hydrogen and oxygen which combine to form water is of immense importance. To obtain accurate results is a task of extreme difficulty, but even a simple experiment affords such good training that it should not be neglected (Fig. 41). Hydrogen (obtained by electrolysis) is

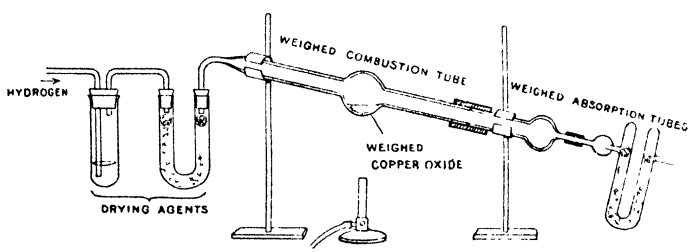


Fig. 41.

dried and passed over a weighed quantity of copper oxide. Part of the steam produced is condensed in the bulb and the remainder absorbed by suitable substances in U-tubes. The increase in weight of the absorption tubes gives the weight of water produced, the loss of weight of the copper oxide is the weight of the oxygen contained in the water produced, and the difference between the weights of the oxygen and of the water, is the weight of hydrogen combined therein.

From what has been said in Chapter I. we should expect the ratio to be exactly 1 : 8, as a matter of fact the result obtained by the ablest of recent experimenters was 1 : 7·94. The discrepancy is due to the rough ratio given for the

density of hydrogen to that of oxygen. The ratio 1 : 8 is sufficiently exact however for ordinary purposes.

Preparation of oxygen from oxides.

When lead is raised to a bright red heat in air, a yellowish oxide is obtained containing 92·82 °/₀ of lead; it is called Litharge. When litharge is kept for some time at dull red heat in air it slowly turns red and increases in weight. This red oxide is called Minium (or by plumbers 'red lead'). Pure minium on reduction yields 90·6 °/₀ of lead. When minium is heated strongly, it loses oxygen, and is reconverted into yellow litharge; if the heating is carried out in a retort some oxygen may be collected over water. This formation and decomposition of minium enables us to obtain oxygen from air, but the process is excessively tedious. The apparatus of Fig. 42 should be employed. To prevent water from travelling back along the delivery tube when the gas, still in the retort, cools and contracts, the tube must be disconnected, or lifted from the water.

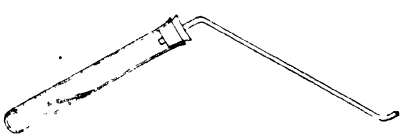


Fig 42.

Oxygen is actually obtained from the air commercially by a somewhat similar process, which will be referred to later.

Oxygen may also be obtained by heating pyrolusite strongly in a retort. This is a black mineral of great importance, which loses oxygen up to 12 °/₀ of its weight. The residue is brown.

When oxide of mercury is heated the metal is left. The metal slowly regains oxygen when heated nearly to its boiling point in air; hence we can obtain oxygen from the air by the formation and decomposition of the red mercury oxide.

PROBLEMS. III.

1. Observe the action, if any, of iron filings, magnesium powder and calcium metal on cold water.

2. To 50 c.c. of air contained in a eudiometer 25 c.c. of hydrogen were added and the mixture was exploded. When the temperature was constant 45 c.c. of gas remained, 5 c.c. of which were hydrogen. What is the composition of air by volume?

3. Find the percentage composition of silver oxide. Crucible weighs 20·11 grams. Crucible + oxide, 28·98 grams, and after strong heating crucible + silver, 28·66 grams.

4. Deduce the percentage composition of litharge and of minium. Two grams of minium were strongly heated leaving 1·953 grams of litharge. On reduction in a current of hydrogen this litharge yielded 1·813 grams of lead.

5. Zinc oxide contains 80·34% zinc; how much zinc is combined with 8 grams of oxygen?

6. Aluminium oxide contains 47·06% oxygen; what will be the increase in weight on burning 10·84 grams of aluminium powder?

7. Deduce the composition of copper oxide from the following:

A. 5·444 grams of copper on oxidation gave 6·811 grams of oxide.

B. 0·810 „ oxide „ reduction „ 0·647 „ copper.

Supposing that the methods are equally trustworthy, which result do you think probably more correct? Would the arithmetical mean of results A and B be preferred to either? State your reasons.

8. What simple experiments would you perform with jars of colourless gases to discover whether they contain oxygen, hydrogen, or nitrogen?

9. How would you obtain a large quantity of atmospheric nitrogen?

10. Find the percentage composition of mercury oxide:

Weight of bulb tube.....11·217 grams.
„ „ „ +oxide ...14·042 „
„ „ „ +mercury 13·833 „

11. Find the composition of water:

A. Morley (1895)
33·2435 grams of hydrogen combine with 263·9387 grams of oxygen.

B. Berzelius and Dulong (1819)
Loss of weight of copper oxide 27·129 grams.
Weight of water produced 30·519 grams.

C. Bunsen (1846)
95·45 c.c. of oxygen at 0° C. and 1000 mm. pressure.
557·26 c.c. of oxygen and hydrogen at 0° C. and 1000 mm.
Volume under same conditions after explosion 271·06 c.c.

12. Find the composition of air:

A. Bunsen (1846)
360·62 c.c. of air at 0° C. and 1000 mm. pressure. Volume after addition of hydrogen read 557·20 c.c. After explosion 330·54 c.c. of gas remained.

B. Dumas and Boussingault (1841)
Vacuous tube containing copper before the experiment ..... = 647·666 grams.
Tube filled with nitrogen and copper after the experiment ..... = 651·415 „
Vacuous tube containing copper after the experiment = 651·346 „
Balloon containing nitrogen at 19° C. and 762·7 mm... = 1403·838 „
„ vacuous at 19° C. and 762·7 mm. ..... = 1391·534 „

CHAPTER III.

COMMON SALT AND ITS COMPONENTS.

COMMON salt occurs locally in mines and springs, and universally in sea water. It is a white crystalline substance possessing a taste both characteristic and intense. It is fairly soluble in cold water, but its solubility does not increase greatly with increase of temperature (Fig. 7). From solution it crystallises in colourless cubes, which are rather more than twice as heavy as water, and melt at 815°C. Fused salt is an electrolyte, by electrolysis it is resolved into a soft lustrous solid which appears at the kathode, and a choking yellow green gas which escapes at the anode.

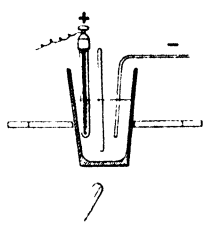


Fig. 43.

Common salt is melted in a large porcelain crucible by means of blowpipe flames (Fig. 43). The iron kathode and carbon anode are separated by a piece of asbestos paper—the diaphragm. The choking gas soon advertises its escape, but the kathode substance will not be isolated without special precautions.

The electrolysis is carried on commercially. Instead of an open crucible a U-tube is employed (Fig. 44), one limb made of iron luted into a broader limb made of earthenware. The iron limb is the kathode, the anode is a carbon rod dipping into the melted salt in the earthenware limb. Both products are collected, and the solid is preserved from air. Neither the gas nor the solid has been further decomposed: both are elements. The solid is called **Sodium** and the gas **Chlorine**[1].

[1] χλωρός = pale green.

Compounds which, like water and common salt, contain only two elements are called **binary** compounds. Common salt then is a binary compound of the electro-positive sodium and the electro-negative chlorine.

Binary compounds containing oxygen are called oxides, those containing chlorine are called **chlorides.**

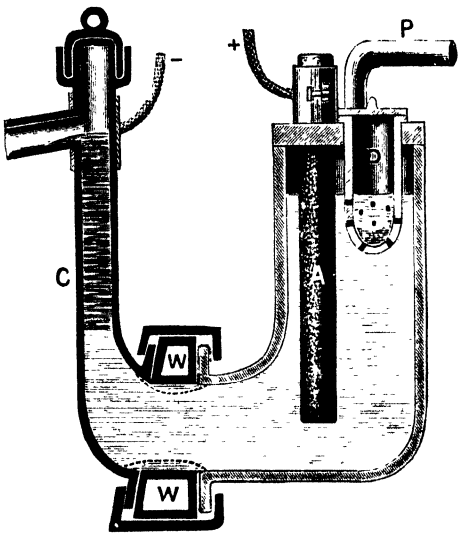


Fig. 44.

Sodium. When sodium is exposed to the air, its metal-like surface is rapidly dulled owing to the formation of a white layer. In oxygen this layer is formed almost instantaneously, whilst in pure nitrogen the lustre is undimmed: the white covering is an oxide.

When sodium (small pieces) is thrown upon water, an energetic action at once begins, hydrogen is liberated whilst the sodium disappears. The solution has acquired the power to turn **blue** a dye called litmus which is obtained from certain lichens. It also exerts a dissolving action on the skin and for that reason feels soapy. The white oxide also dissolves in water but without evolution of hydrogen, and forms a solution whose properties are identical with those of the solution formed by the action of sodium on water. When evaporated, no crystals separate out from either solution, but

in both cases a dry white substance is obtained, which rapidly absorbs moisture from the air. This dry white solid, which we should presume to be the oxide, cannot be reduced by hydrogen, but when electrolysed it yields not only oxygen at the anode and sodium at the kathode but, with the sodium, hydrogen also.

Davy discovered sodium by the electrolysis of this substance in 1807.

The white hygroscopic solid obtained by evaporating the oxide solution contains hydrogen, which therefore must have come from the water, and as in this case no oxygen was expelled, the white substance must contain water added to the oxide. On the other hand the same substance is produced when sodium metal acts upon water, expelling hydrogen. The substance is called **caustic soda** (hence the name sodium for the metal) and consists of sodium, hydrogen, and oxygen: for the present, we must regard it as an oxide which has attached water.

In consequence of the great tendency shown by sodium to combine with oxygen, it must be preserved under petrol which contains no oxygen.

When a saturated solution of common salt is electrolysed, hydrogen escapes at once from the kathode, and, after a short time, chlorine rises from the anode. The appearance of hydrogen instead of sodium at the kathode, is explained by the action of free sodium on water. A drop of litmus placed in the solution near the kathode is turned blue, owing to the presence of dissolved caustic soda.

Caustic soda solution is produced by the electrolysis of brine, special precautions being taken to ensure the separation of the products.

Chlorine.

Chlorine has an unpleasant and choking odour, so that both by its colour and smell it can easily be distinguished from oxygen, hydrogen, and nitrogen. Care must be taken not to inhale it because it has an injurious effect on the tender lining of the throat and nose, and is poisonous. Fortunately its odour is a sufficient warning of its presence.

Experiments in which chlorine is evolved must either be performed in a draught chamber, or other arrangements must be made for carrying off the gas; the chlorine may be passed into slaked lime which absorbs it.

Chlorine is 35·5 times as heavy as hydrogen and should be collected by passing it downwards into a dry cylinder from which it effectually displaces the air. The cylinder is at first partially closed by cardboard, pierced for the delivery tube (Fig. 47). The delivery tube is gradually withdrawn (or the cylinder lowered) during the filling, and finally the cardboard disc is replaced by a ground glass plate.

Chlorine attacks, more or less violently, most of the elements, and especially metals, producing compounds called chlorides, therefore it cannot be collected over mercury. Oxygen, nitrogen, and carbon alone resist its action completely, therefore carbon anodes are used in the electrolysis of chlorides. It bleaches many dyes, for instance, litmus. The combination of chlorine with metals may be shown by throwing powdered antimony into a jar of gas; combination takes place with evolution of heat and light. Thin leaves of brass (a mixture of copper and zinc) burn spontaneously in chlorine. Magnesium powder rapidly forms a white chloride without incandescence. Other metals may need to be warmed to start the combination. Sodium combines with readiness to produce common salt.

When chlorine is bubbled into water it dissolves, and under favourable conditions 50 c.c. of chlorine dissolves in 100 c.c. of water.

This explains its tardiness in appearing at the anode when brine is electrolysed.

The solution has the colour and smell of chlorine, and bleaches litmus. When a solution in an inverted glass tube is exposed to sunlight—or in winter to an arc-light—after a few days, the colour and smell of the solution are lost, a sharp taste is acquired and litmus will be reddened but no longer bleached. A colourless gas collects at the top of the tube, which proves to be oxygen.

In diffused light the reaction is very much slower, and in the dark does not take place.

Now water consists of hydrogen and oxygen, some oxygen has been liberated: what has happened to the hydrogen? Probably it has entered into combination with the chlorine to produce a compound, readily soluble in water and whose

solution has a sharp taste and the power to redden litmus. Attempts to obtain the compound from this solution by evaporation fail, because, although pure water distils over at first, when the solution reaches a certain concentration, it boils without further change, the vapour and the solution having the same composition. And this solution of constant composition has been proved not to be a definite chemical compound, for when it is boiled under a pressure either greater or less than atmospheric pressure, its composition is altered, which could not be true for a compound.

But although the compound cannot be isolated in this manner, it may be synthesised from its elements.

Hydrogen chloride.

A jet of burning hydrogen when lowered into a jar of chlorine continues to burn with the production of a gas, which fumes as it escapes into the moist air. These fumes are the solution of the gas in a myriad of tiny drops.

Hydrogen and chlorine when mixed together in a closed vessel explode, provided they are present in about equal volumes, and the mixture is exposed to bright light. Combination is less violent when either of the gases is in moderate excess, or when weakly illuminated. The exact proportion of the interacting volumes of gases may be discovered by the following experiment. A thick walled tube stoppered at both ends and with a tap at one-third of the length (Fig. 45),



Fig. 45.

has the longer arm filled with pure hydrogen (upward displacement) and the shorter arm with chlorine (downward displacement) produced by electrolysis and dried by vitriol. The gases are allowed to mix by turning the tap, and the tube is left in the light for several days. The tube is then opened under mercury. The mercury is not attacked if the combination is finished and all the chlorine has combined. Mercury does not ascend in the tube nor does gas escape, showing that the product of combination occupies the same volume as the gases which combined. Water coloured with

blue litmus is now poured on the mercury and the tube raised into it. Water makes its way two-thirds up the tube. The residual one-third of the original gas is hydrogen. Hence when hydrogen and chlorine combine, they do so in equal volumes, and the hydrogen chloride produced occupies the same volume as the constituents when free. From this conclusion, and the densities of the gases, we may conclude that 1 gram of hydrogen combines with 35·5 grams of chlorine to produce 36·5 grams of hydrogen chloride, that is, hydrogen chloride contains 97·26 per cent. chlorine and 2·74 per cent. hydrogen. Further, 36·5 grams of the compound occupy twice the volume of 1 gram of hydrogen, hence its specific gravity referred to hydrogen is $\frac{36{\cdot}5}{2} = 18{\cdot}25$.

The combination is exothermic; when 1 gram of hydrogen combines with 35·5 grams of chlorine to produce 36·5 grams of hydrogen chloride, 22,000 calories of heat are evolved. The mixture of hydrogen and chlorine, which has the same density as the compound, may be separated by diffusion even more rapidly than a mixture of hydrogen and oxygen. The rates of diffusion are approximately as $\sqrt{36} : \sqrt{1}$, that is, hydrogen diffuses nearly six times as fast as chlorine.

So far no method suitable for preparing large quantities of hydrogen chloride has been mentioned, and this is of no great consequence, for a saturated solution of the gas is sold under the name of Hydrochloric Acid. When heated this solution gives up a large part, but by no means all, of the dissolved gas.

To obtain the gas the concentrated solution is heated in a flask, and the gas collected in the same way as chlorine, or over mercury. If necessary it may be dried by oil of vitriol.

The gas is one of the most soluble known, 503 litres dissolve in 1 litre of water at 0° C. The specific gravity of the solution increases with the amount of gas dissolved; curves are constructed from which the percentage composition of any solution may be found from its specific gravity.

When the saturated solution is boiled, hydrogen chloride escapes until a solution is obtained having the same composition as that obtained by concentrating a dilute solution. This constant solution has specific gravity 1·1, it contains

about 20 per cent. of its weight of hydrogen chloride. It boils at 110° C.

The great solubility of this gas in water may be shown by filling a dry flask (Fig. 46), closed with a rubber stopper through which passes a long tube drawn out to a jet, which reaches nearly to the bottom of the flask, and a fountain pen filler partly filled with water. The open end of the long tube is placed in a dish of water and the water in the filler expressed. This water dissolves some of the gas, causing a diminution of pressure within the flask, and water is then forced by atmospheric pressure from the basin up the long tube until the flask is full.

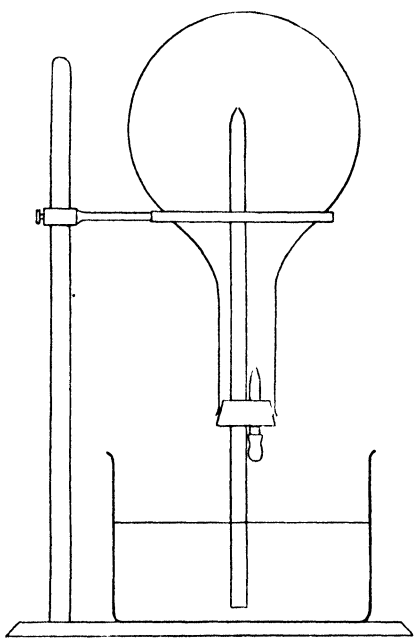


Fig. 46.

It is important to remember that the commercial hydrochloric acid is only a solution, and at the best never contains half its weight of hydrogen chloride. But the pure gas can be obtained and has been liquefied by cold and pressure. This liquid is pure hydrogen chloride without water: it boils at 80° below zero, and therefore is never used in laboratories.

Preparation of chlorine.

When the 1·1 S.G. solution of acid is electrolysed, hydrogen and chlorine are given off in equal volumes as soon as the solution is saturated with chlorine.

As this is not a very convenient method of obtaining chlorine, it is usual to oxidise the hydrogen of hydrogen chloride to water—the reverse of the action of chlorine on water in sunlight. When air, or oxygen, mixed with hydrogen chloride gas, is passed through a heated tube, a piece of litmus paper held in the issuing gases will not be bleached, but if the mixture is passed through a heated tube containing pumice stone, whose surface and pores are coated with copper chloride, the smell and bleaching properties of the issuing gas proclaim the presence of chlorine.

Pieces of pumice stone are dipped in a saturated solution of copper chloride, and then gently heated to drive off moisture. The pumice stone is packed in the combustion tube and the whole is heated to dull redness during the passage of the mixed gases.

By this method (Deacon's process), chlorine was for many years prepared on a large scale. It was absorbed by slaked lime to form the substance sold as 'Chloride of Lime' or 'Bleaching Powder.' The reaction is especially remarkable in that the copper chloride is still copper chloride at the end of the experiment. The function of the pumice is merely to afford a large surface for contact of the gaseous mixture with the copper chloride.

Chemical reactions are common in which substances promote changes in other bodies, but themselves appear to under-

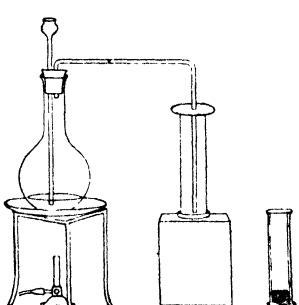


Fig. 47.

go no change. Such substances are called **catalytic agents** and the reactions are included in the term **catalysis**[1]. To give a general name to this class of reagents does not explain

[1] κατά = downwards, λύσις = the act of loosing.

their action, and in many cases the parts they play are entirely unknown. The oil of vitriol used to promote the electrolysis of water is, in this sense, a catalytic agent, although the course of its action is probably known.

A much more convenient—though more expensive—laboratory method of oxidising the hydrogen of hydrogen chloride, is to heat a solution of the latter in a flask with pyrolusite (Fig. 47).

The solution is poured upon the pyrolusite through a safety funnel and the flask gently heated on a sand bath. The chlorine is collected according to previous directions.

During the reaction the pyrolusite gradually disappears. By shaking the residue with water and evaporating the solution, pink crystals of manganese chloride are obtained.

We note here for future reference that when these crystals of manganese chloride are formed from pyrolusite, some oxygen of the latter is used for the liberation of free chlorine from hydrogen chloride.

QUESTIONS. IV.

1. Describe three methods of obtaining chlorine from hydrogen chloride, and two from sodium chloride.

Which method would you make use of in the laboratory, and why would you choose it?

2. Suggest a method of obtaining a chloride of iron from chlorine and the metal; the chlorine must not contaminate the air of the laboratory. Sketch the apparatus you would use.

3. What volumes at S.T.P. do (*a*) 35·5 grams of chlorine, and (*b*) 36·5 grams of hydrogen chloride occupy?

4. How many cubic centimetres of hydrogen chloride solution S.G. 1·1, containing 20·9 per cent. of the compound, must be taken to make 1 litre of a solution containing 3·65 grams of hydrogen chloride?

5. 0·461 gram of sodium was treated in a tube with chlorine; the resulting chloride weighed 1·17 grams. Find the percentage composition of common salt.

6. One gram of copper powder was heated in a current of chlorine and gained 1·116 grams. What is the percentage composition of copper chloride?

CHAPTER IV.

THE CHLORIDES.

EQUIVALENT MASS. THE SECOND LAW OF CHEMICAL COMBINATION.

The action of hydrogen chloride with metals.

AT the beginning of the previous chapter it was stated that chlorine combines directly with metals to form chlorides. Certain chlorides are also formed when hydrogen chloride gas is passed over some heated metals, and in these circumstances hydrogen is liberated. Suitable metals such as iron, copper and magnesium (contained in boats in the form of powder or filings) are placed in a tube and heated in a furnace, whilst dried hydrogen chloride is passed over them. Some hydrogen may be collected, and some dry chloride of the metal will be found in the boats. The copper chloride forms a thin white coating to the metal, and on exposure to the air slowly turns green; from the iron may be collected colourless or slightly green flakes, which in air turn yellow. Magnesium chloride is white.

The yield of chloride by the last method is small, and it is far more convenient to use the *solution* of hydrogen chloride. All metals do not attack the solution with equal readiness. Magnesium, even with very dilute and cold solutions, liberates hydrogen and forms its chloride. This at once dissolves in the water. Zinc and aluminium, especially when pure, are only attacked by moderately concentrated solutions, and for tin concentrated solution is used. Copper will scarcely attack the solution, however hot or concentrated it may be.

In the above examples, as soon as the chloride is formed

it dissolves, and as the chloride solution is often colourless, at first sight one gains the impression that the metal is being dissolved, and one talks loosely of the hydrogen chloride solution dissolving the metal, whereas, of course, the metal is transformed into the chloride which dissolves. At the same time the hydrogen chloride is used up: tinkers speak of this as 'killing' the 'spirits of salt.

On evaporating the solutions nearly to dryness, the solid chlorides are obtained, although few can be induced to crystallise unless the solutions are immersed in a freezing mixture; with zinc chloride, for instance, a syrupy liquid is obtained which at ordinary temperatures only slowly deposits tiny crystals.

When metals react with hydrogen chloride solution, leaving no residue, we find that

(1) the same mass of the same metal always displaces a definite mass of hydrogen, and

(2) equal masses of different metals displace different masses of hydrogen.

Now, because in hydrogen chloride every gram of hydrogen is combined with 35·5 grams of chlorine, it follows, that every chloride has a constant composition (in agreement with the Law); and, that for every gram of hydrogen displaced from hydrogen chloride, 35·5 grams of chlorine have combined with the reacting metal.



Fig. 48.

If the mass of metal attacked is known, and also the weight of hydrogen displaced by it, the composition of the chloride so formed may be calculated. The form of apparatus used varies with the properties of the particular metal. For magnesium a straight tube (Fig. 48) of about 200 c.c. capacity is taken, some 40 c.c. of concentrated hydrogen chloride solution poured into it, and then distilled water until it is full. The tube is inverted over water in a small dish. A piece of well-scraped magnesium ribbon (about 0·18 gram),

accurately weighed, is put into a tube rather smaller than those commonly used for weighing, and all air is expelled by filling it to the brim with water. The small tube, held vertically, is now introduced under the inverted collecting tube. (The thumb should not be placed over the magnesium tube.) The hydrogen chloride soon diffuses into the small tube

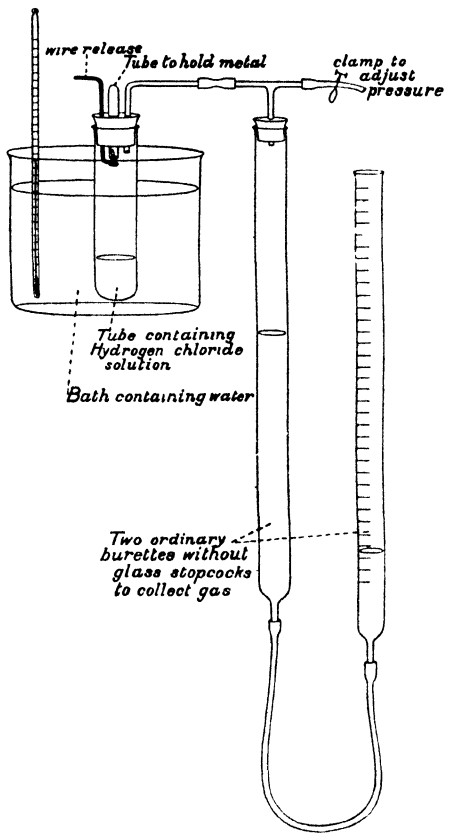


Fig. 49.

and attacks the magnesium. When all the metal has disappeared and the temperature is constant, the gas tube is depressed (or elevated) until the water within and without the tube is at the same level. This place is marked by a thin rubber band, and the exact capacity of the tube up to

that mark measured by running water in from a burette. This volume is reduced to S.T.P. and the weight calculated.

If the dish is too shallow for sufficient depression of the measuring tube, the latter may be removed to a more suitable vessel by placing the end, still under water, in a crucible full of water and lifting both together.

For other metals, such as aluminium and zinc, and for magnesium also, a convenient apparatus is shown in Fig. 49 (but that of Fig. 17 is commonly used instead of the burettes of Fig. 49).

A piece of weighed metal (about ·03 gram aluminium, ·1 gram zinc, and ·045 gram magnesium) is placed in the short sealed tube, and the copper wire is adjusted to retain it there. The test tube containing solution of hydrogen chloride is fitted on, and the beaker of water is brought into position. With the pinchcock open, the movable tube (graduated to $\frac{1}{10}$ c.c.), is raised or lowered until the level of the water is nearly at the bottom graduation. With the pinchcock closed, the water in both tubes is brought to the same level, and this position noted. The metal is now released. To prevent undue pressure, the movable tube is lowered during the evolution of hydrogen to keep the same level in both tubes. When the metal has quite disappeared, the level is again adjusted and the new position noted. The difference in the two observations is the volume of the damp hydrogen at the temperature (which may be taken as that of the water in the beaker) and pressure of the laboratory

This apparatus must on no account be used for determining the equivalent of sodium, but it is suitable for finding that of calcium (take about ·7 gram), using water with a trace of acid.

By the former method the following result was obtained for magnesium:—

Composition of Magnesium Chloride.

Barometer	764 mm.
Temperature of water	15·8° C.
Pressure of aqueous vapour at 15° C.	13·4 mm.
Weight of magnesium	0·131 gram
Volume of hydrogen collected	127·5 c.c.
" " " reduced to S.T.P.	119 c.c.
∴ Weight " "	0·0107 gram

1 gram of hydrogen is displaced by 12·24 grams of magnesium.

∴ Magnesium chloride has:

Magnesium	12·24 grams
combined with Chlorine	35·5 "

Preparation of hydrogen.

For obtaining large quantities of hydrogen, the most convenient method is to displace it from the diluted commercial acid by a cheap and moderately pure metal. The purity of the hydrogen depends upon the purity of the reagents; the impurities are often odorous.

A layer of granulated zinc is placed in a small flask, and dilute hydrogen chloride solution poured down a thistle funnel reaching almost to the bottom of the flask (Fig. 50). Hydrogen should not be collected until all air has been displaced.

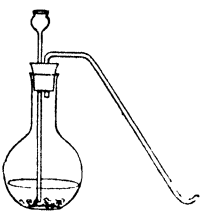


Fig. 50.

The condition of the sample must first be ascertained by filling a test tube over water, and then applying a light; the hydrogen is not free from air until it burns quietly. Serious accidents sometimes happen when this precaution is omitted, and special care must be taken to ensure the air-tight condition of the whole apparatus.

Considerable heat is evolved, the reaction being strongly exothermic. Hydrogen obtained in this way may be burnt at a jet and the water collected as described in Chapter II. (Fig. 35). In this case especial care must be taken not to ignite the hydrogen until all the air is displaced from the apparatus.

When a steady supply of hydrogen is wanted the Kipp apparatus (Fig. 51) is very useful. It consists of two parts: the lower and larger part is a vessel constricted about the middle; the upper part is funnel-shaped with shoulder, ground to fit the neck, and with a stem which, passing easily through the waist of the lower vessel, reaches nearly to the bottom. Granulated zinc is placed in the middle part and is prevented from falling through the annular crevice by a few small glass marbles. With the stopcock open, the solution of hydrogen chloride is poured down the funnel and, ascending in the lower chamber, forces the air before it and passes through the waist and between the marbles until it meets the zinc. The hydrogen generated drives out the air. When the stopcock is closed the hydrogen, as it accumulates and no longer able to escape, forces the solution away from the zinc, down into the lower chamber, and partly into the funnel until the pressure is equalised.

The action of hydrogen chloride on oxides.

When dry hydrogen chloride gas is passed over heated caustic soda, sodium chloride and water are produced. The experiment is more conveniently performed with a less deliquescent oxide. Zinc or copper oxide is placed in a boat within a tube, through which *dry* hydrogen chloride gas is passed; as soon

as the tube is heated a powder appears on the copper oxide, and **water** collects in the cooler parts of the tube. The zinc chloride formed retains some of the moisture. With proper precautions, it may be shown that **neither free**

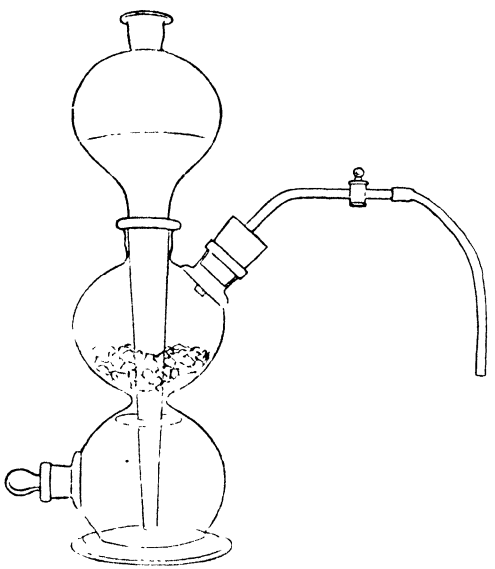


Fig. 51.

hydrogen nor free oxygen is formed: therefore the hydrogen, liberated (from the hydrogen chloride) by the union of the chlorine with the metal (from the oxide), is exactly sufficient to combine with the oxygen displaced from the oxide. This is a most important conclusion, for if the percentage composition of the oxide is known, the composition of the chloride can be deduced.

We know (p. 45) that 12·15 grams of magnesium are combined with 8 grams of oxygen, and that 8 grams of oxygen combine with 1 gram of hydrogen, leaving 35·5 grams of chlorine to combine with the 12·15 grams of magnesium.

$$\left.\begin{matrix}\text{Magnesium... } 12{\cdot}15 \text{ grams} \longleftrightarrow \text{Chlorine ... } 35{\cdot}5 \text{ grams} \\ \text{Oxygen ..... } \quad 8 \text{ „} \quad \longleftrightarrow \text{Hydrogen... } \quad 1 \text{ gram}\end{matrix}\right\}.$$

This result agrees very nearly with that of p. 63. The discrepancy is due to errors consequent upon the methods

employed. The composition of sodium chloride may be sought indirectly by finding the weight of hydrogen displaced from water by a known weight of sodium.

METHOD I. (Mr Bucknell's). Fig. 52.

The hydrogen is collected in a 50 c.c. tube graduated in tenths of a c.c. When this tube is full of water, there must be no air bubbles. The weighing tube *a* (made from 6 mm. bore glass tubing) is fitted with junction rubber tubing and pinch-cock. After weighing it about 0·05 gram of freshly cut sodium, of convenient shape, is quickly introduced and the cock closed and the tube weighed again. The pinch-cock is now removed and the weighing tube joined to the delivery tube (also 6 mm. bore) *which must be* quite dry. The end of the latter is placed under water, and

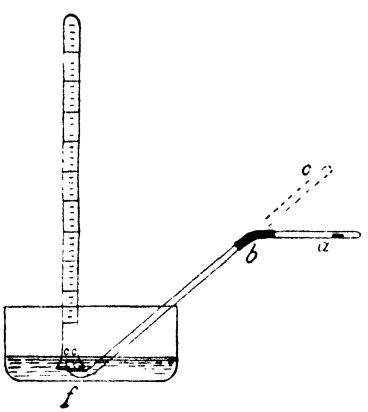


Fig. 52.

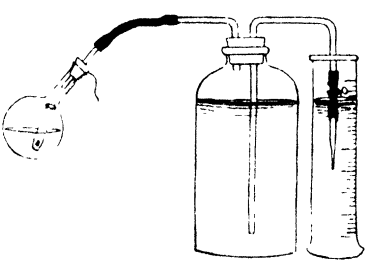


Fig. 52 A.

as soon as the bubble of air has escaped is placed into position. Then the sodium tube is tilted to position *c* and the metal runs into the collecting tube.

METHOD II. (Mr Hale's). Fig. 52 A.

In this method the hydrogen is collected in the apparatus of Fig. 17 (p. 22). The gas generating chamber is a flask with delivery tube leading to this collector. In the flask is nearly 'absolute' alcohol which may be regarded here as a little water greatly diluted with alcohol. The weighed sodium is put in a short open tube suspended above the alcohol by a thread. When all is ready it is jerked into the alcohol. The reaction proceeds gently and without danger.

It is found that 23 grams of sodium displace 1 gram of hydrogen from water; hence 23 grams of sodium combine with 8 grams of oxygen to produce sodium oxide, and with 35·5 grams of chlorine to produce sodium chloride.

Neutralisation of soluble oxide.

It will be remembered that caustic soda solution turns litmus blue, and so delicate is the reaction that a mere trace of caustic soda produces the change. An equally delicate reaction is the reddening of litmus by hydrogen chloride solution. But when caustic soda and hydrogen chloride interact, the sodium chloride produced has no effect on, or, is '**neutral**' to litmus. Therefore, when to a solution of hydrogen chloride a solution of sodium oxide is gradually added, litmus will lose its red colour—but yet will not turn blue—as soon as the quantity of caustic soda added is just sufficient to react with the whole of the acid, producing sodium chloride and water. That point is called the 'end' point of the 'neutralisation,' the 'indicator' being litmus. The sodium chloride may be recovered by crystallisation. Advantage is taken of this sensitiveness of litmus (and other indicators) to a slight excess either of acid or of base, for estimating the concentrations of solutions of acids and bases. The operation is called **titration**[1], and is a process in volumetric analysis.

The concentration of any solution of caustic soda may easily be estimated by finding what volume of a solution of hydrogen chloride, whose concentration is known, will exactly neutralise a definite volume of the given caustic soda solution.

As 36·5 grams of hydrogen chloride neutralise (23 + 8) = 31 grams of caustic soda (considered as oxide), a simple calculation gives the concentration of the solution titrated.

It is found that the quantity of hydrogen chloride, which will neutralise a solution formed by the action of 23 grams of sodium on water—that is, will neutralise (23+8)=31 grams of **sodium oxide**, will also neutralise the solution formed by dissolving 40 grams of **caustic soda** in water. Hence 40 grams of caustic soda contain 31 grams of true sodium oxide, and the residual 9 grams are water.

For volumetric analysis, solutions of known concentration (standard solutions) are made up according to a definite plan. For instance, a convenient solution of hydrogen chloride contains 1 gram of replaceable hydrogen per litre of solution. Such a solution could be prepared by passing pure hydrogen chloride gas into a weighed quantity of water, and then weighing again to determine the exact weight of

[1] From Fr. *titre* = a standard.

the gas added. As 1 gram of hydrogen is contained in 36·5 grams of the gas, an easy calculation indicates to what volume the whole solution shall be diluted, in order to be of the correct concentration. Such a solution is said to be '**normal,**' and all other solutions of which 1 litre is exactly neutralised by a litre of 'normal' hydrogen chloride are also said to be normal. To prepare a normal solution of caustic soda, small pieces of sodium, whose weight is accurately known, may be thrown cautiously into water, and then the solution diluted to the volume that will contain 23 grams of sodium per litre, or perfectly pure caustic soda can be used, and the solution made up to 40 grams per litre. Or, if a standard solution of hydrogen chloride has been already obtained, this may be used to find the exact concentration of an unknown more-than-normal solution of caustic soda, and the latter then diluted to the proper volume. In the same way a solution of hydrogen chloride of unknown concentration may be 'standardised' by titration with a normal solution of caustic soda. Normal standard solutions are very convenient for purposes of calculation, but of course *any* standard solution may be used for titration. 10 c.c. or 20 c.c. of the unstandardised solution are transferred to a clean beaker by means of a dry and clean pipette, a little litmus is added, and then the standard solution allowed to fall into the beaker drop by drop from a burette, with constant shaking or stirring until the end point is just reached. The mean of three titrations is taken to represent the volume added. All the data, the name of the indicator, and any other particulars of importance must be included in the notes.

The standard solution may not be poured into a dirty or *wet* burette, and care must be taken that no bubbles of air are left near the tap or clamp. Whenever caustic soda solutions have been used in a burette, the latter must be thoroughly rinsed and allowed to dry with the stopcock removed.

Normal solutions are too concentrated for accurate work, and solutions of one-tenth the concentration are more commonly used. In every cubic centimetre of decinormal hydrogen chloride there is only ·0001 gram of replaceable hydrogen, and as about ten drops go to the cubic centimetre, the method is very accurate.

The word 'normal' is used in Chemistry to express at least three different ideas. For a solution containing 1 gram per litre of replaceable hydrogen it is therefore better to use the term '**equivalent-per-litre** (E.P.L.),' which has a well-defined meaning. A tenth-equivalent solution is denoted by $E/10$ or $N/10$.

Acid base and salt.

Hydrogen chloride is one of a class of chemical compounds called 'acids,' rather difficult to define satisfactorily, but a general idea of the **type acid** may be gained by recapitulating the properties of the one already studied. Hydrogen chloride has (in solution) a sharp taste and it reddens litmus. It shows a marked inclination to part with its hydrogen in exchange for metals to form metallic chlorides by direct action either with the metal or with the metallic oxide; in the former case hydrogen is liberated, in the latter water is formed.

Oxides which react with acids in this manner are called basic oxides or, shortly, '**bases.**' In addition, soluble bases like caustic soda are called **caustic bases** or alkalis. These in dilute solution colour litmus blue, have a bitter taste and a soapy feeling to the fingers.

The products of the interaction of a base and an acid are water and a **salt.** The salts formed from hydrogen chloride are the metallic chlorides. It must not be forgotten, however, that they may also be produced from the metal and chlorine, and this method is in some cases the more useful, especially when a chloride free from water is desired. Hydrogen chloride is generally referred to as **hydrochloric acid.**

In France the order is transposed to chlorhydric acid, and this is probably the better expression, because the termination -ic is used in a special sense, which will be explained shortly.

The chlorides are for the most part soluble salts. Calcium chloride is exceedingly soluble, sodium chloride fairly so. Silver and lead chlorides are very insoluble, but the latter dissolves in hot water.

Equivalent.

It was shown above that when an oxide reacts with hydrogen chloride, the proportions of metal and oxygen in the oxide are such that they severally combine exactly with the proportion of chlorine and hydrogen

contained in the acid: and we deduced that the mass of metal which combines with 8 grams of oxygen will also displace 1 gram of hydrogen from the acid.

That particular mass, even more than melting point, conductivity for electricity, or any other physical measurement, at once characterises a metal and distinguishes it from all others. It is called the **'equivalent mass.'** Hence the equivalent of magnesium is 12·2 grams as given by the mean of the above experiments. The most accurate experiments have fixed the equivalent of magnesium as 12·2 grams.

It is now made obvious why the term 'equivalent solution' was preferred to 'normal solution.'

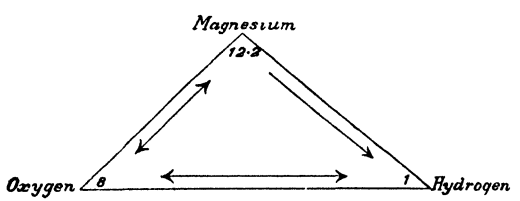
The equivalent mass of an element is that mass of it which will combine with or displace 1 gram of hydrogen, or, extending the definition, will combine with or displace the equivalent mass of any other element, for instance, 8 grams of oxygen or 35·5 grams of chlorine.

The second Law of Chemical Combination.

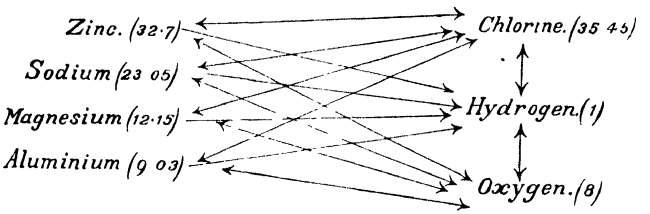
The latter part of the above definition contains the germ of a second Law of Chemical Combination called the Law of Equivalent Ratios (reciprocal proportions) which states that:

'When two elements severally combine with a third, the different masses of the two elements which combine with a fixed mass of the third are in the ratio in which they combine together.'

And this law is true not only for oxides and chlorides but for all compounds. We have actually proved its truth for magnesium, hydrogen, and oxygen; 1 gram of magnesium combines with $\frac{8}{12{\cdot}15}$ grams of oxygen and displaces $\frac{1}{12{\cdot}24}$ grams of hydrogen from acid. These weights are in the proportion 8 : 1, which is the ratio of the masses of oxygen and hydrogen in water. Particular cases may be represented by a closed triangle



or more generally



PROBLEMS. V

1. 0·326 gram of zinc oxide was heated in a current of chlorine, oxygen was expelled and 0·545 gram of zinc chloride was formed. Calculate the percentage composition of zinc chloride given that of the oxide. (Probs. III. 5, p. 50.)

2. 12·35 grams of litharge were heated in a current of hydrogen chloride. What masses of lead chloride and of water were produced?

3. 1 gram of iron heated in a current of chlorine gained 1·9 gram. 1 gram of iron liberated 397·3 c.c. of hydrogen at S.T.P. Was the same chloride formed in both experiments?

4. Find the composition of the chlorides from the following:

(*a*) 1 gram of tin displaces 187·6 c.c. of hydrogen.

(*b*) 1 „ zinc „ 341·2 c.c. of „

5. Reynolds and Ramsay (1887) found that 3·3665 grams of zinc displaced 1212·09 c.c. of hydrogen measured at 747·84 mm. and 10·73° C. Find the equivalent mass of zinc (1 litre of hydrogen at S.T.P weighs 0·0898 grams).

6. Calculate the percentage amount of zinc contained in a sample of zinc dust of which one gram when attacked by chlorhydric acid yields 240 c.c. of dry hydrogen measured at 15° C. and 742 mm. of mercury.

Equivalent of zinc = 32·5 grams.

7. 1 gram of aluminium liberates 1·236 litres of hydrogen. How much aluminium would liberate the hydrogen necessary to produce 4 grams of water?

8. Bismuth chloride contains 33·85 per cent. chlorine. Find percentage composition of oxide.

9. Cobalt oxide contains 78·67 per cent. cobalt. Find percentage composition of chloride.

10. Bismuth oxide contains, according to Classen, 89·696 per cent. metal. Find the equivalent of bismuth.

11. Calculate the equivalents of zinc, tin, aluminium, cobalt, and sodium from the above data.

12. Stas found that 969·35485 grams of silver formed 1287·7420 grams of silver chloride. Deduce the composition of the latter and the equivalent of silver.

13. Stas found that the chlorine in 145·70775 grams of potassium chloride combine, in special circumstances, with 210·85488 grams of silver. Deduce the equivalent mass of potassium.

14. 1·328 grams of silver chloride were heated in a current of hydrogen. Hydrogen chloride was formed and 1 gram of silver was left. Find the equivalent of silver, given the equivalent of chlorine 35·45.

15. A mean of three titrations gave 19·4 c.c. of $\frac{E}{10}$ caustic soda as neutralising 10 c.c. of a solution of hydrogen chloride. Of this solution 8·6 c.c. neutralised 10 c.c. of a solution of caustic potash (dissolved potassium oxide). How many grams of potassium oxide are contained in 1 litre of solution, given that equivalent mass of sodium = 23, of potassium = 39. What must be done to make both the acid and the caustic potash solutions tenth-equivalent?

16. 1 gram of pyrolusite on heating with hydrochloric acid solution caused the evolution of 0·816 gram of chlorine. If the residual salt weighed 1·448 grams and was found to contain 56·35 per cent. of chlorine, deduce the percentage composition of pyrolusite (see end of Chapter III.).

17. Find the equivalent mass of tin by means of the apparatus of Fig. 53. Place a weighed piece of tin in the flask. Expel air from flask and delivery tube by boiled water. Bring collecting tube over delivery tube. Displace water in flask by concentrated solution of acid. If necessary, heat; to accelerate action a drop or two of platinum chloride may be admitted with the acid. Particles of metal may be prevented from escaping by a glass wool plug in delivery tube. Finally displace hydrogen from flask and delivery tube by water.

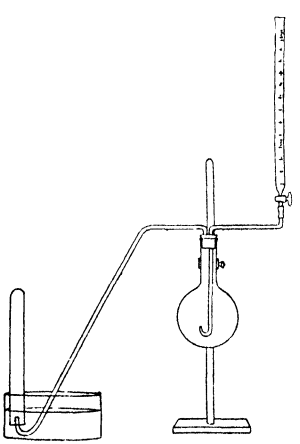


Fig. 53.

CHAPTER V.

THE PREPARATION OF OXYGEN.

WE have already found that when chlorine water is exposed to sunlight, a slow reaction between the water and chlorine takes place, producing hydrogen chloride and free oxygen.

Action of chlorine on litharge suspended in water.

When a slow current of chlorine is passed into warmed water to which litharge is added little by little, and with constant stirring so that it remains suspended in the water, chlorine is continuously absorbed, and although the solution becomes acidic no oxygen escapes. At the same time the litharge becomes dark brown. Now this brown substance is not the chloride of lead for that is white, and moreover if it were formed, oxygen would be displaced from the litharge. But hydrochloric acid is produced: the oxygen liberated from water may be combined in the brown substance. When the latter is washed and dried and then heated in the apparatus of Fig. 42, oxygen is indeed liberated and yellow litharge remains in the tube.

The experiment may be carried out conveniently with chlorine water instead of a current of chlorine.

The brown solid is washed several times with hot water by decantation and then transferred to a filter funnel whose stem is lightly plugged with glass wool, washed again and then dried over a sand-bath cone.

When a known weight of this brown substance is heated in a current of hydrogen, lead and water alone are produced. Calculation shows that whereas litharge contains 7·2 per cent. of oxygen, this new substance contains 13·4 per cent. and therefore is called lead peroxide (per is short for hyper).

It is important to notice, that although still not rapid,

the action of chlorine on water becomes greatly accelerated when litharge is present to combine with the liberated oxygen.

Action of chlorine on hot caustic potash

If instead of suspending litharge in water, we use a hot solution of caustic soda, chlorine is readily absorbed with little or no evolution of oxygen. For this experiment it is better to use caustic potash, a compound in almost all respects similar to caustic soda, the metal potassium (Equiv. = 39) taking the place of sodium.

Potassium like sodium attacks water, but more violently, liberating hydrogen and forming a solution of caustic potash; on evaporation no crystals are deposited from solution, but eventually a mass is left resembling caustic soda. This likewise absorbs from the air moisture in which it dissolves, in fact there is scarcely any limit to its solubility. Neutralisation with hydrochloric acid yields potassium chloride (corresponding to common salt) which crystallises slowly from solution in cubes. These cubes have a salty taste with a cooling sensation to the tongue. At high temperatures potassium chloride is more soluble than common salt.

Before the chlorine is passed into the solution the latter is strongly caustic, but as the chlorine accumulates the causticity becomes less pronounced. After a time no more chlorine dissolves and the action ceases. From the cooling solution a quantity of crystals separates out and the liquid above them (the 'mother-liquor') should be decanted into another beaker; the crystals are dried on filter paper, redissolved in the least quantity of hot water, and allowed to crystallise again. The new crystals are not very soluble in cold water, their solution is neutral to litmus, and their form (they crystallise well) is totally unlike a cube. They cannot therefore be either caustic potash or potassium chloride. Their appearance should be observed, they are flaky and have a lustre. To the taste they are sharp and cooling. How can we account for this new substance?

We know that when chlorine acts on water, hydrogen chloride and free oxygen are produced,

$$\left.\begin{matrix}\text{Hydrogen (1)}\\ \text{Oxygen (8)}\end{matrix}\right\} \text{and Chlorine } (35\tfrac{1}{2})$$

give

$$\begin{matrix}\text{Hydrogen (1)}\\ \text{Chlorine (35·5)}\end{matrix} \text{ and Oxygen (8),}$$

and that hydrogen chloride and caustic potash neutralise each other with production of potassium chloride and water.

$$\begin{cases}\text{Potassium (39)}\\ \text{Oxygen (8)}\end{cases} \text{ and } \begin{cases}\text{Chlorine (35·5)}\\ \text{Hydrogen (1)}\end{cases}$$

give

$$\begin{cases}\text{Potassium (39)}\\ \text{Chlorine (35·5)}\end{cases} \text{ and } \begin{cases}\text{Hydrogen (1)}\\ \text{Oxygen (8)}\end{cases}$$

The potassium chloride, being very soluble, would not be deposited from solution and must therefore still be in the decanted 'mother-liquor.' From one drop of this, allowed slowly to crystallise on a glass slide under the microscope, cubical crystals of potassium chloride are seen to appear as well as a few of the new substance. The argument may be represented thus

$$\left.\begin{array}{l}\text{Chlorine (35·5)}\\ \text{and}\\ \text{Hydrogen (1)}\\ \text{Oxygen (8)}\end{array}\right\} \longrightarrow \begin{cases}\text{Oxygen (8)}\\ \text{Potassium (39)}\end{cases} \quad \begin{cases}\text{Chlorine (35·5)}\\ \text{Hydrogen (1)}\\ \text{Oxygen (8)}\end{cases} \longrightarrow \begin{cases}\text{Potassium (39)}\\ \text{Chlorine (35·5)}\end{cases} \quad \begin{cases}\text{Oxygen (8)}\\ \text{Hydrogen (1)}\\ \text{Oxygen (8)}\end{cases}$$

We have therefore to account for some oxygen which we know has not escaped, and on the other hand for the crystals which have been deposited. If the reaction has proceeded in a manner similar to that which occurred with litharge, the crystals would be potassium peroxide and should yield again oxygen and caustic potash when heated. To test this assumption the dried crystals are heated in a retort (Fig. 42). They first melt and then evolve copiously a colourless gas which proves to be oxygen. As the temperature rises the melted salt solidifies again and there is a temporary cessation of gas evolution; with increase of temperature the solid melts again and a further quantity of oxygen is evolved. Finally a quiescent liquid is left, which, on the cooling of the retort, solidifies to a white substance having the appearance of dry caustic potash, but which is not deliquescent and only moderately soluble in water. A drop of solution crystallises under the microscope depositing the cubes of potassium chloride. Evidently the oxygen has added itself to some of the chloride and not to caustic potash. The reaction may be represented

	Caustic potash	water and	
Water and Chlorine	→ Hydrochloric acid and Oxygen	→ Potassium chloride (free) Potassium chloride (with oxygen)	new substance.

The new substance containing potassium, chlorine, and oxygen is called potassium chlor**ate**; it must on no account

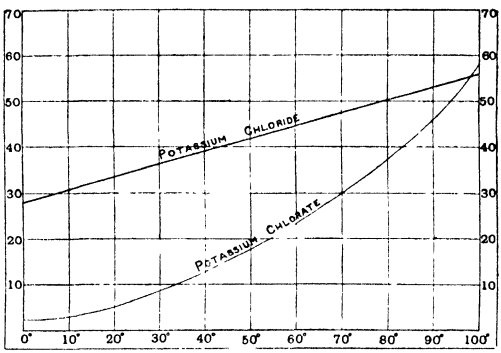


Fig. 54.

be confused with potassium chlor**ide**—the salt of hydrochloric acid which contains no oxygen. The ending -ate as used in chemistry denotes additional oxygen.

It is important to find the percentage of oxygen contained in potassium chlorate.

Preparation of oxygen.

This can be done by heating cautiously a weighed quantity until no more oxygen is evolved, and weighing the residue. If in addition the oxygen evolved is collected and measured, the density of oxygen can be calculated.

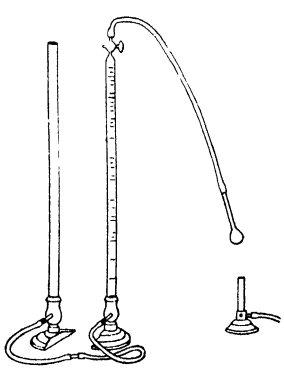


Fig. 55

A hard glass bulb tube is weighed, and when about ·5 gram of the chlorate has been added it is weighed again and connected by thick rubber tubing to a gas

burette (Fig. 55) which may contain water, or even better, mercury. The bulb is gently heated and the tap of the burette opened. The heating must be gradual throughout the experiment, and the top of the mercury in the open arm of the burette kept very slightly below that in the graduated arm, otherwise the bulb when red hot may be either blown out or sucked in. When no more gas is evolved the whole apparatus is left to cool, the level of the mercury being constantly adjusted as long as the bulb is soft. When the temperature is constant the stopcock is turned off and the volume of gas in the burette read. The air driven out of the bulb is of no consequence as it is displaced by the same volume of oxygen. The bulb tube is disengaged and weighed again.

Instead of the gas burette the air tight apparatus described in the Introduction can be used, and a greater volume of oxygen collected.

It will be found that pure potassium chlorate contains about 39·2 per cent. of oxygen. As this substance is manufactured in large quantities, it is a very convenient source of oxygen in the laboratory, and is especially valuable, because, when pure, it yields pure oxygen.

Now take some powdered chlorate and mix with it about one-third of its weight of powdered pyrolusite. On heating the mixture in a retort we notice that the oxygen is evolved with comparatively gentle heating, and that the total evolution of gas ceases long before the mixture is red hot.

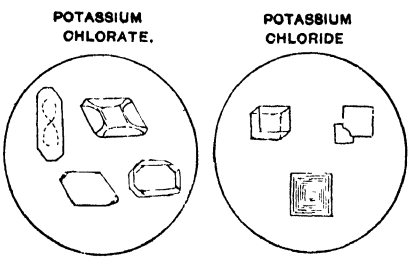
By taking weighed quantities of the two substances it may be shown not only that the oxygen evolved is that which would be given by the chlorate alone, but that the residue, treated with water to dissolve out the potassium chloride, leaves the same weight of pyrolusite that was originally taken.

This proves the extraordinary fact that the pyrolusite, although it is capable of supplying oxygen on its own account (Chapter II.) has merely accelerated the decomposition of the chlorate without itself suffering decomposition: it acts as a catalyser. For obtaining oxygen readily this method is generally adopted, although the oxygen is contaminated with slight traces of chlorine, evidently due to some secondary reaction with the pyrolusite.

NOTE.—If when the first evolution of oxygen from chlorate has finished, the reaction is stopped and the residue dissolved, a drop of the solution evaporated under the microscope yields crystals of potassium chloride and chlorate as before, but also a considerable number of a new form. This substance may be isolated by continued crystallisation from the least quantity of hot water, as it is even less soluble at high temperature than chlorate. When heated it yields 46 per cent. oxygen and is therefore called potassium perchlorate. Its formation may be represented thus

$$\left\{\begin{array}{l}\text{Potassium}\\ \text{Chlorine}\\ \text{Oxygen (39 per cent.)}\end{array}\right. \longrightarrow \left\{\begin{array}{l}\text{Potassium}\\ \text{Chloride}\end{array}\right. + \left\{\begin{array}{l}\text{Potassium}\\ \text{Chlorine}\\ \text{Oxygen (46 per cent.)}\end{array}\right.$$

While much chlorate has decomposed into oxygen and chloride, some of it has been oxidised still further at the expense of the rest of the chlorate.



Crystals growing from a drop of solution as seen under the microscope (Those of the chlorate should be compared with larger ones grown in the usual manner)

Fig. 56.

PROBLEMS. V A.

What happens when

(α) magnesium burns in air?

(β) a burning jet of hydrogen is lowered into a cylinder containing chlorine?

(γ) the product of β is passed over the heated product of α?

(δ) in γ, magnesium is substituted for the product of α?

(ϵ) chlorine is passed over heated magnesium?

From your answers provide a solution for this question:

'What evidence can you cite in support of the statement that the gas which is evolved when magnesium is placed in dilute solution of hydrochloric acid comes not from the water but from the acid?'

(ζ) What happens when powdered magnesium is placed in distilled water?

(η) What happens when steam is passed over heated magnesium ribbon?

How do these reactions bear on your previous answer?

CHAPTER VI.

THIRD LAW OF CHEMISTRY.

NOMENCLATURE.

IN Chapter II. the law of fixity of ratios was enunciated. No exception to the law has yet been discovered, and all chemical calculations are based upon its truth. The law is not self-evident however, as beginners are wont to suppose, and in fact was denied by a great chemist rather more than 100 years ago, but because it offers such a simple explanation of the constancy of properties of chemical substances, one accepts it readily and deems a proof superfluous. But the truth conveyed in the Law of Reciprocal Proportions strikes one at first as something unexpected and inexplicable. It is quite as wonderful in its way as the law of conservation of matter.

Now we have already obtained some evidence for a third Law of Chemical Combination. By analysis it was shown that litharge and lead peroxide contain 7·18 per cent. and 13·39 per cent. of oxygen respectively, and no very striking relation between the composition of the two oxides is revealed; but if the composition is stated in another way, as in litharge,

The third Law of Chemical Combination.

1 gram of lead is combined with ·0773 gram oxygen,

and in the peroxide

1 gram of lead is combined with ·1546 gram oxygen,

a remarkable relation is disclosed. For the numbers ·0773 and ·1546 are in the ratio 1 : 2, that is, in these two oxides the different quantities of oxygen combined with the same quantity (1 gram) of lead are in the simple ratio of one to

two. The same relation holds good of course for the different masses of lead combined with a fixed mass of oxygen in the two oxides. It follows also that lead has two equivalents, namely $103\frac{1}{2}$ and $51\frac{3}{4}$, one double the other. But this is only one of numerous cases.

Amongst the ores of copper are two oxides, **melaconite** the black oxide, containing 79·9 per cent. copper, with which we have already become acquainted; and a red one called **cuprite** which exists in much larger quantity. The red oxide may be formed by heating the black to a white heat. Analysis shows that it contains 88·8 per cent. copper. These results, like those of the oxides of lead, are not remarkable unless expressed in a particular way.

In cuprite

7·85 grams of copper are combined with 1 gram of oxygen.

In melaconite

3·93 grams of copper are combined with 1 gram of oxygen.

Again these two masses are in the ratio of 2 : 1.

Although we have not yet discussed how to analyse chlorides, the results of such analyses are available; they show that the relations existing between the proportion of chlorine and metal are precisely similar to those between oxygen and metal in oxides.

When iron reacts with chlorine a dark chloride is produced, but with hydrochloric acid a nearly colourless chloride is formed. In the former 1 gram of iron is combined with 1·9 grams of chlorine, and in the latter with 1·267. Hence these two quantities of chlorine which combine with 1 gram of iron are in the ratio of 2 : 3.

Again, when black copper oxide is dissolved in hydrochloric acid, or when copper is heated in a current of chlorine, a chloride is formed whose composition, as deduced from that of the black oxide, is 31·5 grams copper to 35·5 grams chlorine.

When hydrochloric acid gas was passed over copper metal a white chloride was obtained. This when analysed is found to contain 63 grams of copper for every 35·5 grams of chlorine, and therefore corresponds to the lower oxide. Again the masses of copper combined with the same mass (35·5 grams) of chlorine are as 1 : 2.

The white chloride is easily prepared from the higher green chloride by boiling a solution of the latter with copper shavings and concentrated hydrochloric acid. Some of the copper disappears and the solution becomes almost colourless or brown. In this condition it is poured into air-free cold water and the white chloride separates out as a crystalline powder. On exposure to the air it turns green (hence the use of boiled water). The acquisition of colour is due to absorption of oxygen to form a compound, to be mentioned more particularly later on, of this significant composition.

63 grams copper : 35·5 grams chlorine : 8 grams oxygen.

It differs from the higher chloride in the addition of a proportional 8 grams of oxygen instead of a proportional 35·5 grams chlorine to the copper and chlorine of the lower chloride. The white chloride differs in several ways from the green, it is insoluble in water and has the power to absorb oxygen.

The **Law of Multiple Ratios,** formulated by John Dalton (1802), brings together all the above results and many others in the generalisation—

'When two elements form more than one compound, the different masses of one element which combine with a fixed mass of the other, bear a simple relation to one another.'

Nomenclature.

So far the composition of compounds has usually been expressed centesimally: this important mode should never be neglected; but it is evident that the composition may also be expressed in equivalent parts, or multiples of these.

Thus for water the composition is 88·87 per cent. oxygen and 11·13 per cent. hydrogen, or oxygen 8 parts, hydrogen 1 part; hydrochloric acid consists of 97¼ per cent. chlorine and 2¾ per cent. hydrogen, or hydrogen 1 part and chlorine 35½ parts; litharge 92·82 per cent. lead and 7·18 per cent. oxygen, or lead 103½ parts and oxygen 8 parts, but for the peroxide (½ × 103½) parts lead and 8 parts of oxygen.

Potassium chloride, with 39 parts of potassium and 35·5 parts of chlorine, has the composition 52½ per cent. potassium and 47·5 per cent. chlorine, whilst the chlorate, with 39·1 per cent. oxygen, has by parts potassium 39, chlorine 35½, and oxygen 6 × 8.

In connection with the composition of chemical compounds a few remarks are necessary concerning nomenclature.

Before much was known of the composition of compounds,

names were applied to them which rather had reference to their appearance or superficial properties. Such for instance are litharge[1] and pyrolusite[2], and many others, some of which are still in use. As the knowledge of the chemical composition of bodies advanced, chemists endeavoured to find some system of naming compounds which would best indicate their constitution.

Binary compounds were named after both elements, the name of the electro-positive preceding that of the electro-negative element, and the suffix **-ide** being attached to a shortened form of the latter. For instance, magnesium oxide, sodium chloride.

But when several compounds of two elements exist, having different composition, a good nomenclature should clearly distinguish between them. No one system has been exclusively adopted and our present nomenclature is a combination of several systems.

The first is based on the use of affixes to the second word. The commoner compound is frequently called by the ordinary name, for instance the black oxide of copper is merely copper oxide, and litharge is lead oxide. The red oxide of copper is therefore called copper sub-oxide or copper prot-oxide, the affixes **sub-** and **proto-** indicating its lesser percentage of oxygen[3]. To indicate the higher percentage of oxygen the brown oxide of lead is called **peroxide**[4]. Another system employs the suffixes **-ous** and **-ic.** These are affixed to the first name, -ous to the compound containing the greater percentage of metal (or less percentage of oxygen) and -ic to the compound with less percentage of metal (or greater percentage of oxygen, &c.). The terminations are added to the names by which the metal is known throughout the scientific world, and these, for the commoner metals (for which each language has its own everyday word), have been bequeathed by the alchemists who generally wrote in Latin : thus the two oxides of copper are cuprous and cupric oxides, from *cupr(um)* ; the chlorides of iron are ferrous and ferric chlorides, from *ferr(um)*;

[1] λίθος = stone, ἄργυρος = silver.
[2] πῦρ = fire, λύω = to loose.
[3] *sub* = under ; *prot* from πρωτ = first.
[4] ὑπέρ = over.

but we say mercurous and mercuric chlorides to avoid the awkward and ill-sounding hydrargyrum[1]. Both these systems are in use, and it is curious that the oxides of lead are rarely referred to otherwise than as litharge and lead peroxide, whilst the black oxide of copper is as rarely named copper peroxide.

The term peroxide has a restricted meaning to be explained in Chapter XX.

In Chapter XI. another system, based upon totally different ideas of composition, will be explained.

To describe ternary compounds (that is compounds containing three elements) the two systems are combined in a way which will be explained as the necessity arises. We have had one instance in potassium chlorate, where the suffix -ide denoting a binary compound was changed into -ate to indicate the additional oxygen. The green compound formed by the oxidation of cuprous chloride is not called copper chlorate however, but cupric oxy-chloride. The distinction is important and will be established in Chapter XXI.

PROBLEMS, ETC. VI.

1. 10 grams of litharge were transformed into 10·7175 grams of lead peroxide. If litharge contains 7·18 per cent. of oxygen, deduce the two equivalents of lead.

2. Stannous chloride, a light yellow solid, and stannic chloride, a colourless fuming liquid, contain 37·37 per cent. and 54·4 per cent. of chlorine respectively. Show that they illustrate the Law of Multiple Proportion.

3. Mercurous oxide (black) and mercuric oxide (red) contain 96·15 per cent. and 92·59 per cent. of mercury respectively. Do they support the Law of Multiple Proportion?

4. 0·4 gram of chlorate of potassium, when strongly heated, gave 110·8 c.c. of oxygen at S.T.P. The residual potassium chloride weighed ·2423 gram. Calculate the density of oxygen.

5. Stas found that after heating 498·6355 grams of potassium chlorate 303·3870 grams of chloride remained. If the chloride contains 52·48 per cent. of metal, calculate the percentage composition of the chlorate.

6. Treat some cuprous oxide with hydrochloric acid. Do you obtain cuprous chloride? Explain the result.

7. Stas found that on evaporation with hydrogen chloride solution 302·8425 grams of potassium chlorate gave 184·2735 grams of chloride. How does the composition of chlorate found by this method agree with that found by ignition (Question 5)?

[1] ὕδωρ and ἄργυρος = water silver.

CHAPTER VII.

SULPHUR AND ITS OXIDES.

SULPHUR is a brittle yellow substance, slightly more than twice as dense as water. In air it burns languidly with a blue flame and the evolution of a pungent gas; in pure oxygen the action is more vigorous. Its colloquial name brimstone (brenstone or burning-stone) indicates its combustibility. When sulphur is heated in a retort it melts to an amber-coloured mobile liquid, which, as the temperature rises, grows dark and viscous; at a yet higher temperature it is still dark but again mobile. During cooling, the changes take place in the reverse order.

Allotropy of sulphur.

At 445° C. the liquid boils. The reddish vapour condenses in the neck of the retort to a dark mobile liquid which flows down and ignites at the mouth.

If the boiling liquid is cooled suddenly by allowing it to fall from the end of the retort into cold water (Fig. 57), it solidifies as an amber-tinted semi-transparent solid of waxy consistency, which may be drawn out into elastic threads. This **'plastic' sulphur** is rather less than twice as heavy as water. On standing, and more quickly when kneaded, it becomes lemon yellow, opaque, and brittle, and as dense as ordinary sulphur. If, however, the liquid sulphur is allowed

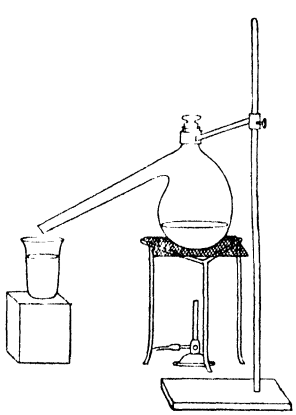


Fig. 57.

to cool slowly, another form is produced. Brimstone is melted in a large crucible and allowed to cool slowly; on the more rapidly cooling surface a crust forms, this is pierced to allow the liquid within to be poured off. Lining the cavity so produced and projecting obliquely into it will be seen a mass of needles. If some of these are carefully detached and placed on a microscope slide, a definite crystalline form will be recognised, but the ends are generally shapeless. They are called β-sulphur. Larger and more perfectly formed crystals can be grown under more favourable conditions;

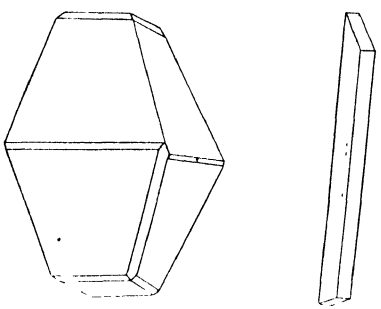


Fig. 58.

their shape gains for them the name monoclinic sulphur (Fig. 58). This **monoclinic** (or β-sulphur) has almost the same density as the plastic form, and like the latter, it becomes denser and opaque on standing.

Brimstone, the common form of sulphur, is not soluble in water, but it is soluble in one of its own compounds called carbon bisulphide.

This substance is formed by passing sulphur vapour over heated charcoal. It is a liquid which evaporates very readily, producing a heavy vapour, both poisonous and excessively inflammable (hence it must *never* be brought near a flame). When impure, and it usually is slightly impure, it is yellow and has a disagreeable odour; when pure it is not unpleasant and is colourless.

When 'flowers of sulphur'—formed by rapid cooling of sulphur vapour—are shaken up with carbon sulphide, the greater part will dissolve. The solution is decanted from the insoluble part and allowed to evaporate slowly. Beautiful

sparkling crystals of definite shape are deposited, whose form is only perfect, however, on those faces freely exposed to the solution (Fig. 58). Better crystals of unimpeded growth may be obtained by suspending a thread in the solution. These crystals have exactly the same density as brimstone, indeed it has been proved that ordinary sulphur is but an aggregation of numberless microscopic crystals of the same form, which, by an infinitude of reflection of light, render the brimstone opaque. This form is called α-sulphur or **rhombic sulphur.** α-sulphur is rather less soluble than β-sulphur in carbon sulphide, whilst plastic sulphur is insoluble. The insoluble part remaining when flowers of sulphur are treated with carbon bisulphide, is found to have no crystalline form, it is therefore called **amorphous** or **white** sulphur; when heated to 100° C. it changes to α-sulphur and becomes soluble. Another method by which this amorphous variety may be prepared is by exposing a solution of rhombic sulphur to bright sunlight; the ordinary sulphur slowly changes to the insoluble form which settles at the bottom of the vessel.

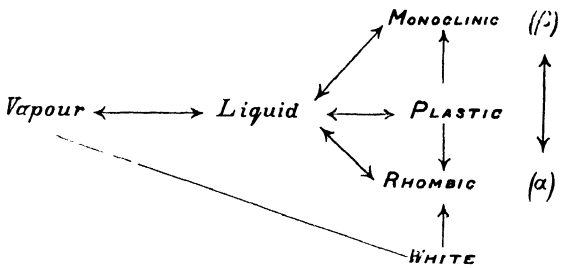
A discovery of considerable importance must be recorded. When sulphur is kept at a temperature above 96° C. it slowly changes into the β-form, whilst, if the temperature of the latter is not allowed to fall below 96° C., it never changes to the α-form. This temperature 96° C. is called the **'transition' temperature**; below it the β-form is unstable, above it the α-form is unstable.

Transparent crystals of the α-form may be placed in a test tube immersed in boiling water. They *gradually* become opaque, falling to minute β-form crystals. The tardiness of the change from α to β sulphur enables one to determine the melting point of rhombic sulphur. This point is about 114·5°. Monoclinic, which is stable above 96°, melts at 119° C.

Another important relation between these two varieties of sulphur is that below 96° the unstable β-sulphur is more soluble in carbon sulphide, above 96° (the carbon sulphide is under pressure) the unstable α-sulphur is more soluble. At 96° they are equally soluble.

But while these forms differ in so many ways they all agree in this—when equal masses are burnt in oxygen, all yield equal masses of the same gaseous oxide. Therefore sulphur is a substance existing in at least four different forms. All are solid at ordinary temperatures and readily change one into the other. They have never yielded any body

chemically simpler. The interchange may be represented diagrammatically thus—



Gaseous oxide of sulphur.

The gaseous oxide of sulphur is colourless but has an odour which distinguishes it from all other colourless gases. It neither burns nor supports combustion. Being thirty-two times as dense as hydrogen, the gas may be collected in the same manner as chlorine. When sulphur is burnt in pure oxygen, the oxide produced occupies the same volume as did the free oxygen from which it was formed, that is, oxygen takes up sulphur to form sulphur oxide without any change in volume.

This volume relation may be shown in a strong flask with

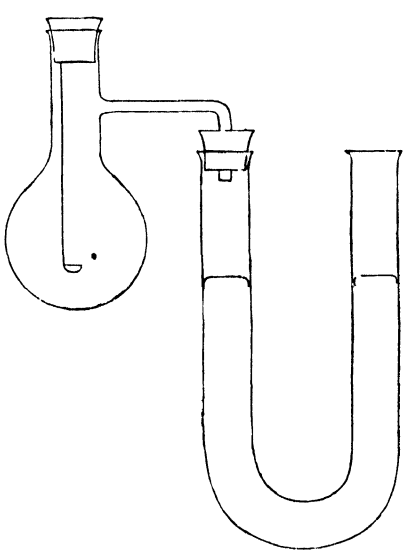


Fig. 59.

a side tube, and of about 600 c.c. capacity (Fig. 59). The side tube is bent and fitted air-tight to a large U-tube which contains mercury to serve as manometer. The rubber stopper carries a glass rod in which is fused a platinum wire; to the latter a piece of boat-shaped platinum foil is attached. A small piece of roll sulphur is placed in the boat, ignited in the air and then quickly thrust into the flask previously filled with oxygen. The stopper must at once be made quite secure. The sulphur burns brilliantly, and the expanded gas drives the mercury down the nearer limb of the U-tube. When the gas has cooled to the original temperature, the level of the mercury will be the same as at the start.

For the lecture bench the apparatus of Fig. 60 is more convenient. The glass stopper is pierced by two copper wires, one of which is expanded into a horizontal cup, whilst the other, tipped with platinum, ends just above it. The apparatus is filled with oxygen, the stopper, with a piece of sulphur in the cup, is replaced, and the level of the mercury adjusted and observed. Mercury is then run out to lower the pressure, and the sulphur ignited by electric sparks passed between the cup and the platinum. When the temperature is constant again, mercury is run in and becomes level at the original position.

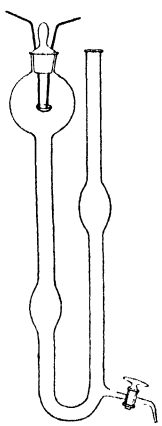


Fig. 60.

From this result and the relative densities of the gases it is possible to determine the composition of the oxide. Thirty-two grams of the oxide occupy the same volume as 16 grams of oxygen. Therefore 32 grams of the oxide contain 16 grams of oxygen and, by subtraction, 16 grams of sulphur. Hence sulphur oxide contains 50 per cent. sulphur and 50 per cent. oxygen, or 8 parts of sulphur to 8 of oxygen. The equivalent mass of sulphur is 8 grams.

This oxide of sulphur readily dissolves in water. A solution may be made by burning a piece of sulphur near one end of a short tube which is connected at the other end with a flask which contains water. Air is aspirated through the apparatus and the oxide dissolves. The oxide may be completely expelled from solution by boiling. The solution has the characteristic odour of the oxide, and first reddens and then slowly bleaches a piece of litmus paper. These reactions recall those of chlorine.

Magnesium ribbon, placed in the saturated solution, is steadily corroded; hydrogen is evolved and the smell of the solution gradually disappears. Magnesium oxide is likewise dissolved, but *without* the evolution of hydrogen. From *both* solutions a white solid may be obtained by evaporation.

These reactions appear similar to those of a solution of hydrochloric acid; in the latter case the hydrogen is expelled from the acid, but in the former the only possible source of hydrogen is the water in which the oxide is dissolved. Bearing in mind that magnesium oxide dissolves in the solution of the gaseous oxide, we can explain the first reaction as due to the intermediate formation of magnesium oxide from water, with liberation of hydrogen. When the white solid obtained by evaporation, referred to above, is treated with dilute hydrochloric acid, the odorous oxide of sulphur is evolved, and magnesium chloride remains in solution. It would seem then that in solution this oxide forms a compound with magnesium oxide. We shall return to this subject a little later.

Solid oxide of sulphur.

Although this gaseous oxide will not burn in air, yet, in certain circumstances, it will combine readily with oxygen to produce a higher oxide. In conformity with the nomenclature explained in the previous chapter, we shall refer to the lower oxide as Sulphurous oxide and to the higher oxide as Sulphuric oxide.

There is more than one mode of inducing sulphurous oxide to combine with oxygen; we shall choose the method easiest to understand and to perform. When the two dried gases are passed together through a moderately heated tube which contains very finely divided platinum metal, they promptly combine.

The platinum is deposited on the threads of woolly asbestos by dipping the latter in a solution containing 'platinum chloride,' and then heating strongly; the platinum is left behind as a black powder, distributed on the asbestos so that, in spite of its small mass, it exposes a large surface to the gases. The action of the platinum is entirely catalytic.

Dry oxygen and sulphurous oxide are passed together slowly over the 'platinised asbestos,' and into a receiver immersed in a good freezing mixture (Fig. 61).

Cork is attacked by sulphuric oxide, so that when the sulphuric oxide is

to be preserved the receiver must be provided with well-fitting glass stoppers.

The experiment may be carried out with simpler apparatus if the reaction alone is to be illustrated.

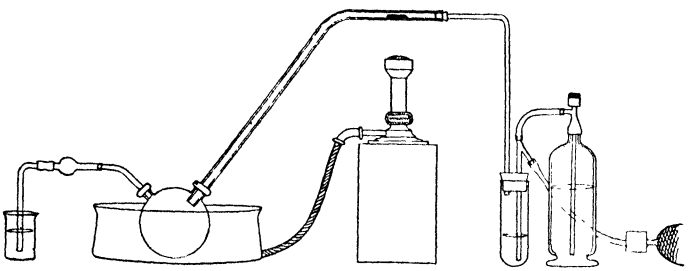


Fig. 61.

When the mixed gases are passed through the cold tube no combination takes place, but the reaction proceeds as soon as the platinum is raised to a dull red heat, a cloud forming if the apparatus contains any moisture. The oxide is obtained in fine needles if the whole apparatus is dry, otherwise it condenses to a fuming liquid. When sufficient has been collected, oxygen alone should be passed through the apparatus for some time, and lastly the receiver disconnected and quickly stoppered.

Sulphuric oxide is very dangerous to handle, and bad wounds result from its contact with the skin. Cork and indiarubber are charred at once.

This oxide is formed with evolution of heat, and when the heat is returned, it dissociates (hence for the synthesis the platinum must not be heated too strongly) into two volumes of the lower oxide and one of oxygen again. That is, two volumes of the lower oxide (S.G. = 32) combine with one volume of oxygen (S.G. = 16); therefore 64 grams of the lower oxide combine with 16 grams of oxygen to produce 80 grams of the higher oxide. Now 64 grams of the lower oxide contain 32 grams of each element, consequently 80 grams of the higher oxide contain $\frac{64}{2}$ grams of sulphur and $(\frac{64}{2} + 16)$ grams of oxygen, that is 8 grams of sulphur to 12 grams of oxygen. The composition of the two oxides supports the law of multiple proportion, and the equivalent mass of sulphur in this oxide is $8 \times \frac{2}{3} = 5\frac{1}{3}$ grams.

Sulphuric oxide fumes instantly in air, and dissolves so energetically when put in water, that even a small quantity is rather dangerous to deal with.

The crystals obtained by the above method are transparent and melt on warming; but on standing for some time they undergo (allotropic) transformation into long radiating silky fibres which no longer melt on heating, but, passing directly into vapour, form a sublimate of the same variety in a cooler part of the receiver.

The solution of the oxide in water is strongly acid even when very dilute; most metallic oxides are dissolved by it with ease, and many metals are corroded with evolution of hydrogen; indeed it seems no whit inferior to hydrochloric acid in these respects.

The solids, obtained by evaporating the oxide or metal solutions, are not decomposed by hydrochloric acid; most of them crystallise well and must be called salts, for they are formed by the expulsion of hydrogen by metals from an acid solution or by the neutralisation of bases.

How are we to regard these oxides of sulphur and their solutions? There have been several views: one of the earliest proceeds on the lines of our previous explanations. The metal, under the influence of the dissolved oxide, attacks the water and, liberating hydrogen, forms its own oxide, which at once combines with the acidic oxide to form the salt. According to this hypothesis the salt is a compound of metallic and acidic oxides. Later on it became certain that the sulphurous oxide and sulphuric oxide themselves combine with water *upon solution*, and this compound of acidic oxide and water is the acid; the oxide (before its solution) was renamed the **anhydride** of the acid because it was regarded as acid *less* water. The salt-formation was explained as the exchange of the metallic oxide for the combined water. This hypothesis received some support for the following reason: barium oxide forms the salt of the higher acid not only by solution of the oxide in the acid solution but also by direct combination with dry sulphuric oxide, and in the latter case the combination is so violent that the product is raised to incandescence.

Views held concerning acids.

At the time these ideas were current the composition of

hydrochloric acid was misunderstood, and every acid was believed to be formed by the solution of an oxide, hence the term oxygen[1], from ὀξύς = sharp, and γέννᾶν = to produce. Davy and Gay Lussac, working independently, proved that hydrochloric acid contains no oxygen. Thenceforward the idea that acids must be compounds of an oxide and water was gradually discarded, and now they are defined as particular compounds of hydrogen with another element, or group of elements, which passes into their salts unchanged.

It is not easy to appreciate these distinctions at once, especially as it is occasionally convenient to regard the reactions of an acid from the original point of view. We explain what happens when an acidic oxide dissolves in water as in two stages:

(1) that it combines with a small but definite mass of the water to produce its acid, and

(2) that this new compound is dissolved in the rest of the water.

The oxygen and hydrogen of water, once combined in the acid, have no longer the same relation as they had when they were still water.

Sulphurous and sulphuric acids.

The two acids formed from the oxides of sulphur are called Sulphurous and Sulphuric acids respectively. Their salts are distinguished by changing the suffix -ous into -ite and the suffix -ic into -ate.

The awkward trisyllabic words are shortened to **sulph-ite** and **sulph-ate**. These terms must be carefully distinguished from each other and from **sulph*ide***.

Sulphurous acid is unstable, and, when boiled, its solution is broken down again into water and sulphurous oxide: the latter escapes from the solution. Moreover it is a weak acid. Sulphuric acid on the other hand is strong, and so stable that it will bear a considerable degree of concentration. In concentrated form it is the well-known 'oil of vitriol,' and in this condition must be treated with care, for, like the oxide, it may cause very serious wounds; so great is its attraction for water that it chars the skin, and such wounds are most difficult to heal.

[1] German Sauerstoff.

Here it is necessary to remind the student that the words *strong* and *weak*, and *dilute* and *concentrated*, are not to be used indiscriminately. Sulphurous acid is a weak acid whether it is in dilute or saturated solution, whilst sulphuric acid remains a strong acid although diluted.

Sulphurous acid, in addition to being weak, is so unstable that it has never been obtained pure; its salts however are obtained as stable solids of well defined composition.

Sulphurous and sulphuric acids differ from hydrochloric acid in several particulars. First of all hydrochloric acid is a *gas*; when it dissolves it does not combine with the water to form a more complex substance. The hydrogen evolved when its *solution* acts on metals, was already contained in it in the gaseous condition, and the gaseous acid will, as we have seen (Chapter IV.), react with metals, yielding hydrogen and the salt. It is the best representative of the **hydr-acids**, the acids containing no oxygen, and it most nearly approaches the 'type' that is in our mind when we try to frame a definition of an '**acid.**' Sulphurous and sulphuric acids, on the other hand, obtain their hydrogen from the water in which the oxide of sulphur is dissolved; they are ternary compounds of hydrogen, sulphur, and oxygen; their hydrogen is replaced by metals to form salts, the sulphites and sulphates, so that, on the analogy of hydrogen chloride, we may call these acids hydrogen sulphite and hydrogen sulphate, thereby bringing into due prominence the essential feature of acids—compounds of hydrogen of a particular kind.

Acids which contain oxygen are called **oxy-acids** to distinguish them from hydracids. The oxygen, though derived from two sources—from the so-called anhydride and from water—is combined with the sulphur in such a way that one metal may displace another in the salts without disturbing the relation between the oxygen and sulphur (Chapter IX.). Such a combination of two elements *common to an acid and to all salts derived from it*, is called an '**acid radicle**': in the case of the acids studied in this chapter the two radicles are designated sulphite and sulphate.

The composition of the acids is a matter of importance. Consider sulphuric acid first. But for the danger, the following experiment might be performed in the laboratory.

A weighed quantity of sulphuric oxide might be dissolved in water, and the acid solution treated with magnesium until it is neutral to litmus, the hydrogen being collected and its weight deduced. From the weight of hydrogen displaced the weight of water which had combined with the acidic oxide could be calculated. Analysis has yielded the following composition of sulphuric acid: for every 1 gram of hydrogen there are 16 grams of sulphur and 32 grams of oxygen, that is, 40 grams of sulphuric oxide combine with 9 grams of water to produce 49 grams of sulphuric acid. A significant result. Oil of vitriol is very nearly pure sulphuric acid. The acid perfectly free from water has been obtained by freezing methods; just as pure water separates out as ice when sea water freezes, leaving the dissolved solids still dissolved in the bulk of the water, so from oil of vitriol some crystalline sulphuric acid settles out, and leaves the impurity *water* dissolved in the remainder of the oil of vitriol.

Equivalent solutions of sulphuric acid may be obtained by standardising (dilute) solutions of unknown concentration against $\frac{E}{10}$ caustic soda solution, and diluting to the calculated volume.

The composition of sulphurous acid is represented as hydrogen 1 part, sulphur 16 parts, oxygen 24 parts.

When sulphurous acid solution is exposed to the air it is gradually oxidised to sulphuric acid.

$$\left\{\begin{matrix}\text{Hydrogen (1)}\\ \text{Sulphur (16)}\\ \text{Oxygen (24)}\end{matrix}\right. \longrightarrow \left\{\begin{matrix}\text{Hydrogen (1)}\\ \text{Sulphur (16)}\\ \text{Oxygen (32)}\end{matrix}\right.$$

The oxidation is rather more rapid if the sulphurous acid solution is placed in a corked flask with an atmosphere of air, or better still oxygen, and *exposed to bright sunlight.*

Solutions of sulphites oxidise more rapidly than sulphurous acid.

The sulphates.

The **sulphates** are prepared by the action of sulphuric acid (1) on metals, (2) on oxides. The second method is more general.

In no case should the concentrated acid be used if the diluted acid will serve.

When oil of vitriol is diluted, much heat is evolved, and the dilution must be carried out with great care; the vitriol should be added little by little to water (never water to vitriol), best by letting it flow down the side of the containing vessel, and cooling if necessary after each addition of vitriol.

Caustic (soluble) bases are neutralised by dilute sulphuric acid and the salts obtained by crystallisation. With insoluble oxides care should be taken not to use an unnecessary quantity of acid. Metals should first be treated with cold dilute acid. Not all metals are easily attacked by the acid. Dilute sulphuric acid does not affect copper, but a hot fairly concentrated solution of the acid corrodes it. Sulphurous oxide, not hydrogen, is evolved. How is this to be explained? Sulphurous oxide may have been produced by the decomposition of sulphurous acid and the latter must previously have been produced from sulphuric acid by loss of oxygen.

We can *imagine* the reaction to take place in three stages:

A. Hot concentrated acid reacts with copper to produce copper sulphate (which dissolves) and hydrogen. As a matter of fact a little free hydrogen does escape.

B. The hydrogen reduces more hot concentrated sulphuric acid to sulphurous acid.

C. The sulphurous acid formed decomposes into water and escaping sulphurous oxide.

The reaction may then be illustrated *quantitatively by equations.*

A. $\left\{\begin{matrix}\text{Hydrogen (1)}\\ \text{Sulphur (16)}\\ \text{Oxygen (32)}\end{matrix}\right\} + \text{Copper (31·8)} = \left\{\begin{matrix}\text{Copper (31·8)}\\ \text{Sulphur (16)}\\ \text{Oxygen (32)}\end{matrix}\right\} + \text{Hydrogen (1)}$

B. $\text{Hydrogen (1)} + \left\{\begin{matrix}\text{Hydrogen (1)}\\ \text{Sulphur (16)}\\ \text{Oxygen (32)}\end{matrix}\right\} = \left\{\begin{matrix}\text{Hydrogen (1)}\\ \text{Sulphur (16)}\\ \text{Oxygen (24)}\end{matrix}\right\} + \begin{matrix}\text{Hydrogen (1)}\\ \text{Oxygen (8)}\end{matrix}$

C. $\left\{\begin{matrix}\text{Hydrogen (1)}\\ \text{Sulphur (16)}\\ \text{Oxygen (24)}\end{matrix}\right\} = \begin{matrix}\text{Hydrogen (1)}\\ \text{Oxygen (8)}\end{matrix} + \begin{matrix}\text{Sulphur (16)}\\ \text{Oxygen (16)}\end{matrix}$

In the above equations the sign of equality means that all the elements are accounted for, both before and after the reaction; it may be translated as '*yield*' or '*become*'; the sign of addition on the left-hand side as '*reacts with*,' the same sign on the right-hand side as '*and*.' The sign ↑ is often used to represent the escape of a gas, the sign ↓ as the formation of an insoluble from a dissolved substance. Acid radicles alone will, in future, be bracketed.

According to the above suggestions the sulphuric acid has played two separate and distinct parts; first it attacked the copper to produce a salt, that is, it acted as **an acid**, and then it acted as an **oxidising agent**, oxidising hydrogen to water, and being reduced to sulphurous acid in the process.

By the reduction of sulphuric acid as described above, sulphurous oxide is usually prepared in the laboratory. Copper shavings and a little water are placed in a flask fitted with safety funnel and delivery tube. A little concentrated acid is added through the funnel, and the flask cautiously warmed on a sand bath. The delivery tube can lead into water, or the gas may be collected by downward displacement. If the gas is passed through a worm or U-tube surrounded with an efficient freezing mixture it is obtained liquid (Fig. 62). Provided excess of sulphuric acid is avoided, fine blue crystals of copper sulphate may be recovered from the residue.

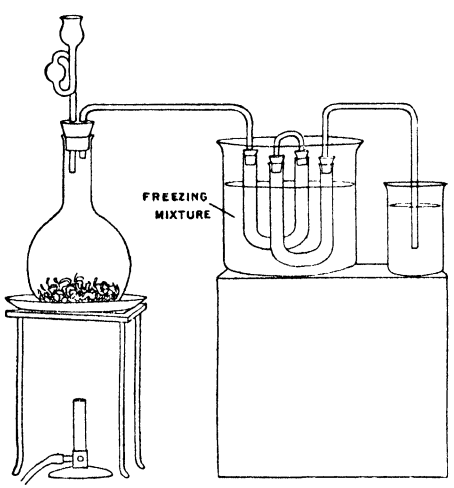


Fig. 62.

Sulphurous oxide is one of the easiest of gases to liquefy. The liquid in syphons is sold very cheaply.

The sulphates, as a rule, are soluble in water and crystallise much more easily than the majority of chlorides: some how-

ever are insoluble, the extreme case being barium sulphate.

Quantitative work with barium sulphate.

This is prepared as a precipitate[1] by the method of '*double displacement*' or '*double decomposition.*' Potassium sulphate and barium chloride are brought together in solution. The insoluble barium sulphate is precipitated throughout the liquid as a cloud of excessively fine particles. These gradually subside leaving the colourless solution of potassium chloride above.

$$\text{Potassium (39)} \left\{\begin{matrix}\text{Sulphur (16)}\\ \text{Oxygen (32)}\end{matrix}\right. + \text{Barium } (x) + \text{Chlorine (35·5)} = \text{Barium } (x) + \left\{\begin{matrix}\text{Sulphur (16)}\\ \text{Oxygen (32)}\end{matrix}\right. + \text{Potassium (39)} + \text{Chlorine (35·5)}$$

Barium sulphate may also be precipitated by using a dilute solution of sulphuric acid instead of its potassium salt.

The reaction does not differ essentially from the other methods of formation of salts, but the term applied to the method is convenient.

Barium sulphate is so insoluble that at ordinary temperatures only ·0025 gram dissolves in 1000 grams of pure water. Advantage is taken of this insolubility for finding the equivalent mass of barium, a metal very difficult to obtain pure, and whose oxide cannot be reduced. A known weight of potassium sulphate is dissolved and the whole of the potassium displaced by barium, the precipitated sulphate is then collected and weighed. By referring to the above equation it will be noticed that, of all the data, only (x), the equivalent mass of barium, is unknown: it may therefore be calculated. Denoting the weighed masses of potassium sulphate and barium sulphate by A and B respectively, we may state the equation thus:

$$(39 + 16 + 32) \text{ is to } (x + 16 + 32) \text{ as } A \text{ is to } B,$$

therefore $$A\,(x + 16 + 32) = B\,(39 + 16 + 32).$$

By substituting the actual weighings for A and B, x may be determined.

A weighed quantity of pure potassium sulphate is dissolved, to the hot solution a little hydrochloric acid is added, and then a hot solution of barium chloride until no more precipitate is formed. The beaker is heated for some time to make the precipitate granular and more easily filtered. The precipitate is carefully filtered, washed with hot water, and the funnel

[1] *praecipitatum* = cast downwards.

containing it is placed over a drying cone. When dry the filter paper is carefully detached from the funnel and placed on a piece of black glazed paper, and as much as possible of the sulphate is shaken into a weighed crucible which has previously been heated strongly and allowed to cool in a desiccator. The last trace of sulphate is transferred to the crucible by means of a small camel-hair brush. There still remains some precipitate in the pores of the filter. To obtain this the filter is carefully rolled in a long platinum wire (Fig. 63) and then, whilst held over the crucible, is ignited by

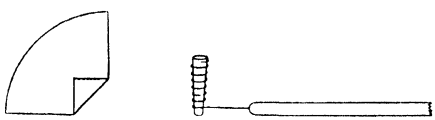


Fig. 63.

a Bunsen, and burnt to white ashes which are allowed to drop into the crucible. Owing to a reaction, which we shall explain in a later chapter, there is a slight loss of weight.

Special filter papers, the weight of whose ash is less than a milligram, are used. The crucible is alternately heated strongly and cooled in a desiccator until the weight is constant.

When barium sulphate is precipitated by the addition of a solution of barium chloride to dilute sulphuric acid, hydrochloric acid is formed. Now the most distinctive property of an acid is its propensity to form salts. In this case it almost seems that the hydrochloric acid has been dispossessed; at any rate it has been set free, which is the reverse action of forming a salt.

$$\text{Barium (68·5)} + \text{Chlorine (35·5)} + \begin{Bmatrix}\text{Hydrogen (1)}\\ \text{Sulphur (16)}\\ \text{Oxygen (32)}\end{Bmatrix} = \text{Barium (68·5)} + \begin{Bmatrix}\text{Sulphur (16)}\\ \text{Oxygen (32)}\end{Bmatrix} + \text{Hydrogen (1)} + \text{Chlorine (35·5)}$$

One might therefore argue that sulphuric acid is *stronger* than hydrochloric. Such is not necessarily the case however, for we shall discover cases where sulphuric acid is set free by an acid which is amongst the very weakest; in these cases also insoluble salts are formed. Evidently the acids are not competing on equal terms. As a matter of fact when silver sulphate solution is added to hydrochloric acid, silver chloride is precipitated and sulphuric acid left in solution.

$$\begin{Bmatrix}\text{Silver (108)}\\ \text{Sulphur (16)}\\ \text{Oxygen (32)}\end{Bmatrix} + \text{Hydrogen (1)} + \text{Chlorine (35·5)} = \text{Silver (108)} + \text{Chlorine (35·5)} + \begin{Bmatrix}\text{Hydrogen (1)}\\ \text{Sulphur (16)}\\ \text{Oxygen (32)}\end{Bmatrix}$$

We have not yet considered a means of comparing the strengths of the two acids.

The sulphates of iron.

It will be remembered that there are two chlorides of iron; there are also two sulphates of iron. Ferrous sulphate readily takes up oxygen from the air, especially when its solution is heated, so that precaution must be taken to avoid contact with air. The salt is best obtained by dissolving iron in moderately diluted sulphuric acid.

A flask is fitted with a Bunsen valve (Fig. 64), a contrivance which hinders the entrance of air from without, but does not prevent the gases from leaving the flask. The valve consists of a piece of narrow rubber tubing in which is a longitudinal slit about half an inch long; one end of the tube is closed with a stopper of glass rod, the other is fitted to a short delivery tube from the flask. The flask containing iron wire and dilute acid is heated, and the experiment is so arranged that when all the iron has been dissolved a little free acid still remains (this may be ascertained by trial). The solution is then boiled until it has been diminished considerably in bulk. Soon after the solution has ceased to boil, a small piece of washing soda is dropped in and the valve inserted. The reason for the last precaution will be explained later. The sulphate separates out in fine large green crystals.

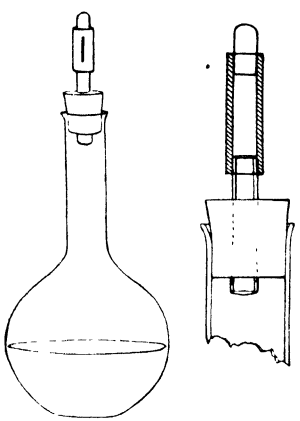


Fig. 64.

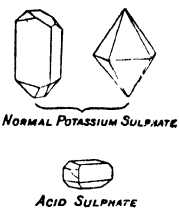
Ferric sulphate does not crystallise well, it is a yellow body which may be obtained by dissolving iron rust in sulphuric acid; although simple this method is not usually employed.

The sulphates of potassium.

Potassium, like iron, forms two sulphates, but the relation between them is quite different from that existing between the two iron compounds, for they are both derived from the *same* oxide. The ordinary potassium salt, prepared by neutralisation, crystallises well in prisms which are usually six-sided and capped by pyramids (Fig. 65*a*), and in general appearance recall 'rock crystal' (quartz). Its aqueous solution is neutral to litmus. If to a solution of caustic potash just double the quantity of sul-

phuric acid needed for neutralisation is added, on evaporation crystals of different form are deposited. They are tabular (Fig. 65*b*) and their solution is strongly acid. Their composition is

Potassium (39)
Hydrogen (1)
Sulphur (16 + 16)
Oxygen (32 + 32)



Figs. 65*a* and 65*b*.

This sulphate is called **acid potassium sulphate**: at one time it was called potassium bisulphate, indicating that the potassium had twice its share of acid radicle. The first name is to be preferred. To avoid confusion the ordinary salt is called **normal potassium sulphate.**

Preparation of hydrochloric acid.

When to solid sodium chloride concentrated sulphuric acid is added, and the mixture warmed, hydrochloric acid gas is evolved. This is the laboratory method of preparing the acid. The apparatus generally employed is a flask with a cork fitted with a safety funnel and a delivery tube. The gas may either be collected by downward displacement or passed into water. In the latter case it is best to avoid the possibility of cold water running back into the flask, by joining a small funnel on to the end of the delivery tube and arranging it so that the rim just meets the water (Fig. 66). The flask is warmed on a sand bath. Acid sodium sulphate is left in the flask.

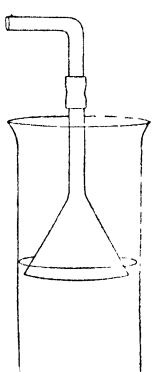


Fig. 66[1].

$$\begin{array}{lll} & & \text{Hydrogen (1)} \\ \text{Sodium (23)} & \text{Hydrogen (1) (1)} & \text{Sodium (23)} \quad \text{Hydrogen (1)} \\ \text{Chlorine (35·5)} & \left\{\begin{array}{l}\text{Sulphur (16) (16)}\\ \text{Oxygen (32) (32)}\end{array}\right. = & \left\{\begin{array}{l}\text{Sulphur (16+16)}\\ \text{Oxygen (32+32)}\end{array}\right. + \text{Chlorine (35·5)} \end{array}$$

This action appears to be another example of a stronger acid driving out a weaker: but later we shall study a case in which an undoubtedly weaker acid, at a high temperature, displaces sulphuric acid. Beginners are wont to be misled on this point, because their judgment is biassed by the extra-acid properties of sulphuric acid. Whereas hydrochloric

[1] See also note on Fig. 92 *a*, p. 212.

acid is an acid pure and simple, with the disadvantage of being a gas whose solution cannot be indefinitely concentrated, sulphuric acid is a liquid which may be obtained all but free from water. We find, as a general rule, that an acid with a higher boiling point will replace one of lower boiling point from combination in its salt; in this particular case, sulphuric acid, which boils well above 200° C., displaces hydrochloric acid which boils at −80° C.

Preparation of chlorine.

As a consequence of the previous reaction chlorine may be prepared from sodium chloride in one stage. Instead of salt alone a mixture of salt and pyrolusite is treated with concentrated sulphuric acid.

Great care must be taken in this experiment.

Hydrogen chloride is first formed but is immediately oxidised to water and chlorine (Question 15).

PROBLEMS. VII.

1. Compare the allotropy of oxygen with that of sulphur.

2. How would you attempt to separate a mixture of sulphurous oxide, hydrogen chloride, and air?

3. What volume of sulphurous oxide will be formed when 1 gram of sulphur is burnt?

4. Treat cuprous oxide with sulphuric acid. Explain the result.

5. Sodium chloride was heated cautiously and then strongly in a platinum crucible with drops of concentrated sulphuric acid, until only sodium sulphate was left. Given that 35·45 grams of chloride radicle are equivalent to 48 grams of sulphate radicle, find the equivalent of sodium when

The weight of crucible	26·59625	grams
„ „ +chloride	27·876	„
„ „ +sulphate ...	28·14925	„

6. Given the equivalent of sodium as 23 grams, how does the fact that 1 gram of sodium chloride is converted into 1·2137 grams of sodium sulphate confirm the view of the composition of sulphuric acid adopted in the text?

7. What volume of hydrogen chloride will be evolved and what weight of acid sodium sulphate will remain when sulphuric acid is heated with 5 grams of common salt?

8. What weight of sulphuric acid must combine with 10 grams of normal potassium sulphate to transform it into acid potassium sulphate?

9. What is the concentration of a solution of sulphuric acid of which 6·4 c.c. neutralises 10 c.c. of an unstandardised caustic soda solution, which is also neutralised by 9·7 c.c. of $\frac{E}{10}$ hydrogen chloride solution.

10. 2 grams of a solution of sulphuric acid were diluted with water and a solution of barium chloride added. 1·631 grams of barium sulphate were collected. Find the percentage composition of the acid solution.

11. Find the equivalent of a metal, of whose sulphate 1 gram yielded 1·114 grams of barium sulphate.

12. 10 c.c. of a solution containing both hydrochloric and sulphuric acids were neutralised by 37·6 c.c. of *normal* caustic soda. Another 10 c.c. yielded 2·402 grams of barium sulphate. Find the concentration of each acid per litre of solution.

13. When pure aluminium sulphate is calcined, it is decomposed entirely into alumina (aluminium oxide) and sulphuric oxide which escapes. According to Baubigny 6·2135 grams of the sulphate gave 1·8537 grams of alumina. Find the equivalent mass of aluminium.

14. Criticise the old term 'spirit of salt' for hydrochloric acid.

15. Investigate the action of concentrated sulphuric acid on pyrolusite; explain the above method of preparing chlorine.

16. Find two values for the equivalent mass of sodium and also the percentage composition of hydrogen chloride from the following results.

(i) 0·8854 gram of sodium was placed in water, 450 c.c. of hydrogen at 12·1° C. and 772·15 mm. pressure were collected (Aq. v.p. at 12·1° C. = 10·56 mm.; 1 litre of gas at S.T.P. weighs ·09 gram).

(ii) The solution was neutralised by hydrochloric acid and the salt formed obtained by evaporation. This salt weighed 2·2532 grams.

17. What law do the following results illustrate? From the results determine the equivalent of aluminium.

(*a*) 1 gram of aluminium was corroded by sulphuric acid; the hydrogen collected measured 1236 c.c. at S.T.P.

(*b*) The sulphate solution was evaporated down and the residue heated strongly. It decomposed into sulphuric oxide, which escaped, and aluminium oxide which remained behind. This oxide weighed 1·889 grams.

(*c*) In a new experiment the hydrogen displaced by 1 gram of aluminium was not collected, but was burnt in oxygen and the water thus formed was absorbed by calcium chloride. It was found to weigh ·999 gram.

CHAPTER VIII.

THE SULPHIDES.

The effect of heating a mixture of iron and sulphur.

BOTH constituents in a mixture of iron filings and powdered sulphur retain their properties unmodified. Carbon sulphide will dissolve out the sulphur leaving the iron, or the iron may be separated from the sulphur by magnetic attraction; dilute hydrochloric acid corrodes the iron (with evolution of hydrogen and formation of ferrous chloride solution) leaving the sulphur unattacked. But if one attempts to boil off the sulphur from the iron in a mixture containing seven parts of iron to four parts of sulphur, very soon the mass begins to glow and, once started, the glow will spread throughout the mass even if heating is discontinued. On cooling, a compact black mass remains in which neither constituent can be distinguished, and, though from the powdered mass a little sulphur may still be removed by solution and a little iron attracted by a magnet, the main portion is indifferent to both reagents. Dilute hydrochloric acid will still react but with a different result. Instead of hydrogen, a colourless gas with most offensive smell is evolved; as before, a solution of ferrous chloride is obtained, but there is now no residue of sulphur.

For success in the experiment, clean iron filings (not turnings) should be mixed well with flowers of sulphur. They may be heated in a test tube.

It seems probable therefore that the gas contains sulphur as well as the hydrogen from the acid, and this view is supported by the fact that it burns at a jet (blue flame) with the formation of water and sulphurous oxide; moreover, if the jet is lowered into a flask containing air, so that

there is a *limited* supply of oxygen, sulphur is soon deposited and water condenses on the side of the vessel.

Hydrogen sulphide.

The gas is therefore hydrogen sulphide, obtained from iron sulphide and hydrochloric acid. It is liquefied either by increase of pressure or decrease in temperature. It dissolves in cold water to form a solution which has its own offensive smell: it may be completely expelled by boiling. The solution has a slight reddening action on litmus paper, and, although it will not attack magnesium ribbon, when shaken up with 'reduced' iron powder a slow but steady stream of hydrogen is evolved. Hydrogen sulphide must therefore be regarded as an acid, albeit a weak one. It is an hydr-acid and may be called **sulphydric acid.**

When its solution in a corked flask is exposed to direct sunlight sulphur is precipitated, the odour of the gas disappears and only water is left. But if contact with oxygen is prevented by making the solution with air-free water and completely filling the flask and corking it securely, no change occurs.

Hydrogen sulphide may be synthesised by passing hydrogen through a tube in which sulphur is warmed. At moderate temperatures the gas is decomposed into hydrogen and sulphur. When heated with many metals it forms salts with evolution of hydrogen (compare hydrogen chloride). This reaction provides a simple method of ascertaining its composition; a pure specimen of the gas must be obtained: for this purpose it is prepared from a pure sulphide.

Antimony sulphide, a mineral called stibnite, is generally used. When found in nature this substance is gray, prepared in laboratories it is red.

The pure sulphide is heated in a flask with concentrated hydrochloric acid; the gas is dried by passing it through a U-tube containing calcium chloride. Besides having a disagreeable smell the gas is poisonous and therefore any excess must be absorbed by concentrated caustic potash solution. (Why?)

For finding the composition the apparatus of Fig. 59 may be used; tin is first placed on the *bottom* of the Jena flask and then all the air displaced by hydrogen sulphide. A rubber stopper is then inserted, and the tin gently heated

by a moving flame. When the gases cool the manometric mercury will regain its original position. From the above experiment it follows that hydrogen sulphide occupies the same volume as the hydrogen resulting from its decomposition.

Now hydrogen sulphide gas is 17 times as heavy as hydrogen, therefore 17 grams of the gas contain 1 gram of the hydrogen; hence 16 grams of sulphur are combined with 1 gram of hydrogen. The equivalent mass of sulphur as shown by this compound is 16 grams. We can now construct the equation for the preparation of the gas.

$$\begin{matrix}\text{Hydrogen (1)}\\ \text{Chlorine (35·5)}\end{matrix} + \begin{matrix}\text{Iron (28)}\\ \text{Sulphur (16)}\end{matrix} = \begin{matrix}\text{Hydrogen (1)}\\ \text{Sulphur (16)}\end{matrix} + \begin{matrix}\text{Iron (28)}\\ \text{Chlorine (35·5)}\end{matrix}$$

As ferrous chloride is derived from the iron sulphide we seem justified in assuming the iron salt to be ferrous sulphide.

Hydrogen sulphide cannot be dried by oil of vitriol as it is oxidised by the latter, the sulphuric acid at the same time being reduced to sulphurous acid; sulphurous oxide escapes.

Preparation of metallic sulphides.

When a solution of hydrogen sulphide is added to a solution of copper sulphate, an immediate precipitate (black) is formed and dilute sulphuric acid solution is left; the *weak* acid dispossesses the *stronger*.

$$\begin{matrix}\text{Copper (31·8)}\\ \left\{\begin{matrix}\text{Sulphur (16)}\\ \text{Oxygen (32)}\end{matrix}\right.\end{matrix} + \begin{matrix}\text{Hydrogen (1)}\\ \text{Sulphur (16)}\end{matrix} = \begin{matrix}\text{Hydrogen (1)}\\ \left\{\begin{matrix}\text{Sulphur (16)}\\ \text{Oxygen (32)}\end{matrix}\right.\end{matrix} + \begin{matrix}\text{Copper (31·8)}\\ \text{Sulphur (16)}\end{matrix}$$

If, instead of a solution of copper sulphate, ferrous chloride is used little or no ferrous sulphide is precipitated. Supposing the reaction had taken place it would be represented thus—

$$\begin{matrix}\text{Iron (28)}\\ \text{Chlorine (35}\tfrac{1}{2}\text{)}\end{matrix} + \begin{matrix}\text{Hydrogen (1)}\\ \text{Sulphur (16)}\end{matrix} = \begin{matrix}\text{Iron (28)}\\ \text{Sulphur (16)}\end{matrix} + \begin{matrix}\text{Hydrogen (1)}\\ \text{Chlorine (35}\tfrac{1}{2}\text{)}\end{matrix}$$

This is the reverse of the preparation of hydrogen sulphide from ferrous sulphide. The hydrochloric acid which would be formed, would at once attack the iron sulphide reproducing the original system. This can be made evident by adding a drop or two (not more than necessary) of caustic potash solution to neutralise the liberated acid; a black precipitate of ferrous sulphide appears as soon as the hydrogen chloride is neutralised. In the same way when solutions of other metallic chlorides are treated with hydrogen sulphide solution, some

sulphides will be precipitated in spite of the strong acid produced at the same time; such are those of antimony (orange red), arsenic (yellow), mercury (black), etc. These sulphides will be found insoluble in dilute strong acids. From solutions of some other metallic salts, precipitation will occur only when the acid is neutralised. In such cases, instead of hydrogen sulphide to precipitate the metallic sulphide a solution of potassium or sodium sulphide is used.

(These are prepared by passing the gas into the caustic base solution.)

$$\begin{matrix}\text{Sodium (23)} \\ \text{Oxygen (8)}\end{matrix} + \begin{matrix}\text{Hydrogen (1)} \\ \text{Sulphur (16)}\end{matrix} = \begin{matrix}\text{Hydrogen (1)} \\ \text{Oxygen (8)}\end{matrix} + \begin{matrix}\text{Sodium (23)} \\ \text{Sulphur (16)}\end{matrix}$$

When sodium sulphide is used, instead of the acid its sodium salt is formed.

$$\begin{matrix}\text{Iron (28)} \\ \text{Chlorine (35·5)}\end{matrix} + \begin{matrix}\text{Sodium (23)} \\ \text{Sulphur (16)}\end{matrix} = \begin{matrix}\text{Iron (28)} \\ \text{Sulphur (16)}\end{matrix} + \begin{matrix}\text{Sodium (23)} \\ \text{Chlorine (35}\tfrac{1}{2}\text{)}\end{matrix}$$

The sulphides are usually insoluble in water. They may be formed

(1) By direct action of metal and sulphur (for instance ferrous sulphide).

(2) Action of hydrogen sulphide gas on the metal (tin sulphide).

(3) Action of hydrogen sulphide solution on soluble bases (sodium sulphide).

(4) Double decomposition (cupric sulphide).

Comparison of hydrogen chloride and hydrogen sulphide.

The student will have noticed that in the preparation of sulph-hydric acid and of its salts the sulphides, there is an exact parallel with the preparation of chlor-hydric acid and its salts. The differences between the two hydr-acids are

(1) the greater ease with which hydrogen sulphide is oxidised, making it a reducing agent,

(2) the comparative instability of the sulphur hydr-acid;

(3) whilst the chlorides are generally soluble, the sulphides are generally insoluble; and lastly

(4) whilst chlor-hydric acid is one of the strongest, sulph-hydric is one of the weakest acids.

Hydrogen sulphide is almost always referred to as 'sulphuretted hydrogen,' a hardy survival which expresses its composition no better than hydrogen sulphide, and is an unnecessary excursion from the terminology.

Oxidation of sulphides.

If some of the powdered iron sulphide (formed by method 1) is moistened and exposed to the air, it rapidly turns into rust with liberation of sulphur. The oxidation is very rapid when the *precipitated* sulphide is exposed. On the other hand, when precipitated cupric sulphide is exposed to the air and new portions are continually brought to the surface, and the whole is kept moist, a blue sheen appears on the sulphide. If, after a few days, the still moist sulphide is shaken with water, the solution will be coloured blue, and with care the solution will be sufficiently concentrated to prove that copper sulphate has been reformed.

$$\begin{matrix}\text{Copper (31·8)}\\ \text{Sulphur (16)}\end{matrix} \longrightarrow \begin{matrix}\text{Copper (31·8)}\\ \text{Sulphur (16)}\\ \text{Oxygen (32)}\end{matrix}$$

Thus in air ferrous sulphide oxidises at ordinary temperatures to oxide and free sulphur, whilst cupric sulphide oxidises to cupric sulphate.

On the other hand when oxidation is accelerated by heating the sulphide in air (roasting), oxides are formed in *both* cases and the sulphur is further oxidised to sulphurous oxide, but even during rapid oxidation some sulphate may be formed.

Sulphur in nature.

Sulphur occurs uncombined on the earth, especially near volcanoes. In the gases evolved from volcanoes are found both hydrogen sulphide and sulphurous oxide. The occurrence of native sulphur has been attributed to the interaction of these gases. The reaction may be illustrated by passing the two gases at the same time into an empty flask. Sulphur will form in clouds and will settle with the moisture on the walls of the flask.

$$\begin{matrix}\text{Sulphur (16)}\\ \text{Hydrogen (1)}\end{matrix} + \begin{matrix}\text{Sulphur (8)}\\ \text{Oxygen (8)}\end{matrix} = \begin{matrix}\text{Hydrogen (1)}\\ \text{Oxygen (8)}\end{matrix} + \text{Sulphur (16+8)}$$

Streams which have their sources in volcanic regions frequently contain hydrogen sulphide and sulphuric acid. One in South America, called R. Vinaigre, is said to contain ·5 per cent. of sulphuric acid.

In combination sulphur occurs in metallic sulphides, which are found in great quantities. Some of the minerals, for instance, the sulphides of lead, mercury, zinc and copper, are used as ores.

The most important are :—

Galena (lead, 103½ : sulphur, 16).
Marcassite (iron, 28 : sulphur, 32).
Iron pyrites (iron, 28 : sulphur, 32).
Copper pyrites (ferrous sulphide and cupric sulphide).
Blende (zinc, 32½ : sulphur, 16).
Cinnabar (mercury, 100 : sulphur, 16).
Stibnite (antimony sulphide).
Realgar (red arsenical sulphide).
Orpiment (yellow arsenical sulphide).

Some of these minerals, where they become exposed to the moist atmosphere, oxidise to their respective sulphates or oxides. To such oxidation is to be imputed the occurrence of some native sulphates, such as zinc sulphate (white vitriol), from blende ; ferrous sulphate ('copperas' or green vitriol) from marcassite ; copper sulphate (blue vitriol) from copper pyrites ; and lead sulphate from galena. At Leadville in Colorado, and at Leadhills in Scotland, the surface of the galena is concealed by the products of its oxidation, minium and the sulphate.

Other native sulphates of importance are :—

Barytes or heavy spar (barium sulphate).
Celestine (strontium sulphate).
Alabaster or gypsum (calcium sulphate).
Epsom salts (magnesium sulphate).
Glauber's salt (sodium sulphate).
Alum and alumstone (sulphate of aluminium and potassium).
Potassium sulphate also occurs in large quantities in the famous salt beds of Stassfurth in Prussian Saxony.

Several of the native sulphides are important metallurgically.

Cinnabar is heated in special furnaces by hot gases mixed with air, the sulphur burns to sulphurous oxide, whilst the impure mercury condenses in cooling chambers.

Blende is 'roasted' in air till completely changed to zinc oxide and sulphurous oxide. The zinc is afterwards obtained from the oxide.

Galena is first 'roasted' in a furnace with air until about two-thirds is oxidised to oxide and sulphurous oxide. The

remaining sulphide is then heated with the oxide to a higher temperature, when the following reaction takes place:

$$\begin{matrix}\text{Lead } (103\tfrac{1}{2}) \\ \text{Sulphur } (16)\end{matrix} + \begin{matrix}\text{Lead } (103\tfrac{1}{2}+103\tfrac{1}{2}) \\ \text{Oxygen } (8+8)\end{matrix} = \begin{matrix}\text{Sulphur } (16) \\ \text{Oxygen } (16)\end{matrix} + \text{Lead } (3\times 103\tfrac{1}{2})$$

During the roasting some of the galena is oxidised to sulphate which subsequently reacts with some of the sulphide.

$$\left.\begin{matrix}\text{Lead } (103\tfrac{1}{2}) \\ \text{Sulphur } (16) \\ \text{Oxygen } (32)\end{matrix}\right\} + \begin{matrix}\text{Lead } (103\tfrac{1}{2}) \\ \text{Sulphur } (16)\end{matrix} = \begin{matrix}\text{Lead } (207) \\ \text{Sulphur } (32) + \\ \text{Oxygen } (32)\end{matrix}$$

Some crude copper is obtained from the native sulphide by a similar method.

All the above reactions, with cinnabar, lead sulphide and copper sulphide, may be imitated successfully in an ordinary hard glass test tube, or better, in a hard glass J-tube (open at both ends).

PROBLEMS. VIII.

1. What do you think would happen upon mixing solutions of chlorine and hydrogen sulphide? Explain your reasons. Go to the laboratory and test the truth of your conclusions.

2. What volume of hydrogen sulphide will be evolved when 3·94 grams of ferrous sulphide are treated with hydrogen chloride solution? What weight of sulphurous oxide will be formed by burning the evolved hydrogen sulphide?

3. What weight of mercury (E. = 100) should be obtained by heating 5 grams of cinnabar in a current of air?

4. 0·6723 gram of zinc blende was oxidised to sulphate. The sulphate formed was dissolved in water and barium chloride added. 1·57475 grams of barium sulphate were deposited. Find the purity of the blende.

5. What volumes of hydrogen sulphide and sulphurous oxide, by interaction, would yield just 1 gram of sulphur?

6. Deduce the composition (by parts) of sulphuric acid from the following:

1 gram of cadmium (Eq. mass = 56·2) was dissolved in a slight excess of hydrochloric acid and hydrogen sulphide passed into the solution. 1·2843 grams of yellow cadmium sulphide were collected. This sulphide was oxidised completely to sulphate, dissolved in water, and barium chloride added to the solution. 2·073 grams of barium sulphate were collected.

7. Suggest a method of obtaining lead sulphide from lead sulphate without dissolving it. Carry out your suggestion and report on what takes place. Test your product.

8. Pass hydrogen over weighed cupric sulphide and heat (Fig. 37). Investigate the product.

9. What are the products of treating zinc with sulphuric acid of various concentrations?

CHAPTER IX.

DEPOSITION OF METALS FROM THEIR SALT SOLUTIONS.

By Electrolysis.

WHEN a current of electricity is passed through a solution of sodium sulphate, hydrogen and oxygen are evolved at their respective electrodes, in the proportion of 2 to 1 by volume. This is exactly the result of electrolysing water to which a little dilute sulphuric acid has been added. We can account for the appearance of hydrogen instead of sodium by the reaction of the latter element with water (Chapter III.). The appearance of the oxygen at the anode is not so easy to explain.

When a solution of sodium sulphate, to which has been added a little litmus, is electrolysed, very soon the whole solution will be divided quite sharply into blue kathode and red anode regions. The blue around the kathode we should expect; the red about the anode shows the presence there of acid, probably sulphuric acid. Possibly the acid radicle of sulphuric acid journeys like that of hydrochloric acid to the anode. But whereas the acid radicle of hydrogen chloride can exist as chlorine, we know of no free compound containing sulphur and oxygen in the mass proportion of 16 : 32. We can, however, imagine that oxygen is lost at the anode by the radicle leaving sulphuric oxide (16 : 24) which would combine at once with water to produce sulphuric acid (1 : 16 : 32).

But it is evident that we must obtain some clearer insight into the movement of the radicle before we can understand properly what happens during electrolysis.

If instead of sodium sulphate, copper sulphate solution is electrolysed, copper is deposited on the kathode, and oxygen

is liberated at the anode as before, whilst a colourless dilute solution of sulphuric acid eventually remains. This agrees well with our previous assumptions, for we know that copper does not attack water.

By using a weak current and a very clean kathode a closely adhering layer of copper of a beautiful cerise tint is obtained. If the electrode is removable the weight of the deposited copper may be found, and if, during the whole time of the electrolysis, the oxygen also is collected, it will be found that for every 8 grams of oxygen evolved 31·8 grams of copper are deposited, that is, these elements are set free in masses proportional to their equivalents.

When a circuit includes a water voltameter, a solution of cupric sulphate, and a solution of cuprous chloride, it is found that the various kathode products are deposited in the following ratio: 1 of hydrogen, to 31·8 copper from cupric sulphate, to 63·6 copper from cuprous chloride. These masses are again in the ratio of the equivalents and are specially noteworthy because both equivalents of copper occur in the ratio.

Determination of chemical equivalents.

As a consequence of many such experiments, Faraday (1834) formulated his laws of electrolysis, the second of which states that—

When a current of electricity is passed successively through any number of electrolytes in solution, the whole forming one circuit, the masses of metal deposited, or of gases liberated, from their respective compounds, are in the ratio of their chemical equivalents.

This law enables us to compare the equivalents of two metals; and when the equivalent of one of the metals is accurately known, the equivalent of the other may be calculated from such an experiment. The equivalent of copper may be determined absolutely by finding the mass deposited by the same current which liberates a measured volume of hydrogen. Copper sulphate is electrolysed in a voltameter in which the anode is of copper and the kathode of platinum. In the same circuit is included a water voltameter so arranged that the volume of hydrogen can be measured. As it is desirable to collect a large volume of gases the arrangement in Fig. 67 may be conveniently employed. The platinum

plate, after being carefully cleaned, dried, and weighed, is replaced in the voltameter and the current started. At the close of the experiment the volume of gas is measured and

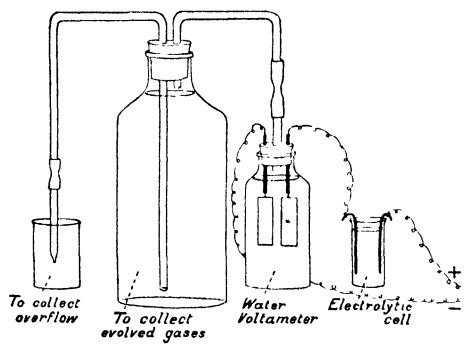


Fig. 67.

its mass calculated; the kathode again washed, dried and weighed, and the mass of copper deposited determined by difference. In order to ensure a firmly adhering deposit of copper, the strength of the current must be adjusted after a trial experiment.

When copper sulphate solution is electrolysed between *copper* anode and kathode, oxygen is not evolved at the anode, on the contrary the anode is corroded at exactly the same rate as the kathode is augmented, and the concentration of the copper sulphate undergoes no change. Pursuing our simple suggestion, we can suppose that the acid radicle attacks the copper to reform the original quantity of copper sulphate, instead of attacking water to form sulphuric acid with liberation of oxygen.

This behaviour is exploited in the refining of copper. A thin sheet of pure (electrolytic) copper serves as kathode and a sheet of crude copper as anode. The current is adjusted so that the copper alone goes into solution whilst the impurities, containing gold and silver, fall as a mud into a muslin bag of fine mesh. The net result is to transfer the anode copper to the kathode in a pure state.

Upon a kathode of any other conducting substance, pure copper may be deposited. By such methods are made the copper plates from which engravings are printed.

By displacement.

It is well known that a knife blade when placed in a solution of copper sulphate is coated with copper. If iron turnings are substituted for the knife blade and the action is allowed to continue for some time the solution becomes nearly colourless. From the solution ferrous sulphate may be crystallised, hence the iron must have displaced the copper from its salt, and as no gas is evolved, it must do so equivalent for equivalent.

$$\begin{matrix} \text{Copper (31·8)} & \text{Iron (28)} & & \text{Iron (28)} & \text{Copper (31·8)} \\ \left\{\begin{matrix}\text{Sulphur (16)} + \\ \text{Oxygen (32)}\end{matrix}\right. & & = & \left\{\begin{matrix}\text{Sulphur (16)} + \\ \text{Oxygen (32)}\end{matrix}\right. & \end{matrix}$$

Such reactions, although not universal, are by no means uncommon, and they afford another method of finding equivalents.

A sheet of pure zinc is well cleaned with emery paper, cut into strips and weighed. It is then immersed strip by strip in an air-free solution of copper sulphate, and as fast as the copper is deposited this is carefully scraped from the zinc by a glass spatula until all the zinc is dissolved. The liquid is poured through a small weighed filter paper. The copper, after being washed several times by decantation with air-free water, is all transferred to the filter paper. There it is washed with a little water and then with absolute alcohol. The filter is dried at 100° C., and weighed again. The accuracy of the experiment depends largely upon washing the copper quite free from zinc sulphate. The copper can be weighed without using a filter paper, but in this case small particles of the copper are invariably lost. Given the equivalent of copper as 31·8 the equivalent of zinc can be calculated.

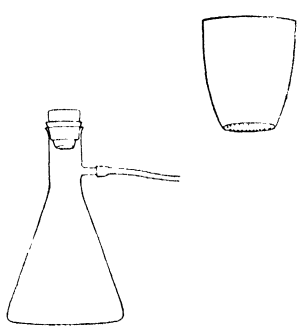


Fig. 68.

The mass of copper can be more accurately determined by substituting a Gooch crucible (Fig. 68) for the weighed filter paper. Such a crucible has its base perforated with very small holes. The crucible is fixed in a suction-filter-flask and a little shredded asbestos, suspended in water, is poured in it, and the suction started. The asbestos,

forming a thin layer over the holes, acts as a very efficient filter. The last trace of water is washed away by a few drops of absolute alcohol and then the crucible is disconnected, dried in an oven, and weighed. It is replaced in the suction flask and the whole reaction substance filtered through. The copper is kept covered with cold air-free water, which itself is displaced by absolute alcohol. The crucible with the copper is then dried and weighed again.

In the same way zinc will displace tin and lead. In the latter case, especially if the zinc rod is wrapped in asbestos paper and suspended in the middle of a 10 per cent. solution of lead salt, the lead often assumes a beautiful crystalline form (a lead tree). The equivalent of silver may also be obtained by the method.

Since zinc displaces iron, silver, lead, &c., it is said to be more electro-positive than these metals. Metals are arranged in an electro-chemical series, such that every metal will be displaced from its salts by those preceding it, and will displace from their solutions those that follow it. The 'alkali metals,' sodium and potassium (whose oxides are very difficult to reduce), are found at the head of the list; whilst the '**Noble** metals,' gold, silver, platinum (whose oxides are decomposed even by heating), are at the foot of the list.

Sodium and Potassium.
Magnesium.
Aluminium.
Zinc.
Iron.
Tin.
Lead.
(Hydrogen).
Copper.
Antimony.
Bismuth.
Mercury.
Silver.
Gold.

PROBLEMS. IX.

1. 0·4286 gram of Lee-Enfield bullet casing was dissolved in a suitable solvent. 0·33475 gram of copper and 0·09175 gram of nickel were deposited by electrolysis. Find the percentage composition of the alloy, assuming that the impurity is iron.

2. During the deposition of the nickel 35·36 c.c. of hydrogen were liberated from a voltameter by the same current. Find the equivalent mass of nickel.

3. From two solutions containing salts of copper and silver respectively, ·0214 gram of the former and ·0727 gram of the latter were deposited. Compare their equivalents.

4. Calculate the equivalent of magnesium when 0·113 gram of it displaces 1·008 grams of silver from its salt.

5. Hardin electrolysed salts of silver and of mercury, and found that 92·66 grams of mercury and 100 grams of silver were deposited by the same current. Find the equivalent of mercury.

6. Calculate the equivalent of gold from the following data: 100 c.c. of hydrogen at S.T.P. were obtained by the action of dilute sulphuric acid on zinc. In another experiment, using the same quantity of zinc and acid to which some gold chloride had been added, only 44·5 c.c. of hydrogen at S.T.P. were obtained and ·3258 gram of gold was deposited.

(Univ. Scholarship.)

7. Richards found that 100 grams of copper displaced 339·40 grams of silver (E. = 107·93). Calculate the exact equivalent of copper, and from the result and the following data calculate the equivalent of zinc:

Weight of Gooch crucible + asbestos.....16·024 grams.
" " " + copper.....17·908 grams.
" zinc which displaced copper ..... 1·934 grams.

8. Find the equivalent of zinc from the following results:

(*a*) A current of electricity was passed successively through acidulated water and through a solution of a silver salt. It was found that while ·437 gram of silver was deposited, 46·7 c.c. of hydrogen at 7° C. and 759 mm. (barometer) was collected over water. [Aq. v.p. at 7° = 7·5 mm.]

(*b*) In another experiment 1·036 gram of zinc was placed in an excess of solution of silver nitrate. The silver deposited weighed 3·422 grams.

CHAPTER X.

CARBON AND ITS OXIDES.

WHEN a piece of wood is burnt in air, the greater part disappears as colourless gases, and by aspirating them through a tube, one, by condensation, may be shown to be steam. Only a little infusible ash remains. When, however, the wood is heated out of contact with air in a retort (destructive distillation), gases are likewise evolved, some of which readily condense to form tarry matter, and the rest passing on contains much combustible gas which may be ignited, whilst in the retort remains a black mass, called **charcoal**.

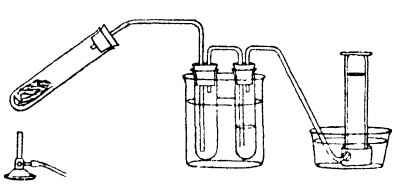


Fig. 69.

Charcoal burns less readily than wood, and leaves behind the same infusible ash. Charcoal is more often obtained by heating wood in air, so that some of the wood is sacrificed completely in order to supply the heat necessary to char the remainder.

Vegetation which has been buried for millions of years has reached a state called **coal**: this when distilled yields **coke**. Coke and charcoal are impure **carbon**[1]. Pure carbon may be prepared by heating in a tube certain vegetable products such as pure sugar, in which the ash constituents

[1] *carbo* = charcoal.

are nearly or quite absent. A charred mass is obtained which may be completely purified by passing over it, when heated, chlorine, which attacks impurities, but, as we have already stated, does not directly combine with carbon. It removes all but a negligible ash.

When pure carbon is heated in oxygen it burns with the production of a colourless gas.

Two substances which occur naturally also give nothing but this gas when heated in oxygen; and further, equal masses of the three bodies give equal mass of gas. These two substances are **Diamond** and **Graphite**. From them and from ordinary carbon nothing simpler has been obtained. Hence they are not only elements but are one and the same chemical element: carbon is an element existing in three allotropic forms.

The chemical history of carbon is one of great interest. Who would surmise that diamond is identical with graphite—the hardest and most brilliant substance with one so soft and dull, or who suspect that either substance is the same as charcoal? Diamond was at one time confused with rock crystal (quartz), which in its turn was considered a variety of congealed water. The discovery that diamond disappears when strongly heated in air led, in 1771, to the further discovery that, during the burning, a gas is evolved like that emitted by burning charcoal. In 1800 it was shown that graphite burns to form the same gas.

Graphite has been a very perplexing substance from the earliest times. About three centuries ago it was first used in writing-pencils (whence the name graphite). Because it marks paper it was confused with lead (whence the name plumbago), and pencils are to this day made of 'black lead.' Besides being confused with lead it was scarcely ever distinguished from a substance named molybdaena[1] which also marks paper and has exactly the same appearance. Molybdaena has since been shown to be a metallic sulphide containing neither carbon nor lead.

Diamonds, when heated *out* of contact with air, swell up and change into graphite, and both forms burn in air at about the melting point of common salt.

[1] μολυβδός = lead.

One of the recent triumphs of chemistry has been the artificial production of diamonds. The late Prof. Henri Moissan, of Paris, dissolved carbon in molten iron, raised to the prodigious temperature of his electric furnace. The molten metal dropped into a cold liquid was suddenly cooled, forming a solid crust which, contracting, exerted a very great pressure. In these circumstances, the greater part of the carbon crystallised as graphite, a lesser portion as 'bort' (a substance like diamond, but dark), and very little as minute colourless diamonds. The metal was variously treated by acids and other reagents to separate the diamonds.

Carbonic anhydride

The gaseous oxide of carbon has a slightly sharp and agreeable taste. It dissolves moderately in water, and from its solution may be entirely expelled by boiling. The solution turns litmus paper slightly red; magnesium ribbon remains unattacked, but magnesium powder is corroded by it with slow evolution of hydrogen. We have here another acid anhydride which, combining with water, produces an acid, although a very weak and very unstable one. The acid is called carbonic acid and the gas carbonic anhydride.

Like all gases which are acids (chlorhydric and sulphydric) or which produce acids in solution (sulphurous oxide) it is completely absorbed by caustic bases to produce a salt—in this case the carbonate. The complete absorption of carbonic anhydride is an operation of great importance in practical chemistry, and many pieces of apparatus have been designed for the purpose. They should be light for weighing, and able to stand upright to avoid spilling the contained liquid; a nice pattern—Geissler's absorption bulbs—is best described by the figure. The apparatus stands quite safely because one small bulb is not in the same straight line with its fellows. The three small bulbs are half filled with concentrated caustic potash solution.

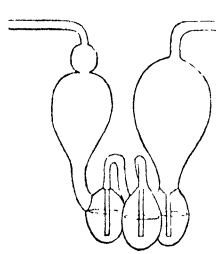


Fig. 70.

The apparatus is easily charged, by suction, through a long rubber tube, care being taken that no potash reaches the mouth. It is easily emptied and washed. The gas is passed from right to left of apparatus.

Carbonic acid is displaced from its salts, the carbonates, by other dilute acids, and at once breaks up into water and carbonic anhydride. This reaction affords a simple method of obtaining the anhydride in large quantities. Marble, a crystalline form of calcium carbonate, is placed in the middle part of a Kipp apparatus, and dilute hydrochloric acid is admitted as before. The gas may be dried by oil of vitriol or calcium chloride.

Carbonic anhydride is frequently used in chemical operations for displacing an atmosphere of air when readily oxidisable substances are being prepared. Wherefore a little washing soda (sodium carbonate) was dropped into the acid solution of ferrous sulphate (Chapter VII.). The carbonic anhydride is heavy and therefore not rapidly diffusible.

Carbonic anhydride is 22 times as heavy as hydrogen. Its composition may be determined both gasometrically and gravimetrically.

In the first method the Lecture bench apparatus (modified) described under sulphurous oxide is used. The pan is replaced by a horizontal spiral of platinum in which a stick of carbon is put. As with sulphur, so with carbon, the volume of the oxide is exactly the same as that of the free oxygen. Therefore 22 grams of the gaseous oxide contain 16 grams of oxygen, leaving 6 grams for the carbon. The equivalent of carbon as found in this oxide must be 3 grams.

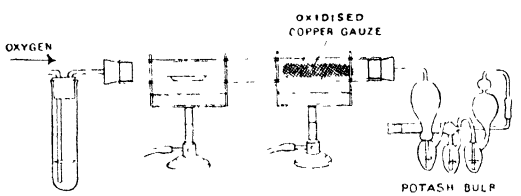


Fig. 71.

In the gravimetric method, dried oxygen or air is passed through a heated hard glass tube which contains a boat with a weighed quantity of carbon; the resulting carbonic anhydride is absorbed in a weighed Geissler apparatus.

Sugar charcoal is dried by first heating it in air and then allowing it to cool in a desiccator. About 1 gram is placed in a dried and weighed boat and the boat reweighed. It is then placed in the middle of the tube, and oxygen passed through at such a rate that the bubbles can easily be counted

as they pass through the drying and absorbing apparatus. The tube is heated by burners below the boat. As soon as the carbon has been oxidised the heating is stopped, but the current of oxygen is continued until the boat is cool, and all the carbonic anhydride formed has been swept into the potash. The boat (and possibly ash) is then weighed again.

Carbonic anhydride does not burn and in the ordinary sense does not support combustion. If, however, a piece of magnesium ribbon which has been ignited in the air is thrust into a jar of the gas, it continues to burn with formation of magnesium oxide (and some carbonate) and soot is set free.

The lower oxide of carbon.

When carbonic anhydride is passed over carbon contained in a porcelain tube heated strongly in a furnace, not all the issuing gas dissolves in caustic potash, a part passes through the solution and may be collected over water. This gas is colourless, and on applying a light burns with the curious blue flame often seen playing over glowing coke. From the flame the gas formed may be aspirated and shown to be carbonic anhydride. The lower oxide is quite poisonous and should not be inhaled.

It can more readily be prepared by passing carbonic anhydride through a well-heated tube which contains zinc dust; zinc oxide is produced at the same time.

The inflammable oxide obviously contains a lesser percentage of oxygen and therefore a greater percentage of carbon than carbonic anhydride. It is a lower oxide. The gas is 14 times as heavy as hydrogen, it has therefore the same specific gravity as nitrogen, which it resembles in two other physical properties, for the solubility in water of the two gases and the boiling points of their liquids differ but slightly.

The lower oxide of carbon, as we have said, combines with oxygen to produce the higher oxide. A mixture of oxygen and the inflammable oxide is explosive; if the explosion takes place in a eudiometer the volume proportions of the lower oxide may be ascertained. The experiment differs little from that performed with hydrogen and oxygen. The dried and purified gases are separately introduced into the eudiometer and their volumes measured. Sparks are passed and the volume is read after the temperature has fallen. A few drops of concentrated potash are admitted, which rise to

the top of the mercury and absorb the carbonic anhydride produced, and the excess of oxygen is measured. The vapour pressure of the concentrated potash solution is so small that it may be neglected. It will be found that when the volume of lower oxide is twice that of the oxygen, the whole combines to produce a volume of carbonic anhydride equal to that of the lower oxide alone. That is, 2 volumes of lower oxide combine with 1 volume of oxygen to produce 2 volumes of higher oxide. Since the specific gravities (H = 1) of the gases are lower oxide 14, oxygen 16, carbonic anhydride 22, it follows that 28 grams of lower oxide have combined with 16 grams of oxygen to produce 44 grams of carbonic anhydride. But it has already been proved that 22×2 grams of carbonic anhydride contain 6×2 grams of carbon and 16×2 grams of oxygen. Consequently the 28 grams of lower oxide, in which the whole of the carbon occurs, consist of 6×2 grams of carbon and 16 grams of oxygen. The equivalent mass of carbon as shown by this oxide is 6 grams.

As the inflammable oxide of carbon combines readily with oxygen it is a very good reducing agent: when passed over the heated oxides of iron and copper it will reduce them to the metals with simultaneous formation of the carbonic anhydride. This reaction suggests a method of ascertaining accurately the composition of the oxide.

The whole operation resembles that described for the gravimetric estimation of water. The differences extend only to details (see Fig. 41). The lower oxide (which must be free from carbonic anhydride) takes the place of the hydrogen, the U-tube of fused calcium chloride is changed to a

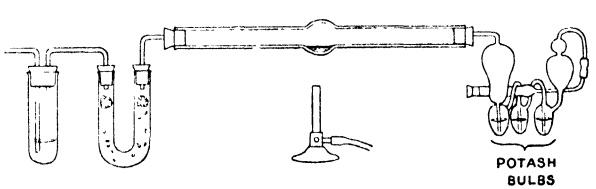


Fig. 72.

set of potash bulbs (Fig. 72). As a condensible substance is not formed, the absorbing apparatus may be simplified.

The increase in the weight of the absorption apparatus is the mass of the carbonic anhydride formed, the loss in weight of the copper oxide is that of the extra oxygen; and the difference of the two is the mass of the lower oxide which has suffered oxidation.

Unlike sulphurous and sulphuric oxides and carbonic anhydride, the solution of this oxide is not acidic. It is called therefore an 'indifferent' oxide.

The lower oxide is easily obtained by several methods, the reactions in which are at present beyond our understanding. One method, though inconvenient if gas is to be collected, will be mentioned because it helps us to understand its origin in grates. The oxide is formed when air or oxygen is passed slowly over a large quantity of carbon heated in a furnace

Carbon 6 + Oxygen 8 = Carbon 6,
Oxygen 8.

Air which ascends from below a grate meets with the lowest 'live coals' and combines with carbon to form the higher oxide; this is carried on by the draught through the middle of the red hot fire where, in contact with red hot carbon and because of lack of oxygen, it is reduced to the lower oxide; this lower oxide on emerging above the coal, where it meets more air, is burnt or escapes up the flue.

NOTE.—The student will have wondered why the two oxides of carbon were not referred to as carbonous and carbonic oxides, according to the system explained in Chapter VI. The inconsistency is a consequence of the confusion that has overtaken the naming of these oxides. By a few Americans the system is adhered to. In England, however, the *lower* oxide is called carbonic oxide, and the higher oxide is called carbonic anhydride or, worse, carbonic acid gas. Some authors of technical and geological books refer to it as carbonic acid, which it certainly is not. These names are the survivals of the early ideas on acids referred to under sulphuric acid.

It is now more usual to distinguish the two oxides according to a nomenclature based upon the accepted theory of the ultimate constitution of matter, which will be studied in the following chapter.

PROBLEMS. X.

1. Roscoe found that 6·4406 grams of transparent Cape diamonds gave 23·6114 grams of carbonic anhydride.

Calculate the percentage composition of the gas and the equivalent of carbon.

2. What volume of carbonic anhydride will be given by burning 1 gram of carbon?

3. Dumas and Stas obtained the following results (1840):

A. 1·216 grams of natural graphite gave 4·461 grams of carbonic anhydride.

B. 0·998 gram of artificial graphite gave 3·662 grams of carbonic anhydride.

C. 1·232 grams of diamond graphite gave 4·517 grams of carbonic anhydride.

Compare the results.

4. Stas (1849) found that when the lower oxide of carbon was passed over heated copper oxide

61·926 grams of carbonic anhydride were formed,
and 22·515 grams of oxygen were lost by the copper oxide.

Taking the composition of the higher oxide as

Carbon 27·278 per cent.,
Oxygen 72·722 per cent.,

deduce the percentage composition of the lower oxide. Show that the Law of Multiple Proportions is supported.

5. 39 c.c. of the lower oxide of carbon were exploded with 24 c.c. of oxygen. 43½ c.c. of gas was left, of which all but 4½ c.c. dissolved in caustic potash solution. Deduce the composition of the lower oxide.

6. How would you separate nitrogen from a mixture of the lower and higher oxides of carbon?

7. Deduce the percentage composition of carbonic acid from the following:

A solution of caustic soda was made from ·4 gram of sodium (Eq. mass = 23). Into this solution carbonic anhydride was passed. The carbonate was obtained by evaporation and dried thoroughly. It weighed ·9217 gram.

8. Anthracite contains 92·56 per cent. of carbon. When 12 grams of carbon burn to form 44 grams of carbonic anhydride 96960 calories are evolved. Find the quantity of water at 100° C. which theoretically should be turned into steam (latent heat 537) by the combustion of 1 kilogram of anthracite.

CHAPTER XI.

THE ATOMIC AND MOLECULAR THEORIES.

In Chapter II. the Law of Fixity of Composition was stated. 'Every definite chemical compound—from whatsoever source obtained—always consists of the same elements combined together in the same proportion by mass.'

The composition of copper oxide was investigated in order to provide, by the ordinary methods of elementary work, a proof of the law: and with the following results:

Oxidation of Copper.

Source of Copper and method of oxidation	Weight of Copper taken	Weight of Copper-oxide collected	Per-centage Copper	Equiva-lent
	grs.	grs.		
I. Displaced from sulphate and oxidised by oxygen ...	3·296	4·121	79·98	31·96
II. 'Reduced' copper—oxidised by oxygen	5·444	6·811	79·93	31·85
III. 'Electrolytic' copper—oxidised by nitric acid ...	2·835	3·546	79·95	31·90
Arithmetic mean =			79·94	31·9
Correct value =			79·90	31·8

Reduction of Copper Oxide by Hydrogen.

	Source of the Oxide	Weight of Copper-oxide taken	Weight of Copper obtained	Per-centage Copper	Equiva-lent
IV.	The mineral melaconite ...	5·787	4·639	80·17	32·32
V.	By heating artificial carbonate	2·459	1·967	80	31·98
VI.	By heating natural carbonate (malachite) ...	2·120	1·691	79·76	31·53
VII.	By heating nitrate ...	0·810	0·647	79·88	31·75
VIII.	By heating hydroxide ...	5·057	4·038	79·87	31·7

In II. the use of reduced copper was perhaps inadmissible as to some extent 'begging the question.'

It will be noticed that whilst the numbers in the fourth column agree extremely well, the equivalent is not so constant. This is owing to the whole error being thrown upon the per-centage of oxygen, which is found by difference.

Two extracts from the writings of Proust—who established this law—will not be out of place:

'According to our principles a compound is a..... privileged product to which nature assigns fixed ratios, it is, in short, a being which nature never creates even when through the agency of man, otherwise than balance in hand, *pondere et mesura*. Let us therefore recognise, that the properties of true compounds are invariable as is the ratio of their constituents. Between pole and pole they are found identical in these two respects; their appearance may vary owing to the manner of aggregation, but their properties never.'

And again,

'We must conclude that nature acts not differently in the depths of the earth than on its surface and through the agency of man. These ratios always the same, these constant properties which characterise the true compounds of art or nature, in one word this *pondus naturae*.....is no more left to the power of chemists, than is the law of election which governs all these combinations.'

The Third Law of Chemical Combination—the Law of

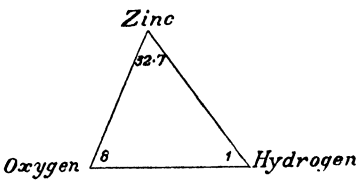
Multiple Proportions—has been sufficiently illustrated in the sixth and following chapters.

The Second Law, the Law of Reciprocal Ratios, deduced in Chapter IV., needs some extension in consequence of the law of multiple proportions. It will then read

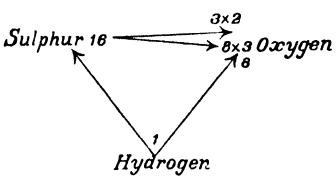
'The masses of different elements which combine separately with any given mass of another element are either in the same ratio as the masses of these different elements which combine with each other, or in simple multiples of that ratio.'

For example,

1. Simple reciprocal



2. Multiple reciprocal



These three laws were stated over 100 years ago. The student should make himself very familiar with them, and especially should he reflect upon their simplicity; he will then recognise that any hypothesis advanced to explain them must have above all things the same stamp of simplicity.

In 1807 Dr Dalton of Manchester published his *Atomic Theory*, which explains in a very clear manner the above three laws. In order to appreciate his notions, it is necessary to anticipate him somewhat. It is a common experience that a block of wood (or any other substance) may be divided into smaller pieces by suitable means. And the limit to the minuteness of division depends only upon the delicacy of our dissecting instruments and our skill in using them. Particles which with a knife cannot be further divided, under a hand lens can still be pulled asunder with fine needles, and so it may be argued that with infinite skill and infinitely delicate and precise instruments there would be no limit to the degree of division we could accomplish.

The doctrine of the infinite divisibility of matter has been maintained since the time of the ancient Greeks. On the other hand, another school of Greek philosophers argued that there is a limit to the extent to which bodies are capable of division, and the ultimate particles which would defy severance they designated **atoms**[1]. Both views persisted even to the time of Dalton, contemporaries like Descartes and Newton holding different opinions on the question.

Dalton, like Newton before him, adopted the second doctrine, and explained that if the particles resulting from ultimate division could be isolated and examined, they would prove for every definite chemical substance to be alike, and, above all other properties, to have equal mass, but that the ultimate particles of a selected chemical substance would differ from the ultimate particles of every other substance, especially in mass. For these ultimate particles he proposed to retain the word 'atom.'

But there are atoms of two kinds, the atoms of elements and the atoms of compounds, the latter formed by union of unlike elementary atoms; and whilst neither kind of atom can be further divided by mechanical means, the compound atom can be resolved into elementary atoms by chemical means.

As regards the method of union amongst elementary atoms to form compound atoms, Dalton laid down the rule that atoms combine together in **simple** ratio by number, and he was led by his own observations to prefer the ratios between, say, the number of atoms of A to the number of B, as either 1 to 1, 1 to 2, or 2 : 1, 1 to 3, or 3 : 1.

It will be seen therefore that Dalton's theory is very simple and may be condensed into a very few words. The mass is a definite and characteristic property of the atom: when different elementary atoms combine to form a compound atom, they do so in numbers whose ratio is simple.

Dalton always assumed that when only one compound of two elements exists, the compound atom consists of one atom of each element. For instance, sodium chloride is said to consist of one atom of sodium combined with one atom of chlorine.

[1] ἀτόμος = a thing which cannot be cut.

The Daltonian theory has been considerably developed since first stated, and to-day the whole language of Chemistry bears eloquent testimony to its complete acceptance.

We have said that the laws of chemical combination are clearly explained by the theory.

Law I.

Inasmuch as all the atoms of a compound are alike, each compound atom of the same substance consists of the same number of simple atoms having each a fixed mass, it follows that any aggregate of atoms (pure specimens) has the same definite proportion of mass as each individual atom. Although it is scarcely within the limits of probability that the actual mass of any elementary atom will ever be directly measured with accuracy, we can *compare* the masses of elementary atoms by comparing the masses in which they are found combined together, provided that we know how many elementary atoms of each kind the compound atom of the chosen compound contains. And in this lies the difficulty, for we cannot determine the intimate composition of particles so minute. And therefore we must fall back on Dalton's rule, that the simplest composition of a compound must be adopted unless there are convincing reasons showing the contrary.

In order to give a clear pictorial representation of his ideas concerning compound atoms, Dalton portrayed elementary atoms as circles, the different elements being distinguished by various ornamentations.

For instance

Oxygen = ○
Hydrogen = ⊙
Nitrogen = ⓘ
Sulphur = ⊕
Carbon = ◉

And he pictured compound atoms by arranging the circles together. For instance water, which according to his rule has the simplest composition, he represented by the symbol ⊙○.

It must be borne in mind that Dalton had no *evidence* for his idea of the constitution of water; its only merit is simplicity, it might for aught he knew to the contrary be truly represented as ⊙○⊙ or ○⊙○.

In water the mass proportion of the two elements is

oxygen to hydrogen as 8 to 1, therefore, according to Dalton's choice, the relative masses of the **atoms** of hydrogen and oxygen are 8 to 1. But from the second formula we get the ratio 16 : 1, and from the third 4 : 1.

The results of analysis prove that in all compounds containing hydrogen the other elements occur in the larger proportion, consequently Dalton chose hydrogen as the **standard** for comparing atomic weights, and the atomic weight of hydrogen he fixed for convenience as 1. In order to determine the atomic weights of other elements, their hydrogen compounds must be accurately analysed. This is not an easy matter in many cases, and, moreover, there are many metals which form no hydrogen compounds. On the other hand all metals form compounds with oxygen, and in practice it is usual to analyse the oxide or other compound containing oxygen. Then by applying reciprocal relations the atomic weight is found, so that only indirectly are the atomic weights of most elements referred to hydrogen. Hence the importance of determining *exactly* the ratio in which hydrogen and oxygen combine.

Berzelius simplified the representation of compounds by substituting for Dalton's circles the initial letter of the universal name of the element, and he added a second small letter for distinction when necessary. In the list appended the universal name is placed in brackets. A few only of the most important elements are included.

Ag (Argentum)	Silver	Mg	Magnesium
Ba	Barium	Mn	Manganese
C	Carbon	N	Nitrogen
Ca	Calcium	Na (Natrium)	Sodium
Cd	Cadmium	O	Oxygen
Cl	Chlorine	P	Phosphorus
Cu (Cuprum)	Copper	S	Sulphur
Fe (Ferrum)	Iron	Sn (Stannum)	Tin
H	Hydrogen	Sb (Stibium)	Antimony
Hg (Hydrargyrum)	Mercury	Pb (Plumbum)	Lead
K (Kalium)	Potassium	Zn	Zinc

When he believed that a compound atom contains more than one atom of the same element, he indicated the fact by

an index. Thus, for water, Dalton's circles would not become HO, HOH, or OHO (although in special cases it is convenient so to represent a compound atom) but HO, H_2O, or HO_2.

Such a representation of a compound is called its **Formula.** When he wished to show *several complete* compound atoms, he placed the number *in front of* the formula 2HO, $2H_2O$. He did *not* write H_2O_2 or H_4O_2 as the case might be.

Law II. As combination can take place only between atoms which are of fixed mass, it follows that any particular element may always be represented in a compound by its atomic mass or by a simple multiple of this, regardless of the element with which it is combined.

Law III. When two elements X and Y form more than one compound, taking the *simplest* proportion, the compound atoms may be represented either by XY and XY_2 or by X_2Y and XY. And each pair of formulae agrees with the proportion 1 : 2 by mass for X and for Y.

But although it is easy enough to *illustrate* the law, it is another matter to decide which of the two sets of formulae truly represents the compound atoms.

For instance, take the case of the two oxides of carbon. The lower oxide contains 8 grams of oxygen to 6 grams of carbon, and the higher oxide contains 8 grams of oxygen to 3 grams of carbon.

Their formulae can be represented thus:

Lower oxide C_2O ..... $2 \times 3 : 8$
Higher oxide CO ..... $3 : 8$

but they are equally well represented thus:

Lower oxide CO ..... $6 : 8$
Higher oxide CO_2 ..... $6 : 8 \times 2$.

In the first set the atomic weight of carbon is 3, and in the second set it is 6 (if $O = 8$). It is merely a matter of personal preference which set of formulae is adopted, and consequently those who choose the first set assign to carbon the atomic weight of 3, while those chemists who prefer the second set of formulae adopt the atomic weight of 6. Such rival systems of formulae and atomic weights caused not a little confusion in the early part of last century.

Equivalent mass and atomic weight.

It will have become evident to the student that the number which represents the equivalent mass of an element is closely related to the number which represents its atomic weight, and in fact is either the same as, or a submultiple of, the latter.

The standard for atomic weights is hydrogen 1, the equivalent mass of an element combines with 1 gram of hydrogen, and this is why the two sets of numbers are often coincident. But had the standard, either for equivalent mass or for atomic weight, been chosen differently, the connection between the numbers would not have been striking.

Law IV.

Soon after Dalton had enunciated his atomic theory, a law of far reaching importance was formulated by M. Gay Lussac (1808).

The student will already have been impressed by the simplicity of the results of experiments performed to discover the volumes of gases which interact; and perhaps he may have thought it strange that his attention has not yet been specially called to this simplicity.

In all cases when two gases (compound or elementary) **combine, they do so in volumes either equal to one another or in simple ratio, and, furthermore, when the product of the reaction is also gaseous, its volume is simply related to those of its components.**

The instances of gaseous interaction so far studied are

I. 2 vols. hydrogen unite with 1 vol. oxygen to give 2 vols. steam.

II. 1 vol. hydrogen unites with 1 vol. chlorine to give 2 vols. hydrogen chloride.

III. 1 vol. oxygen unites with (solid) sulphur to give 1 vol. sulphurous oxide.

IV. 1 vol. oxygen unites with 2 vols. sulphurous oxide to give 2 vols. sulphuric oxide.

V. 1 vol. hydrogen unites with (solid) sulphur to give 1 vol. hydrogen sulphide.

VI. 2 vols. hydrogen sulphide react with 3 vols. oxygen to give 2 vols. steam + 2 vols. sulphurous oxide.

VII. 1 vol. oxygen unites with (solid) carbon to give 1 vol. carbonic anhydride.

VIII. 2 vols. lower oxide unite with 1 vol. oxygen to give 2 vols. carbonic anhydride.

IX. 2 vols. hydrogen sulphide react with 1 vol. sulphurous oxide to give (liquid) water and (solid) sulphur.

These results are generalised in the '**Law of Volumes**' stated above. These ratios in which gases interact by volume recall in their simplicity those from which the Law of Multiple Proportions was deduced. Gay Lussac, having deduced the law from results similar to those just collected, at once drew attention to the similarity between Dalton's hypothesis and his own law.

Elements combine together in simple ratio by atoms.

Elementary gases combine together in simple ratio by volume.

Gay Lussac's Law, however, is equally true for all compound gases.

He pointed out that the similarity could not be dismissed as a mere coincidence, and suggested as a possible explanation, that equal volumes of gases contain equal numbers of atoms.

The molecular theory.

This hypothesis, valuable as it was in supporting his own, was repudiated by Dalton—who indeed denied the truth of the law—although some other chemists, notably Berzelius, welcomed it as a valuable aid for determining atomic weights. When the hypothesis is applied to explain particular cases some inconsistencies are revealed.

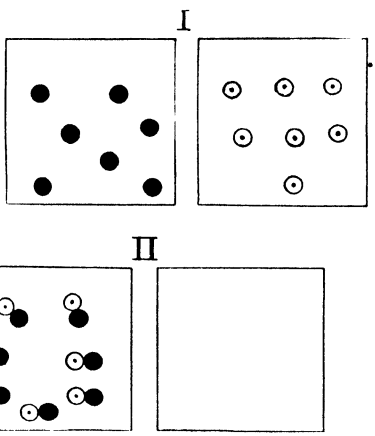
One volume of hydrogen combines with 1 volume of chlorine to produce 2 volumes of hydrogen chloride, therefore x atoms of hydrogen combine with x atoms of chlorine to produce $2x$ atoms of hydrogen chloride. That is, both hydrogen and chlorine *atoms* must be *halved* in order to produce $2x$ compound atoms of hydrogen chloride, every atom of which contains both hydrogen and chlorine. But atoms cannot be halved.

Again, 2 volumes of hydrogen combine with 1 volume of oxygen, therefore $2x$ atoms of hydrogen combine with $1x$ atoms of oxygen; the formula for water should be H_2O. And, to carry on the argument, 2 volumes of steam are formed, hence $2x$ compound atoms of steam should be formed also. But to produce $2x$ atoms of steam—every one of which contains an equal mass of oxygen—we must assume the halving of each atom of oxygen, a denial of the foundation of the Atomic Theory. And the difficulty cannot be avoided by disregarding the volumes of the *compounds* produced,

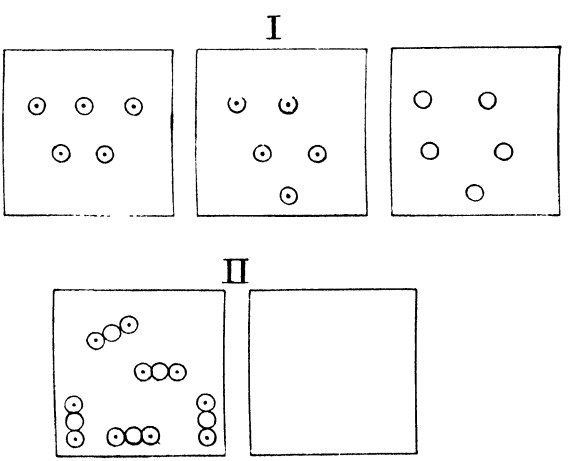
because the Law of Volumes is as true for compound gases as for elementary gases.

The student is strongly recommended to illustrate the above arguments for himself. Several cardboard trays, all of the same size, are taken to represent equal volumes, and cubes, or better still spheres, differently coloured, represent different elementary atoms. To represent compound atoms small holes are drilled into the spheres, so that they may be fixed together by pegs. An equal number of spheres is placed in each tray, and the proper redistribution attempted thus (the student must not be satisfied with the diagrams alone).

Hydrogen Chloride



Water



The matter could not be left in this unsatisfactory position, and shortly afterwards (1810) Avogadro, an Italian, reconciled the apparent inconsistencies by a very simple extension of the Daltonian conception of the ultimate particle.

According to Avogadro, also, the atom of an element is the smallest particle of it that can enter into combination, but the smallest *free* particle of element or compound he renamed **molecule**[1]. Hence all ultimate particles of compounds are molecules. The atoms of elements cannot be further divided, but it does not follow that a free particle of an element necessarily consists of only one atom, on the contrary, Avogadro assumed that each free particle—or **molecule**—of oxygen, hydrogen, chlorine, and other *gaseous* elements, consists of *two* atoms. Hence the molecular weight of hydrogen is 2, whilst its atomic weight is 1.

The compound molecule consists of atoms for the most part unlike, whilst the elementary molecule consists of like atoms. By substituting in Gay Lussac's hypothesis the word molecule for atom, we formulate Avogadro's hypothesis

'**Equal volumes of gases** (under equal conditions of temperature and pressure) **contain equal numbers of molecules.**'

The molecular weight of an element or a compound is the sum of the weights of its several atoms. Compounds have molecular weight only, elements have both molecular and atomic weights.

And now in the new light we can attack the old problems of the composition of water and of hydrogen chloride.

1 volume of hydrogen + 1 volume of chlorine give 2 volumes of hydrogen chloride.

x molecules of hydrogen + x molecules of chlorine give $2x$ molecules of hydrogen chloride.

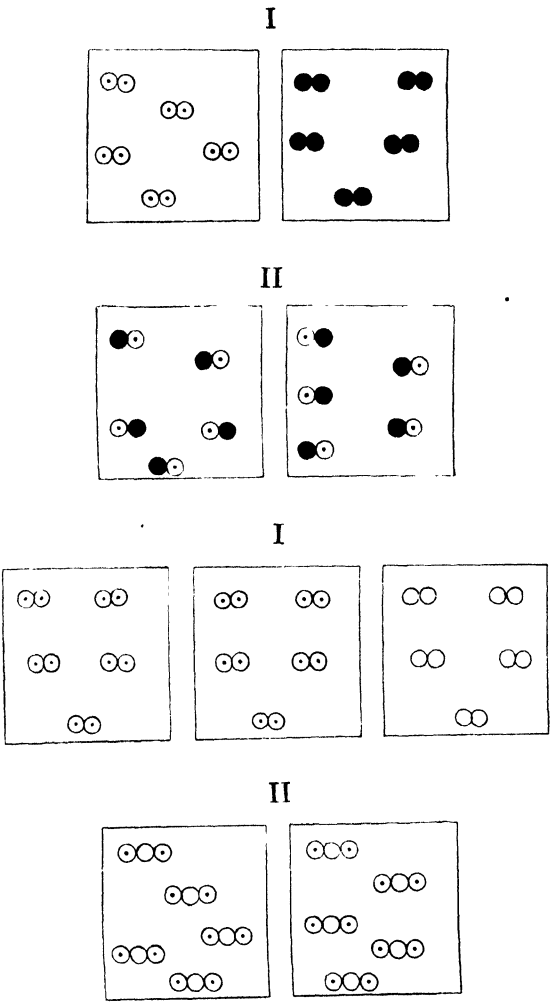
Every molecule of the elements splits into two single atoms, which, changing partners, produce molecules of hydrogen chloride which contain one atom of each element.

2 volumes of hydrogen and 1 volume of oxygen give 2 volumes of steam,

$2x$ molecules of hydrogen and $1x$ molecule of oxygen give $2x$ molecules of steam,

[1] *molecula* = a little mass.

and the molecule of oxygen can split into half molecules, that is, atoms, which help to form separate molecules of steam.



When this hypothesis was accepted the atomic weight of oxygen was settled definitely as **16**, and the atomic weights of all other elements which had been based on oxygen as 8, were doubled.

Unfortunately, when Avogadro stated his hypothesis

chemists were so intent upon other problems that its importance in deciding between alternative formulae (and therefore atomic weights) was not recognised, and the prevailing confusion continued, until about the middle of the last century it became intolerable. Then Cannizzaro, a fellow countryman of Avogadro, restated his views so convincingly that almost every one adopted them, and 'Avogadro's hypothesis' assumed the dignity of the '**molecular theory**' of gases. It is quite in harmony with, and may be deduced from, the Kinetic Theory of gases which is based on the physical laws of Boyle and Charles.

It is important to remember that the Molecular Theory does not assert that molecules of different gases occupy equal spaces—that unlike molecules are of the same size. It does assert that equal numbers of molecules exist in equal spaces under the same conditions. There is a great difference between the two statements. Molecules are not supposed to be in contact, on the contrary the average distance between any two molecules is such that, compared with it, their diameters are negligible, and therefore also, compared with the space in which they move, the volume actually occupied by the molecules is likewise negligible.

A crude mental picture of gaseous volume may be obtained by imagining a room in which 1000 bodies of, say, the size of pinheads, are moving about in all directions, bombarding the walls and cannonading against one another, but inasmuch as the volume of the room remains constant their average distance apart at any time is also constant. If we imagine the pinheads replaced by the same number of bodies as large as peas, the average distance apart of the new bodies is, for nearly all purposes, the same as that of the pinheads.

When a gas is compressed in volume the molecules are not compressed but their *free path* is contracted. Hence when the pressure on a gas is continuously increased, the free path is gradually reduced until the molecules are so near together that new forces come into play.

Therefore conclusions respecting the relative weights of molecules of any particular gases cannot be drawn if the densities are determined under conditions in which the gases deny Boyle's and Charles' laws. Gases support these laws, in general, more exactly the further the temperature departs from their liquefying points.

CHAPTER XII.

FORMULAE AND EQUATIONS.

M = 2D.

If equal volumes of gases contain equal numbers of molecules, it follows that the masses of equal volumes of gases (under the same conditions) are in the proportion of the masses of their molecules or, in other words, **the densities of gases are in the ratio of their molecular weights.** The densities of gases are compared with that of hydrogen, therefore the number which represents the specific gravity of a gas (hydrogen = 1) also represents how many times heavier is its *molecule* than the *molecule* of hydrogen. But as the weight of a molecule is the sum of the weights of its *atoms*, the molecular weight of a gas represents how many times its molecule is as heavy as the **atom** of hydrogen.

But by Avogadro's assumption the molecule of hydrogen consists of 2 atoms, therefore the molecular weight of a gas is not represented by the same number as its specific gravity (hydrogen = 1) but by *twice* that number, that is $M.Wt = 2D$, where D = density relative to hydrogen.

For instance, oxygen is 16 times as heavy as hydrogen, that is, the *molecule* of oxygen is 16 times as heavy as the *molecule* of hydrogen; its molecular weight is 32. And by Avogadro's assumption the molecule of oxygen consists of two atoms [O_2]. In the same way the S.G. of steam is 9 but its molecular weight is 18 [H_2O]. The S.G. of chlorine is 35½ times that of hydrogen: its molecular weight is however 71 [Cl_2]. The S.G. of hydrogen chloride is 18·25, its molecular weight is therefore 36·5 [HCl] and so on.

Determination of atomic weight by the method of densities.

Upon the theory just explained is based a method of determining the atomic weight of an element without first having to assume a formula for any of its compounds.

Suppose that the atomic weight of chlorine is desired. Chlorine is an element having several gaseous compounds and many others which are readily vapourised. It is extremely likely that among so many, at least one, and probably more than one, compound will contain only one atom of chlorine in the molecule; and the greater the number of compounds studied the greater is the probability that such a compound is included. It is obvious that the molecular weight of a compound with only one atom of chlorine in its molecule, contains the atomic weight of chlorine. Therefore, the percentage composition of each being known, the densities of as many as possible gaseous and vapourisable compounds of chlorine are determined. The last step is to arrange the composition of each compound in terms of its molecular weight. The smallest number representing the quantity of chlorine contained in any of these molecular weights must be the highest possible value for, and will probably be the true value for, the atomic weight of chlorine. For, to repeat, if there is included but one compound containing only one atom of chlorine in its molecule, then the mass of chlorine in the mass of that compound, represented by its molecular weight, must be the atomic weight of chlorine. As an illustration, we will find what atomic weight is to be assigned to sulphur. To simplify matters the composition by 'parts' of each compound will be given instead of percentage composition.

Substance analysed	S. G. (H=1)	Molecular Weight (S. G. × 2)	Analysis		Analysis of Molecular Weight	
			Sulphur	Other elements	Sulphur	Other elements
Sulphur Vapour at 500°	98	196	—	—	196	—
Hydrogen Sulphide ...	17	34	16	1	32	2
Sulphurous Oxide ...	32	64	8	8	32	32
Sulphuric Oxide ...	40	80	8	12	32	48
Carbon Sulphide ...	38	76	16	3	64	12
Sulphur Chloride ...	67½	135	32	35·5	64	71

Atomic weight of sulphur 32.

By the same method the atomic weights of many other elements have been fixed.

The atomic weight of sulphur being known, a formula can now be assigned to each compound. In the last two columns the elements are represented in the masses as they occur in the molecular weight. Therefore, *by dividing those masses by the atomic weights of the elements, the* **number** *of the atoms in the molecule is obtained.*

Sulphur hydride becomes SH_2.

The oxides of sulphur (O = 16) SO_2 and SO_3.

The carbide is (C = 12) CS_2. The chloride S_2Cl_2 (not SCl, whose V. D. would be $33\frac{3}{4}$, and M. WT. $67\frac{1}{2}$).

In the same way the oxides of carbon are found to be

Lower oxide CO.
Higher oxide CO_2.

A special nomenclature, which represents compounds in atomic composition, has grown with the atomic theory. Thus the two oxides of carbon are carbon **mon**oxide and carbon **di**oxide.

It is sometimes asserted that the Law of Multiple Proportions enables us to designate the oxides on this model, but if reference is made to the previous argument it will be seen that the Law of Multiple Proportions would not have prevented us from calling both of them monoxides.

C_2O (oxygen dicarbide or dicarbon oxide).
CO (oxygen monocarbide or monocarbon oxide).

In the same way the oxides of sulphur are often called sulphur dioxide and sulphur trioxide.

The densities of ordinary gases are fairly accurately determined by Regnault's method. But the vapour densities of substances which are liquids or solids at ordinary temperatures cannot be so determined, and in order to calculate what their densities would be if at 0° C. and 760 mm. they could still exist as gases, they must be measured and weighed at temperatures so far above their boiling points that they approximately support the gaseous laws.

Two methods of procedure will be shortly described. The oldest but least used method was introduced by Dumas (1827).

A glass balloon drawn out to a tube of fine bore is used (Fig. 73). The

weight and volume of the balloon are determined, and into it is introduced a fair quantity of the liquid whose vapour density is desired. The balloon is then immersed in a bath where its temperature is raised considerably above the B.P. of the contained liquid. The substance vapourises and expels the whole of the air and its own excess, until the balloon is just full of the vapour of the substance at the known temperature and pressure. All that now remains is to find its weight. For that purpose the end of the tube is sealed off and the bulb is taken out of the bath, dried and weighed. By this time the contained vapour has condensed partly to liquid; this does not matter, of course, for the tube is sealed. The volume of the vapour is found by breaking the neck under water, and reweighing the balloon full of water. The small volume of liquid substance is negligible.

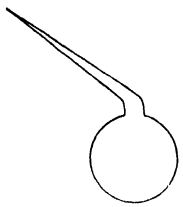


Fig. 73.

It will be seen that Dumas' is only a modification of Regnault's method.

Victor Meyer invented a method so simple that, with care, satisfactory results may readily be obtained by inexperienced students. The apparatus, shown in Fig. 74, consists of a long tube expanded at the bottom and having a short delivery tube of narrow bore near the top. Up to this side tube it is surrounded by a jacket bulbed at the bottom. The inner tube is arranged with the delivery tube under water, and, save for a piece of asbestos at the bottom of the expanded portion, contains air only. A liquid, whose boiling point is well above the vapourising point of the substance investigated, half fills the bulb of the jacketing tube. This liquid is boiled so that its vapour completely envelops the inner tube. Thus the air within gradually rises to the same temperature, and expanding, expels its own excess through the delivery tube. When no more bubbles of air escape, the temperature is constant, and now the inner tube is just filled with air at atmospheric pressure and the temperature of the jacket vapour.

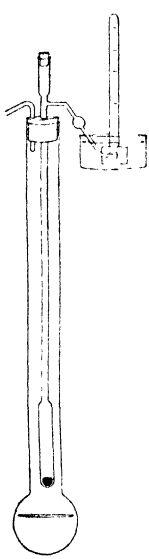


Fig. 74.

In the meantime, a little of the substance under investigation has been weighed out into a tiny stoppered flask. The inner tube is quickly uncorked, the flask dropped on to the asbestos and the cork replaced. The substance vapourises and, pushing out the stopper of the flask, expands in volume until its temperature is also the same as that of the jacket vapour. It therefore expels from the tube its own volume of air at its own temperature. This air collects in the receiving tube and soon cools to the temperature of the water, and its volume contracts in accordance with Charles' Law, just as the vapour which expelled it would have done if it could remain gaseous at so low a temperature. The volume of air collected is reduced to S.T.P. with the usual correction for aqueous vapour pressure.

By either of the above methods only an approximate value for the density of the gas is obtained, and therefore also only an approximate value for the molecular weight. This is of no consequence, for when the approximate value is known the **exact** value may be calculated from the result of an exact analysis. For instance:

The chloride of a certain metal has the composition, metal 63 per cent., chlorine 37 per cent. 0·082 gram of the chloride expels 5·8 c.c. of air measured at 28° C. and 714 mm. pressure. The density (H = 1) = 193·05, hence the approximate molecular weight is 386·1. The molecular weight is actually 381·6.

Determination of atomic weights by the atomic heat method.

But the vapour density method of determining atomic weights applies only to elements which have a fair number of vapourisable compounds, and affords little or no help in the case of some metals.

Fortunately a method for finding the atomic weight of metals exists in the Law of Atomic Heats.

About 100 years ago, MM. Dulong and Pettit, investigating the specific heats of solid elements and chancing to arrange the metals in the order of the increase of specific heats, observed that the metals were, with few exceptions, also arranged inversely in the order of their atomic weights. It occurred to them to multiply the atomic weight of each metal by its specific heat. In nearly every case they obtained numbers which approximated to **6·4**. This constant number they called the **'atomic heat.'**

In consequence of their discovery, they asserted that the number 6·4 approximately would be obtained as the product of the atomic weight and the specific heat of **every** solid element. And they, or their followers, began to justify or revise the atomic weights then generally accepted.

As an instance, silver oxide, which has the composition silver 93·1 per cent., oxygen 6·9 per cent., has been represented by the simplest formula AgO. Hence the atomic weight of silver appears to be 216. But the specific heat of silver is ·0557 and this number divided into 6·4 yields the quotient 115: a number about one half of 216. Therefore, the true atomic weight of silver is 108 and the formula of silver oxide becomes Ag_2O.

Pursue the same method for copper: the composition of the two oxides is

Cuprous oxide 127·2 : 16,
Cupric oxide 63·6 : 16.

If Cu_2O and CuO are adopted as their respective formulae

Cu_2O $2 \times 63{\cdot}6 : 16$,
CuO $63{\cdot}6 : 16$,

then 63·6 must be the atomic weight of copper: but if the choice falls on CuO and CuO_2, the number must be doubled

CuO 127·2 : 16,
CuO_2 $127{\cdot}2 : 16 \times 2$.

But the specific heat of copper was found to be ·0949 and $\frac{6{\cdot}4}{{\cdot}0949} = 67$, therefore 63·6 is the true atomic weight, and Cu_2O CuO are the formulae of the oxides.

Similarly, lead oxides have the composition

Litharge 207 : 16,
Peroxide $103\frac{1}{2} : 16$.

Now for Pb_2O and PbO, the atomic weight is $103\frac{1}{2}$, whilst for PbO and PbO_2 the atomic weight is 207. The specific heat of the metal is ·0293. Therefore the second set of formulae is correct and the atomic weight of lead is 207.

Minium has the composition 155 : 16. Hence its formula is Pb_3O_4.

Lastly, take the chlorides of iron

Ferrous chloride 28 : 35·5,
Ferric chloride 18·6 : 35·5.

The specific heat of the metal is ·1100 which gives (approximately) 58 as the atomic weight of the iron. It follows that the simplest formulae of the chlorides are $FeCl_2$ and $FeCl_3$, and that 56 is the true atomic weight.

The atomic weights of all elements so far mentioned, obtained by various methods, are (taking oxygen = 16 as standard)

Hydrogen	H = 1·008	Platinum[1]	Pt = 195
Oxygen	O = 16·00	Iron	Fe = 55·9
Chlorine	Cl = 35·45	Barium	Ba = 137·4
Nitrogen	N = 14·01	Lead	Pb = 206·9

[1] *plata* (Spanish) = silver.

Carbon	C = 12·00	Tin	Sn = 119·0
Copper	Cu = 63·6	Aluminium	Al = 27·1
Sulphur	S = 32·06	Silver	Ag = 107·93
Sodium	Na = 23·05	Zinc	Zn = 65·4
Potassium	K = 39·15	Magnesium	Mg = 24·36
Phosphorus	P = 31·0	Mercury	Hg = 200·0

The formula of sulphuric acid follows naturally from the results of analysis and the knowledge of atomic weights. We have habitually represented the composition as

Hydrogen 1 part,
Sulphur 16 parts,
Oxygen 32 parts.

Now the atomic weight of sulphur is 32, therefore we must double the numbers

Hydrogen 2,
Sulphur 32,
Oxygen 64,

which corresponds to the formula H_2SO_4: one molecule of sulphur trioxide combines with a molecule of water to produce a molecule of sulphuric acid.

From the analysis of its salts sulphurous acid is represented as H_2SO_3.

How to deduce formulae of salts from those of oxides.

From the above table we can deduce the formulae of other metallic oxides, as BaO, ZnO, MgO, K_2O, and Na_2O.

And **from the formulae of the oxides** and of the acids, **those of their salts follow**, for, as one oxygen atom of the oxides combines with two hydrogen atoms of the acids HCl, H_2SO_4 it follows that the chlorides are represented by $BaCl_2$, $ZnCl_2$, $MgCl_2$, and the sulphates by $BaSO_4$, $ZnSO_4$, $MgSO_4$.

It follows also that the sulphates of iron corresponding to the chlorides are

Ferrous sulphate $Fe(SO_4)$ from $FeCl_2$
Ferric sulphate $Fe(SO_4)1\frac{1}{2}$ from $FeCl_3$.

But as an atom of sulphur cannot be halved, the second formula is doubled $Fe_2(SO_4)_3$. The formulae of copper salts are CuCl, $CuCl_2$, and $CuSO_4$. The lower chloride on exposure to air becomes cupric oxychloride (Cu_2Cl_2O).

NaCl and KCl represent the chlorides of the alkali metals, and the formula of potassium chlorate, whose composition by parts was given in Chapter V. as 39 : 35·5 : 48, becomes $KClO_3$. The corresponding sulphates are K_2SO_4 and Na_2SO_4.

Hydrogen salts.

It will be remembered that there are two sulphates of potassium formed on quite a different type from ferrous and ferric sulphates. According to their method of formation we should distinguish them thus: K_2SO_4 the normal salt, and K_2SO_4, H_2SO_4 the acid salt, and for many years these formulae did duty for them.

Now there are hydrogen salts of sulph-hydric, sulphurous and sulphuric acids, but none of hydrogen chloride, and if the formulae of these acids are compared, H_2S, H_2SO_3, H_2SO_4, HCl, it will be seen that hydrogen chloride differs from the others in having only one hydrogen atom in the molecule. By studying the oxyacids of phosphorus, first Graham and afterwards Liebig were convinced that acid salts must be regarded as half-neutralised acids, so to speak, whilst at the same time they are salts. The hydrogen sulphate is therefore represented as

K H S O_4 and not K_2SO_4, H_2SO_4
39 : 1 : 32 : 64

the proportional composition remaining unaltered.

Acids whose molecules contain two *replaceable* hydrogen atoms are called **dibasic** acids; acids like hydrochloric acid with only one such hydrogen atom (or, when there is more than one hydrogen atom with only one of them replaceable by metals) are called **monobasic** acids.

The student is cautioned against writing the formula of a substance instead of its chemical name. Except in the case of practical text-books on Analysis where the convenience of printing the whole of the directions in the smallest space outweighs all other considerations, he will rarely find that authors use them as a shorthand in description.

Formulae are properly used in equations. The importance of equations to chemists can scarcely be overestimated.

By $H_2O = H_2 + O$

is meant not only that water yields hydrogen and oxygen on decomposition, but that for every 18 grams of water decomposed 2 grams of hydrogen and 16 of oxygen are set free.

The equation is **essentially** quantitative. But the molecule (free particle) of oxygen contains two atoms [O_2], therefore it is correct to write $2H_2O = 2H_2 + O_2$. For the synthesis of water one writes

$$2H_2 + O_2 = 2H_2O$$

an equation giving much information.

(1) The equality sign indicates that equations are based upon the Law of Indestructibility of Matter, and that

(2) Hydrogen and oxygen combine together in the mass proportion of 1 : 8 and the composition of water is invariable.

(3) Because molecular weights of gases occupy equal volumes, any volume of hydrogen combines with half its volume of oxygen to produce its own volume of steam.

But an equation does not express everything that happens during the reaction: the Law of Conservation of Energy finds no expression. When hydrogen and oxygen combine, the water, after cooling to the original temperature, contains less energy than did the uncombined gases; this energy being dissipated as heat. To show complete equality this energy must either be added to the right-hand side or subtracted from the left-hand side of the equation

$$2H_2 + O_2 = 2H_2O + (2 \times 58700) \text{ calories,}$$

or

$$2H_2 + O_2 - (2 \times 58700) = 2H_2O.$$

Before an equation can be written, exactly what substances enter into the reaction and what substances are formed must be known. Equations should be the expressions of chemical truths.

For instance, the following equation

$$CaCO_3 = CaC + O_3$$

is unsatisfactory, although it satisfies the Law of Indestructibility of Matter. Chemically it states that calcium carbonate when heated yields, in given proportions, a modification of oxygen containing three atoms to the molecule and a carbide of calcium whose formula is CaC. Now the formula O_3 does indeed represent ozone, and a carbide of calcium exists but it is *not* represented by the formula CaC; moreover, by heating calcium carbonate neither a carbide nor ozone is formed. Yet it is not unusual for beginners, who have not

appreciated the limitations of equations, to argue that because an equation may be so written the reaction represented by it necessarily takes place. It may or it may not, but experience alone can justify the equation.

The equations representing the simpler reactions described in the preceding chapters can be worked out by the student, and he is **strongly** recommended before proceeding, to revise the first ten chapters, illustrating every reaction by a suitable equation and assigning to every compound mentioned its correct formula, deriving each from the oxide. Only the more complex reactions will be considered here.

The oxidation of litharge.

When chlorine acts on water, oxygen and hydrochloric acid are produced.

$2Cl_2 + 2H_2O = 4HCl + O_2$ would represent the reaction if the oxygen became free. When the litharge is oxidised however, it is unnecessary to double the quantities, for

$$Cl_2 + H_2O + PbO = PbO_2 + 2HCl.$$

The preparation of potassium chlorate.

Taking K_2O (provisionally) to represent caustic potash, we proceed in steps

(1) $Cl_2 + H_2O = 2HCl + O$,

(2) $K_2O + 2HCl = 2KCl + H_2O$,

the oxygen is retained to form chlorate $KClO_3$ ($KCl \longrightarrow KClO_3$) therefore the formulae of both steps are trebled.

$$3Cl_2 + 3H_2O = 6HCl + 3O \text{ (not } O_3)$$
$$3K_2O + 6HCl = 6KCl + 3H_2O,$$

hence the completed equation becomes

$$3Cl_2 + 3H_2O + [3K_2O] = 5KCl + KClO_3 + 3H_2O.$$

The water appearing on each side might be omitted (but wait for Chapter XIII.).

For the **preparation of cuprous chloride** the equations are

(1) $CuO + 2HCl = CuCl_2 + H_2O$,

(2) $CuCl_2 + Cu = 2CuCl$.

The **preparation of sulphurous oxide** from sulphuric acid, by steps

$$Cu + H_2SO_4 = CuSO_4 + H_2,$$
$$H_2 + H_2SO_4 = H_2O + H_2SO_3,$$
$$H_2SO_4 = H_2O + SO_2.$$

and complete

$$Cu + 2H_2SO_4 = CuSO_4 + 2H_2O + SO_2.$$

The metallurgy of lead.

$$PbS + 2PbO = 3Pb + SO_2$$

and

$$PbS + PbSO_4 = 2Pb + 2SO_2.$$

PROBLEMS. XI.

1. When concentrated sulphuric acid is heated with powdered sulphur, sulphurous oxide is produced. Write the equation to represent the reaction.

2. Write down the formulae of the sulphates, sulphites, sulphides, and chlorides, corresponding to the following oxides:

$$X_2O,\ YO,\ Z_2O_3.$$

3. Also write the formulae of the salts corresponding to the above three oxides of a tribasic acid which has the formula H_3QO_4.

4. Plot a curve of atomic weights and specific heats.

5. Compare the atomic weights of hydrogen, oxygen, and nitrogen.

Morley found that 1·429 grams of oxygen were contained in 1 litre at S.T.P.
" " ·08987 " hydrogen was " "
Rayleigh " 1·2505 " nitrogen were " "

6. Deduce the molecular weight of stannic chloride from the following. Dumas method:

Volume of globe.....250 c.c. Barometer.....760 mm.
Temperature of bath...150° C. Weight of globe + air at 0° C....51·125 grams
" + chloride vapour...52·71 grams.

7. Deduce the molecular weight of chloroform from the following:
Victor Meyer method:
Air collected over water...39 c.c. Weight of chloroform...·2 gram.
Temperature ..12° C.
Pressure...755 mm.

8. Deduce the atomic weight of carbon from the following:

Methane.....	75 % carbon,	25 % hydrogen,	v.d. =	·555 (air = 1)
Ethane	80 % "	20 % "	v.d. =	1·076 (air = 1)
Ethylene.....	85·71 % "	14·28 % "	v.d. =	·971 (air = 1)
Acetylene	92·3 % "	7·7 % "	v.d. =	·917 (air = 1)
Benzene.....92·3 %	"	7·7 % "	v.d. =	2·752 (air = 1)
Carbon chloride... 7·8 %	"	92·2 % chlorine	v.d. =	about 5 (air = 1)
Lower oxide .....42·85 %	"	57·14 % oxygen	v.d. =	·967 (air = 1)
Higher oxide..... 27·27 %	"	72·72 % "	v.d. =	1·529 (air = 1)
Ethyl chloride ...37·21 %	"	7·74 % hydrogen, 54·04 % chlorine.	v.d. =	2·219 (air = 1)

9. Deduce the atomic weight of chlorine from the following:

Carbon chloride V.D. = about 5 (air = 1), Composition—carbon 7·8, chlorine 92·2.

Chloroform V.D. = 60 (H = 1), Composition—carbon 10·06, hydrogen 0·84, chlorine 89·2.

Phosphorus chloride V.D. = 68 (H = 1), Composition—phosphorus 22·57, chlorine 77·43.

Sulphuryl chloride V.D. = 4·7 (air = 1), Composition—sulphur 23·72, oxygen 23·72, chlorine 52·56.

10. Deduce the formula of alcohol from the following:

Carbon 52·17 per cent., hydrogen 13·04 per cent., oxygen 34·80 per cent., vapour density 1·6 (air = 1).

[For method see answers.]

11. Deduce the *simplest* formula of oxalic acid.

Carbon 26·66 per cent., hydrogen 2·22 per cent., oxygen 71·11 per cent. Oxalic acid is dibasic. What is its probable formula?

12. Cane sugar contains carbon, hydrogen, and oxygen only. Find its simplest formula when ·30 gram of it completely burnt to water, and carbon dioxide gave ·463 gram of the latter and ·174 gram of the former.

13. Similarly find the simplest formula of a substance of which a quarter of a gram gives ·293 gram of carbon dioxide and ·09 gram of water.

14. What atomic weights might reasonably be assigned to tin from the following analyses. State in each case the probable specific heat.

Stannous oxide contains 88·1 per cent. metal.
Stannic oxide „ 78·73 per cent. metal.

15. Give formulae to the following compounds and find the exact atomic weights of gold and platinum:

Aurous chloride contains 84·78 per cent. gold.
Auric „ „ 65·17 per cent. „
S.H. gold = ·03035.

Platinous chloride contains 73·71 per cent. metal.
Platinic „ „ 57·87 per cent. metal.
S.H. platinum = ·03147.

16. Dumas found that 100 grams of silver combined with the chlorine in 55·993 grams of arsenous chloride. The vapour density of the latter is 6·3 (air = 1) and the specific heat of arsenic = ·0814. Find the exact atomic weight of the element and the formula of its chloride.

17. Strontium chloride contains 44·73 per cent. chlorine. What formulae may it have and, in each case, what would be the atomic weight of strontium? If the S.H. of strontium is ·074, which is correct?

CHAPTER XIII.

COMBINED WATER.

A. *Water of Hydration (Water of Crystallisation).*

FROM a saturated solution of sodium sulphate at ordinary temperatures, crystals are deposited which, on exposure to the air, lose weight; the drier the air the more rapid the loss, and in a desiccator the rate of loss is greatly accelerated. The ordinary crystals, when placed in a test tube which is slowly heated in a water bath, are found to melt at 33° C., and soon separate into two parts, one solid the other liquid. From the liquid portion, which may be shown to be a solution of sodium sulphate, water is driven off a little above 100° C., leaving in the tube a white solid. Either solid dissolves in water forming a neutral solution which on evaporation deposits crystals identical with those at the beginning. The cycle of change may be repeated as often as one may choose. These crystals when converted into the white solid are found to lose 55·9 per cent. of their weight, and as the original crystals are reformed merely by addition of water the entire loss must consist of water. It is evident that a crystalline compound of sodium sulphate and water is formed, unstable not only when heated but also in dry air.

A simple calculation shows that the compound contains ten molecules of water for every molecule of sodium sulphate.

$$\underbrace{Na_2SO_4 . xH_2O}_{142+18x} = Na_2SO_4 + \underbrace{xH_2O}_{18x}$$

$$(142 + 18x) : 18x :: 100 : 55{\cdot}9$$

$$x = 10$$

Potassium sulphate, although so similar to sodium sulphate in its chemical behaviour, crystallises from its solution without any addition of water. But blue vitriol, formed by the solution of copper oxide in, or the corrosion of copper by, sulphuric acid, like sodium sulphate, loses a part of its weight when heated to 300° C.; this loss corresponds to five molecules of water. The grayish white powder which is left, when exposed to damp air attracts moisture therefrom, and whilst remaining dry turns blue again. From its solution the characteristic blue vitriol crystals may be obtained. The five molecules of water appear not to have an equal relation towards the sulphate, for below 100° C. four of them are lost, whilst the last is not detached below 300° C. Zinc and magnesium sulphates have each seven molecules of water to every sulphate molecule; six of these they lose at lower temperatures than the seventh.

From the above few examples several things may be learned.

(1) Some crystalline sulphates do and others do not contain water molecules attached to their own, and that potassium and sodium sulphates differ in this, though similar in many other respects.

(2) Sulphates which attach such water do so in various proportions, and even in the same crystal one portion of the water may be held more tenaciously than another. This water, which may have a profound effect upon the physical properties of the salt, more especially the crystalline form, as a rule, influences but slightly its chemical properties; it is called Water of Hydration. Salts containing it are called hydrated salts, those free of it are termed anhydrous.

This water is usually termed Water of Crystallisation; a term from which one is likely to infer that all crystals contain such water.

Hydrated salts are definite compounds, distinct from the anhydrous salts. It is usual to write the formula in two parts, the water molecule following the salt formula, thus $CuSO_4$, $5H_2O$ represents blue vitriol, very rarely it is written $H_{10}CuSO_9$. The divided formula provides a simple nomenclature.

$CuSO_4 5H_2O$ (blue vitriol) is a pentahydrate,
$CuSO_4 H_2O$ is a monohydrate,

$Na_2SO_4 10H_2O$ (Glauber's salt) is a decahydrate,
$ZnSO_4 7H_2O$ (white vitriol) is a heptahydrate,

and so on.

Sometimes a distinction is made in the formulae of crystals which hold their water with unequal strength.

$$CuSO_4H_2O + 4H_2O. \qquad ZnSO_4H_2O + 6H_2O.$$

The vapour pressure of hydrates.

Just as perfectly dry ice evaporates to steam without forming the ordinary intermediate liquid phase, and at different temperatures has its own definite vapour pressures, so the water of hydrates is vapourisable, and each hydrate has its own specific aqueous vapour pressure, which varies with the temperature. But the combined water differs immensely from ice, in that it can exist in the solid form even at a comparatively high temperature.

Liquid water has a considerable vapour pressure. This increases with the temperature until at 100° C. it equals that of the atmosphere (760 mm). In dry air it is constantly evaporating; the steam in the air exerts its own pressure there. As long as the pressure of the water vapour in the air is less than that exerted by the water, the latter will continue to evaporate, but if for any cause the vapour in the air should exert a greater pressure than that of water, vapour will be deposited as rain or snow, etc., until the pressure exerted by the uncondensed vapour has declined to that exerted by the water. When both pressures are equal there is neither deposition from the air nor evaporation from the water.

The same laws apply to water of hydration. When the hydrate water exerts a pressure greater than that of the atmospheric water-vapour, water evaporates more or less rapidly from the crystal into the air. This leads to a transformation either into a lower hydrate (sodium carbonate), or into the anhydrous condition (sodium sulphate); in either case the crystal surface loses its lustre and transparency, and assumes a mealy appearance, hence the term applied to them '**efflorescent**[1].'

Blue vitriol is slightly efflorescent on dry days, but on damp days is stable. The dehydration of hydrates may be

[1] *efflorescere* = to blossom out.

accelerated by those causes which promote the evaporation of water; confinement in a closed space with a desiccating agent, the passage over them of a current of dry air, or increase of temperature.

The formation of hydrates is not peculiar to sulphates. Washing soda, which is deposited in large crystals from a hot moderately concentrated solution of sodium carbonate, is a decahydrate ($Na_2CO_3 10H_2O$). On exposure to the air it effloresces to become a monohydrate ($Na_2CO_3H_2O$). The decahydrate melts at 34° C., losing 9 molecules of water; at a somewhat higher temperature the tenth molecule is driven off also. When the saturated solution of sodium carbonate is concentrated at higher temperatures, crystals of a hepta-hydrate are deposited ($Na_2CO_3 7H_2O$). All three hydrates of sodium carbonate differ in their crystalline form.

The proportion of water of hydration may vary with the temperature of deposition, and some salts are known which have as many as five different hydrates.

When anhydrous sodium carbonate is moistened with a little water, the latter is absorbed with a considerable evolution of heat to form the dry monohydrate. Some other carbonates form hydrated salts, but many are anhydrous.

Amongst the chlorides the same variation is found: sodium and potassium chlorides crystallise anhydrous at ordinary temperatures, cadmium chloride ($CdCl_2$, $2H_2O$) is an efflorescent duohydrate, whilst barium chloride crystals ($BaCl_2$, $2H_2O$) remain practically unchanged in the air, but are dehydrated at 113° C. Many other chlorides are hydrated, and some are **deliquescent**, that is they attract moisture from the air and dissolve therein. They can be obtained crystalline by very strong cooling of their concentrated solutions.

Substances, like anhydrous copper sulphate, which are capable of taking up again their water of crystallisation from the air are called **hygroscopic**. Deliquescent salts are those whose concentrated solutions have a very low vapour pressure. When the dry substance is exposed to moist air a thin film of moisture is deposited on it and a solution is immediately formed which acts as a region of low pressure. When placed in a closed space with a damp substance, moisture from the latter distils to it. The more moisture attracted the more salt is dissolved; finally the solution becomes so dilute that it is no longer effective. The name deliquesce means literally to *melt* away—a misconceived term. Common desiccating agents are oil

of vitriol, solid caustic potash and soda, and the anhydrous chlorides of calcium, aluminium and zinc. The most effective known is the higher oxide of phosphorus. Anhydrous copper sulphate is sometimes used as a 'reagent' for testing for the presence of water in liquids, because of the acquisition of colour on hydration.

Hydrates occur amongst the acids. Thus oxalic acid crystals have the following composition $H_2C_2O_4$, $2H_2O$, and the two molecules of water are driven off at 100° C. Under certain conditions crystals of the formula $2H_2C_2O_4$, H_2O are formed, the formula of these is sometimes written as $H_2C_2O_4$, $\frac{1}{2}H_2O$ in spite of the absurdity.

Acids which are formed by the union of acid anhydride and water can also form hydrates, and then the water of the anhydrous acid (anhydrous sulphuric acid is H_2SO_4) is called **water of constitution.** (Refer to Chapter VII.)

But hydrates are not confined to compounds. A remarkable hydrate is formed by cooling to 0° C. a saturated solution of chlorine. It is a greenish crystalline substance of definite form which melts a little *above* 0° C., at the same time chlorine escapes. Its formula is Cl_28H_2O.

Chemical reaction between salt and water of hydration.

When the crystalline chlorides, or even the saturated solutions of zinc, iron (ferric), aluminium and magnesium chlorides are heated for the purpose of obtaining the anhydrous salts, an interaction occurs between the water of crystallisation and the chloride molecules with the production of hydrochloric acid and the metallic oxide (or an intermediate compound. See Chapter XV.).

$$2AlCl_36H_2O = Al_2O_3 + 6HCl + 9H_2O.$$

Hence the anhydrous chlorides of these metals cannot be obtained from their solutions.

Analysis.

To determine the proportion of water of crystallisation in a hydrate, a simple preliminary experiment is undertaken to ascertain whether the compound is dissociated (into anhydrous salt and water) or decomposed (into new substances). Upon its behaviour depends the choice of experiment. Three methods are common.

(1) By heating a weighed quantity of the hydrate and weighing the residual anhydrous salt.

(2) By heating a weighed quantity of the hydrate, absorbing the water expelled and weighing it (Fig. 75), or combination of 1 and 2.

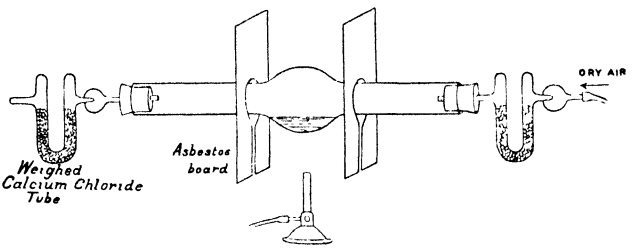


Fig. 75.

(3) Volumetric and precipitation methods for decomposable hydrates.

The apparatus for determination 1 is very simple, the salts should be well powdered and the crucible or other vessel should not be heated much above the temperature of dissociation and must be cooled over a good desiccator and then weighed quickly.

For Method 2, the substance is heated in a tube, and the moisture swept into the absorption U-tube by a current of dry air. Care must be taken that the end of the delivery tube is flush with the cork, any moisture condensed in the tube is evaporated by gentle heat.

Method 3. For sulphates, the acid radicle may be precipitated as barium sulphate, and from the weight of the latter the weight of the anhydrous salt in the crystal may be deduced. For chlorides the acid radicle may be precipitated as silver chloride. Volumetric methods are available for nearly all salts.

Natural hydrated salts.

Hydrated salts occur frequently as minerals, for instance Glauber's salt and Epsom salt. Calcium sulphate occurs both anhydrous (as anhydrite) and as the duohydrate, which according to its appearance and physical properties is called gypsum, satin spar[1], alabaster, or selenite. When gypsum is heated to 120°—130° C. it loses water. This dehydrated powder is used as plaster of paris, which, when made up into a paste with water, slowly rehydrates itself and sets dry and hard as a porous mass of interlacing hydrated crystals.

[1] From Germ. *Spalten*, to split.

B. *The Hydroxides.*

In Chapters III. and V. reasons were given for regarding the white deliquescent substances, caustic potash and caustic soda, as the soluble oxides of potassium and sodium. Such they were supposed to be when their compound nature was first discovered. When they are heated with zinc powder hydrogen is evolved, and this hydrogen must come from attached water, for caustic soda and potash are formed by the solution of the oxides. It was soon shown that these white solids correspond to the formulae Na_2O, H_2O and K_2O, H_2O. The molecule of water cannot be expelled by heating.

Just as sodium and potassium attack water to form their oxides, so calcium metal when placed in water yields a steady current of hydrogen and combines with the oxygen. But calcium oxide is not very soluble, so that soon after the action starts a white precipitate appears which can be separated and dried. Upon heating this strongly, water escapes leaving a white solid **"quick" lime.** Quicklime takes up moisture again with evolution of heat, to reform dry **"slaked" lime.**

$$CaO + H_2O = CaO, H_2O$$

quicklime slaked lime.

The names "quick" (live) and "slaked" (quenched) refer to the above phenomena; a thermometer placed in the midst of good powdered quicklime, during the slaking will read 150° C.

Slaked lime is not deliquescent.

Barium monoxide or "Baryta" (BaO) resembles quicklime in many ways, and far surpasses it in avidity for water. So great is the heat evolved upon slaking, that the mass may become incandescent. Baryta is usually grayish, but the slaked baryta is perfectly white. Whilst all the combined water of slaked lime may be driven off at temperatures below 1000°C., dry slaked baryta loses its combined water only upon prolonged heating in a current of hydrogen. The gas sweeps away the moisture as soon as this is set free.

Magnesium oxide MgO (magnesia) is obviously slaked upon the addition of water. Slaked magnesia has a very weak alkaline action upon litmus, but slaked lime and baryta are caustic.

Zinc oxide, which in many respects resembles magnesia, will not slake, nor is it perceptibly soluble. Alumina (aluminium oxide) behaves like zinc oxide.

Are the slaked oxides to be regarded as oxides containing water of hydration?

The nature of the water combined in slaked oxides.

Take the case of baryta. From solution crystalline slaked baryta separates, corresponding to the formula $BaO, 3H_2O$; when the crystals are heated two molecules of water are driven off with comparative ease, but the third with considerable difficulty, and the anhydrous oxide takes up this molecule again with a vigorous evolution of heat. In all these respects the trihydrate of baryta behaves like the decahydrate of sodium carbonate, and the parallel extends to the behaviour of the anhydrous substances with water. They differ only in degree.

The soluble oxides react in solution with the salts of other metals to produce the hydrated oxides of the latter.

Thus, when a solution of caustic soda reacts with one of aluminium sulphate, a transparent jelly is precipitated, and sodium sulphate is left in solution. The dried jelly readily loses water on heating, leaving the white anhydrous oxide alumina (Al_2O_3). Zinc sulphate gives, in similar circumstances, a similar precipitate (ZnO, H_2O).

In both cases it is important not to add a large quantity of caustic soda solution, else the precipitate redissolves. The cause of the re-solution will be explained in the next chapter.

From ferric sulphate solution $Fe_2(SO_4)_3$, a brown jelly is precipitated. When the dried precipitate is heated it loses water, and brown ferric oxide (Fe_2O_3) is left behind. When ferrous sulphate ($FeSO_4$) solution is similarly treated, a greenish white jelly is precipitated. If air is allowed entrance, this slowly turns brown to form the ferric compound, but if air is scrupulously forbidden, the white jelly may be dried. When heated, this also loses water with the formation of ferrous oxide (FeO) which is black.

From the solution of a lead salt, a heavy white solid is precipitated which, losing water on heating, yields yellow litharge (PbO).

From a cold solution of copper sulphate a blue green jelly is precipitated which may be dried in a desiccator, but

which on moderate heating loses water, and is transformed into black oxide (CuO).

If the solution of copper sulphate is hot when the caustic soda is added, the black *anhydrous* oxide is precipitated instead of the hydrated green jelly, that is to say, the hydrated oxide dissociates below 100° C., even though it be suspended in water. From cold solutions of silver salts, caustic bases precipitate a brown substance which loses water in the attempt to dry it, leaving silver oxide (Ag_2O). And lastly from a cold solution of mercuric chloride, caustic soda precipitates the yellow form of **anhydrous** mercuric oxide (HgO). In **all** cases a sodium **salt** is left in solution.

The substances thus precipitated from solution by the caustic bases are apparently—with the exception of the mercuric compound—hydrated oxides; they may differ in colour or consistency or both from the anhydrous oxides.

$$HgCl_2 + Na_2O, H_2O = HgO + 2NaCl + H_2O,$$
$$CuSO_4 + Na_2O, H_2O = CuO, H_2O + Na_2SO_4.$$

The tabular statement should be well studied:—

Metal	Anhydrous oxide	Hydrated oxide
Potassium ...	white, slakes energetically	white, very soluble, deliquescent, strongly caustic, undecomposed by heat
Sodium ...	„ „ „	
Barium ...	„ „ „	white, fairly soluble, caustic, very difficult to decompose
Calcium ...	„ „ „	white, not very soluble, less when hot, moderately easy to decompose, caustic
Magnesium ...	„ feebly slaked ...	white, slightly soluble, feebly caustic, easily decomposed
Zinc ...	„ does not slake ...	white, insoluble, not caustic, easily decomposed
Aluminium ...	„ insoluble ...	white jelly, insoluble, not caustic, easily decomposed
(Ferrous) Iron	black „ ...	white jelly, insoluble, not caustic (oxidises to ferric)
Lead ...	yellow „ ...	white powder, insoluble, not caustic, easily decomposed
Copper ...	black „ ...	blue jelly, insoluble, not caustic, unstable below 100° C.
Silver ...	„ „ ...	brown, insoluble, not caustic, very unstable
Mercury ...	yellow „ ...	not known

This method of obtaining oxides, namely, by heating the precipitated hydrated oxides, is sometimes very convenient, and is distinguished as the "Wet" method.

Its drawback is the difficulty of washing away the precipitant completely. The finely divided particles of copper oxide, obtained by the wet method, absorb some caustic soda which cannot be washed away entirely, no matter how often one boils them with water.

Why the compounds are called hydroxides.

The oxides containing combined water were for many years regarded as hydrated oxides and are still frequently described as such.

Caustic potash and caustic soda are, unfortunately, sometimes described on reagent bottles as *sodium* hydrate and *potassium* hydrate.

Another view concerning the composition of these compounds was advanced about the year 1850, and met with such immediate and complete approval that now their composition is rarely questioned.

The entire argument cannot be stated here, because it is based upon the reactions of compounds unsuitable for inclusion in an elementary book.

Professor Williamson, as the result of very important researches upon ether and alcohol, showed why, in the latter, whose formula is C_2H_6O, the group or 'radicle' (OH) probably exists. This group is called 'hydroxide' (or hydroxyl[1]). According to him, alcohol must be regarded as a substance in which one of the hydrogen atoms of water is displaced by the radicle (C_2H_5) or 'ethyl,' thus alcohol is ethyl hydroxide $C_2H_5(OH)$. Alcohol behaves like caustic bases in their most important and characteristic property, namely, the formation of salts; under suitable conditions it reacts with hydrochloric and sulphuric acids to form water and 'salts' whose formulae are

$$(C_2H_5)Cl\,;\ (C_2H_5).HSO_4 \text{ and } (C_2H_5)_2SO_4,$$
$$(C_2H_5)OH + H_2SO_4 = (C_2H_5)HSO_4 + H_2O.$$

Professor Williamson suggested that the caustic alkalis are hydroxides of metals, that is, compounds of metals and the radicle hydroxide (OH). This view, enthusiastically supported by Odling and Kekulé, has been universally adopted.

[1] *-yl* from ὕλη = matter.

Recently a theory of solutions has arisen (the Ionic theory), based upon such physical properties as electrical conductivity, which leads to the same conclusion.

With the new formulae we write these equations:

$$Na_2O + H_2O = 2NaOH,$$
$$2Na + 2HOH = 2NaOH + H_2,$$
$$Ca + 2HOH = Ca(OH)_2 + H_2,$$
$$CaO + H_2O = Ca(OH)_2.$$

The crystalline compound of slaked baryta contains both water of constitution and water of hydration, $Ba(OH)_2\ 2H_2O$.

$$NaOH + HCl = NaCl + H_2O,$$
$$NaOH + H_2SO_4 = NaHSO_4 + H_2O,$$
$$2NaOH + H_2SO_4 = Na_2SO_4 + 2H_2O.$$

The formation of other hydroxides by double decomposition.

$$3NaOH + AlCl_3 = Al(OH)_3 + 3NaCl.$$

The oxides are formed from the hydroxides by dissociation.

$$2Al(OH)_3 = Al_2O_3 + 3H_2O.$$

Caustic soda is called sodium hydroxide. Slaked lime is called calcium hydroxide. Mercury has no hydroxide.

Hydroxides react with acids to form salts more readily than do the anhydrous metallic oxides.

The extension of the idea.

If the above view is correct, both basic oxides and acid 'anhydrides' (SO_3, CO_2, SO_2) combine with water to produce compounds in which the water ceases to exist as such. When these compounds are heated, the hydrogen and oxygen may be expelled again as water, but both basic hydroxides and oxy-acids exist which are not thus decomposed by heat.

Professor Williamson and those who adopted his idea of hydroxide formation extended it to include the oxy-acids. According to them, the water of constitution becomes hydroxyl, and that is why the hydrogen in water has properties distinct from those of the same hydrogen in the acid. The difference between the basic hydroxide and the acidic hydroxide is then one of exchange, the acid exchanges only

the *hydrogen* of the hydroxyl whereas the basic hydroxide exchanges the *whole of the hydroxyl.*

$$\begin{matrix} Na \\ Na \end{matrix}\left|\begin{matrix} OH & (H \\ OH + & (H \end{matrix}\right|\begin{matrix} O) \\ O) \end{matrix} SO_2 = Na_2SO_4 + 2HOH.$$

Both basic and acidic hydroxides can be arranged in order of strength.

$$\downarrow \begin{matrix} KOH \\ Ca(OH)_2 \\ Mg(OH)_2 \\ Al(OH)_3 \end{matrix} \qquad \begin{matrix} SO_2(OH)_2 \\ SO(OH)_2 \\ CO(OH)_2 \end{matrix} \downarrow$$

Natural metallic hydroxides.

The student is urged to study carefully the foregoing arguments and to form his own opinion of their probable truth. He must be prepared to modify his opinion, as he encounters more evidence bearing on the subject.

The changes and development since 1780 of ideas concerning the nature of oxy-acids may be represented by the following series of formulae:

Lavoisier's oxygen theory (1783) in Berzelius' symbols (1811)	(1812—1834) Berzelius' 'copulated' formula dualistic system	(1815—present day) Davy's hydrogen theory	(1852—present day) Williamson's hydroxide theory (water type)
SO_3	SO_3, H_2O	H_2SO_4	$SO_2(OH)_2$

Metallic hydroxides occur as minerals: limonite (or brown haematite) is a hydrated ferric oxide, the outer layer often changed by contact with atmosphere to carbonate. The anhydrous ferric oxide also occurs and is known as red haematite. Hydrated oxide of aluminium occurs as bauxite, diaspore and gibbsite; and alumina (anhydrous oxide) occurs as corundum or emery and in rarer forms as ruby and sapphire.

N.B. Some authors apply the term **Water of Constitution** *to the molecules of water of hydration which are extra-tenacious; according to this usage, the complete molecule of blue vitriol has one such molecule of water.*

PROBLEMS. XII.

1. Find the number of molecules of water of hydration in:

A. **Green vitriol** ($FeSO_4 xH_2O$), given that 1 gram of crystals yields 0·84 gram barium sulphate.

B. **Magnesium chloride crystals**, given that 1 gram yields 1·3645 grams of silver chloride.

C. A sample of sodium carbonate, given that 1 gram gave 1·5887 grams of barium carbonate.

D. Lithium carbonate (At. = 7), given that ·6 gram of the carbonate was dissolved in 100 c.c. of water and that

10 c.c. of the solution was neutralised by 17·91 c.c. of $\frac{E}{10}$ HCl.

2. The following weighings were made when crystals of barium chloride were strongly heated in a hard glass tube. Find the molecules of water.

Weight of glass tube.....40·74475 grams.
" " and crystals ...43·75675 grams.
Weight of calcium chloride tubes before experiment 32·94925 grams.
" " " after " 33·393 grams.

3. Compare the results for finding the water of hydration of blue vitriol.

A. 1·1055 grams of crystals gave ·352 gram of copper oxide when treated with caustic soda.

B. 1·0672 grams of crystals gave 1·002 grams of barium sulphate.

4. What formulae would you give to hydroxides, corresponding to the following oxides:

$$XO,\ X_2O,\ X_2O_3,\ XO_2,\ X_2O_5,\ XO_3.$$

Suppose the third, fourth, fifth and sixth lost one molecule of water, what would remain? and also if the last two lost two molecules of water?

5. Prepare cuprous oxide by dissolving cuprous chloride in hydrochloric acid and adding caustic soda to the warm solution.

CHAPTER XIV.

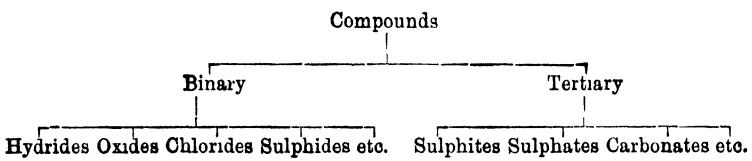
ACIDS AND BASES. HYDROLYSIS.

Classification.

CHEMICAL substances are divided into two classes, Elements and Compounds, these which have and those which have not been resolved into simpler substances. The distinction, founded on *composition*, is sharp; both divisions may be further subdivided. The elements are usually classified into metals and non-metals, the oxides of the former are basic, of the latter are acidic; this distinction, founded upon *properties* is not sharp, and in consequence an intermediate group of elements is often made, called the metalloids; yet so ill-defined are the groups that few authors agree in which of them to place certain elements.

Another and more satisfactory arrangement sorts them according to their inter-relations.

The compounds also may be sharply classified according to their composition.



Such a system is very simple but is very mechanical. The sulphides and sulphates are separated although they are clearly related, whilst substances as unlike as carbon monoxide, water, sulphur dioxide and calcium oxide are included under one heading. Again, hydrochloric and sulphuric acids are treated as though they had nothing in common. In fact when compounds having similar properties are found together it is mainly accidental.

Acids and bases.

The student will recognise that almost every compound dealt with so far falls, according to its *properties*, into one of the three classes—acid, base, and salt. These three outstanding groups are used for classifying, but any system founded upon differences in properties is very difficult to apply, and we shall learn shortly that the terms acid and base are to some extent relative.

If asked to name a compound which most nearly coincides with one's conception of a 'base,' one would almost certainly choose potassium or sodium hydroxide, for both will react with the very weakest acids to form salts. One's choice of a typical acid might well fall upon sulphuric acid.

Because bases interact with acids to produce salts, one has a tendency to look upon a base as the very antithesis of an acid; yet it is quite difficult to give a general definition of an acid which shall exclude the above bases chosen as representative.

The special character of an acid is salt formation: the reddening of litmus and the sharp taste of its solution are but useful diagnostic properties. The following are often used as definitions of acids:

I. "Acids are substances containing hydrogen and are characterised by the fact that they give up their hydrogen very easily and take up other elements in place of it."

II. "Acids are particular compounds of hydrogen in which the latter can be replaced by metals."

III. "An acid may be defined as a compound containing one or more atoms of hydrogen which become displaced by a metal when the latter is presented to the compound combined in an 'hydroxide'."

IV. "Acids possess a sour taste, turn blue litmus red and neutralise the basic oxides."

And yet undoubted acids are known whose taste is not sour—and may even be bitter—which do not affect litmus, and which do not react with metals. On the other hand sodium hydroxide, whilst indeed it turns litmus blue and has a bitter instead of a sour taste, corrodes zinc, aluminium, boron and silicon, with evolution of hydrogen to form substances which are recognised salts. But, that sodium

hydroxide is a strong base has never been in doubt, in spite of the fact that it only transgresses the least important points in the above definitions of an acid and fulfils the most important. The cause of this apparently anomalous behaviour is to be imputed to the zinc and aluminium rather than to the sodium hydroxide, and for the following reason:

Admitting Williamson's ideas concerning them, we may regard the class of hydroxides as a series of compounds which includes strong bases at the one extreme, and strong acids at the other. Beginning at each extreme, we may arrange the series more or less satisfactorily, so that strong bases or strong acids shall precede weaker ones. The half series are united in hydroxides whose propensity to form salts is so weakened, that they differ but little from each other, and may react either as weak base, or as weak acid, according to circumstances.

Aluminium possesses a hydroxide so uncertain that when brought under the influence of the strong sulphuric acid, it behaves as a base and reacts to form aluminium sulphate and water.

$$2Al\left|\overline{(OH)_3 + 3H_2}\right|SO_4 = Al_2(SO_4)_3 + 6H_2O.$$

While compared with the strong base caustic soda it is a weak acid (aluminic acid), and so reacts to form sodium **aluminate.** Sodium aluminate may be precipitated from solution by the addition of alcohol in which it is insoluble.

$$Al(O\left|\overline{H)_3 + 3HO}\right|Na = Na_3AlO_3 + 3H_2O.$$

For the sake of simplicity the sodium compound has been given the above formula; it has actually the composition $NaAlO_2$ derived from $AlO(OH)$, that is $Al(OH)_3$ less one molecule of water.

This is the compound formed when aluminium is corroded by caustic soda,

$$\underset{(2\times 27)}{6NaOH + 2Al} = \underset{(3\times 2),}{2Na_3AlO_3 + 3H_2}$$

quite a different reaction from that which takes place with an acid, although in both cases a salt is formed.

$$\underset{(2\times 27)}{6HCl + 2Al} = \underset{(3\times 2).}{2AlCl_3 + 3H_2}$$

In the same manner sodium hydroxide corrodes zinc to form sodium zincate (Na_2ZnO_2), and silicon—which has no metallic properties—to form sodium silicate.

The terms acid and base convey general ideas but are not easy to define, and when applied to the bases and oxyacids must be considered as relative terms.

An acid has been defined as

'A compound of hydrogen and an electro-negative element, or group of elements, the hydrogen being replaceable either entirely or in part by a metal when presented to it combined in a hydrated oxide or base; a salt and water being produced.'

The same difficulties of definition are even more pronounced in other sciences and for this reason:—Classification is for the purpose either of lessening the labour of scientists or of expressing relations and distinctions between the things studied. Thus Botanists once classified plants according to the number of their stamens; a system easy of application but of very little assistance to research. The present system sorts plants into closely related families, orders, genera and species, a method most difficult to apply in many cases because in nature there are very rarely sharp divisions.

A still more significant illustration is this: biologists class beings into animals and plants. There is no difficulty in placing a horse or an oak, but research has discovered beings so little specialised that they are claimed for the respective kingdoms both by Zoologists and Botanists.

Hydrolysis.

Water reacts chemically upon some salts dissolved in it: this kind of reaction is termed 'Hydrolysis[1].'

A solution of normal potassium sulphate does not affect litmus; it may be prepared by neutralising caustic potash with sulphuric acid. Hydrogen potassium sulphate turns blue litmus red, behaving like an acid.

A solution of normal potassium carbonate is strongly alkaline to litmus, that is, its solution turns red litmus blue just as if it were potassium hydroxide. A solution of potassium hydroxide is not 'neutralised by absorbing carbonic anhydride (acid in solution), judging by the fact that, with litmus as indicator, a decided red colouration is never produced. If, instead of litmus, an indicator called phenol-phthalein is used, an end point (the discharge of a pink tint) is reached when the solution contains hydrogen potassium carbonate. Thus whilst the normal carbonate is

[1] ὕδωρ, water; λυσις, the act of loosing.

alkaline in solution the hydrogen carbonate (corresponding to the *acid* sulphate) is neutral in solution. Similarly the normal potassium and sodium salts of sulphur*ous* acid as well as the soluble sulphides are alkaline to litmus. The chlorides of the same metals, like the normal sulphates, are neutral; that is, the normal potassium salts of those acids which already we have had reason to regard as strong, are neutral in solution to litmus, whilst the normal potassium salts of the weaker acids are alkaline to litmus.

On the other hand, the chlorides and the normal sulphates of iron, copper and aluminium, when dissolved in water yield solutions which redden, that is are acidic to, litmus; and these are the salts of strong acids with bases which we have reason to regard as weak.

Those normal salts alone are neutral in solution which are derived from both a strong base and a strong acid; the normal salts of weak acid and strong alkali are alkaline in solution, and the normal salts of weak base and strong acid are acidic in solution.

To what causes shall this behaviour be ascribed? The results of two simple experiments supply the answer; to follow them clearly a slight digression is necessary.

Dialysis.

Graham discovered that solutions of substances like sugar and common salt are able to make their way (diffuse) slowly through animal and vegetable membranes such as pig's bladder or parchment, but that the white of egg (albumen) and many jelly like substances are unable to do so. The former substances, which are usually crystalline, he called 'crystalloids'; such are *most* acids, bases and salts. The non-diffusible substances he called 'colloids.' When a colloid and a crystalloid are mixed they may be separated by diffusion, or as Graham termed it, by '**dialysis**[1]' through a membrane.

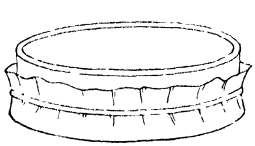


Fig. 76.

The apparatus used for dialysis is called a dialyser and consists of a broad ring of glass or tinned iron with a piece of parchment securely tied over one rim. The vessel has the appearance of a diminutive drum with one parchment missing (Fig. 76). The 'solution'

[1] διαλύω = to loose through.

is placed in the dialyser, and the dialyser half immersed in pure water which must be renewed frequently. The separation is more rapid when the dialyser is placed in running water. The crystalloid escapes through the parchment leaving the pure colloid.

We are now in a position to understand the two experiments referred to above.

Amongst bases, the weak aluminium hydroxide, and amongst acids, the weak silicic acid, are colloids.

Aluminium chloride may be prepared *directly* from its metallic and gaseous elements; its aqueous solution is strongly acidic. If the solution is placed in a dialyser partly immersed in water, the solution in the dialyser gradually becomes neutral to litmus, whilst the water without soon reddens litmus. Hydrogen chloride has passed through the parchment. Aluminium hydroxide in an exceedingly fine state of division remains behind, and may be obtained by the evaporation over a water bath of the liquid in which it remains suspended.

It is obvious that the water has reacted with the chloride to produce the free acid and the free base

$$AlCl_3 + 3HOH = \underset{\text{(colloid)}}{Al(OH)_3} + \underset{\text{(crystalloid)}}{3HCl}$$

and that the complete hydrolysis was favoured by the removal of the acid.

Similarly, if a solution of potassium silicate—which is alkaline to litmus—is dialysed, the water without the parchment soon turns litmus blue, whilst the liquid within the dialyser loses the property and indeed acquires the feeblest acid reaction; on evaporating the liquid over a water bath, the jelly of pure silicic acid is deposited. The solution of potassium silicate has been hydrolysed into the crystalloid potassium hydroxide and the colloid silicic acid.

In practice, this method of obtaining silicic acid is modified and the process hastened.

And, therefore, we may conclude that the salts of weak bases or of weak acids are hydrolysed by water into free acid and base, and whichever of these is stronger influences the litmus. It is important to notice that a normal salt is not necessarily neutral in solution, nor is an 'acid' (hydrogen)

salt acidic to litmus. A normal salt is one in which all the hydrogen of an acid is displaced by metal.

It happens that normal salts are called neutral salts by many chemists, although only the normal salts of both a strong acid and a strong base are really neutral in solution.

Salts in which some replaceable hydrogen of the acid still remains are called hydrogen salts rather than acid salts, for whilst hydrogen potassium sulphate is acidic to litmus and phenol-phthalein, the corresponding hydrogen potassium carbonate is neutral to phenol-phthalein.

PROBLEMS. XIIA.

1. Add lead acetate solution little by little to a hot dilute solution of caustic soda. Observe the reaction and suggest an explanation.

2. Discover the best conditions for preparing chromic hydroxide $Cr(OH)_3$.

3. Prepare potassium hydrogen oxalate, KHC_2O_4.

   A. From the normal salt, and the acid $C_2O_4H_2$, $2H_2O$.

   B. From the acid and caustic soda solution.

4. Add copper sulphate gradually to large excess to a *boiling* solution of caustic soda, and suggest explanations for the results.

CHAPTER XV.

THE CARBONATES.

A. *Preparation and Properties.*

The Normal and Hydrogen Carbonates.

The carbonates are an important series of compounds forming a considerable part of the crust of the earth. Of the normal carbonates, only those of the alkali metals (potassium and sodium) are even moderately soluble in water.

Sodium and potassium carbonates are of great importance, and are prepared for commercial purposes on a vast scale and by special methods. In the laboratory they may be obtained by saturating a solution of the caustic base with carbon dioxide, $2NaOH + H_2O + CO_2 = Na_2CO_3 + 2H_2O$; upon evaporation the hydrated sodium salt settles from the solution. The potassium salt is much more soluble than the sodium salt; at 20° C., water dissolves more than its own weight of potassium carbonate, but only one-fifth of its weight of sodium carbonate.

When carbon dioxide (+ water = carbonic acid) is passed into a **cold saturated** solution of normal sodium or potassium carbonate, the respective hydrogen carbonate settles from the solution. These are far less soluble in water than the normal carbonates; the hydrogen potassium salt is about one quarter as soluble, and the hydrogen sodium salt about one half as soluble as the corresponding normal salt.

When ***solutions*** of the hydrogen salts are heated there is partial decomposition, carbon dioxide escapes leaving solutions of the normal carbonates: therefore the hydrogen salts can be obtained by saturation at low temperatures only.

When the *solid* hydrogen carbonates are heated, they are completely decomposed into the normal anhydrous carbonate and carbon dioxide and water (dissociated carbonic acid).

$$2NaHCO_3 = Na_2CO_3 + H_2O + CO_2.$$

By the decomposition of these carbonates the formula of carbonic acid may be confirmed. As both normal and hydrogen salts are known, carbonic acid is dibasic and contains at least two replaceable atoms of hydrogen. Wollaston took equal known quantities of the potassium bi-carbonate, and heated one part till it was converted entirely into the normal carbonate. When the heated and the unheated portions were treated with dilute acid, the latter was found to evolve just twice the volume of carbonic anhydride. These results are represented by the following formulae and equations.

$$[2NaHCO_3 \rightarrow]Na_2CO_3 + 2HCl = 2NaCl + H_2O + CO_2,$$
$$2NaHCO_3 \text{ (unaltered)} + 2HCl = 2NaCl + 2H_2O + 2CO_2.$$

Carbonic acid is H_2CO_3.

The insoluble carbonates are, in the laboratory, usually precipitated from a solution of some salt of the metal by the soluble alkali carbonates. Barium carbonate, for instance, is formed by adding sodium carbonate solution to barium chloride solution, $BaCl_2 + Na_2CO_3 = BaCO_3 + 2NaCl$.

Barium and calcium carbonates may be precipitated by passing carbon dioxide (+ water = carbonic acid) into solutions of their hydroxides, $Ca(OH)_2 + H_2O + CO_2 = CaCO_3 + 2H_2O$.

Slaked lime absorbs carbon dioxide when exposed to the air, and becomes carbonate: hence the use of slaked lime in mortars for building purposes. It will be noticed that, even with dry slaked lime, water is liberated in the reaction. This accounts for the moisture on the walls in new houses when first occupied. Although the walls seemed dry, not all the lime had changed to carbonate.

$$\underset{\text{(dry)}}{Ca(OH)_2} + CO_2 = CaCO_3 + \underset{\text{(moisture)}}{H_2O}.$$

When carbon dioxide is passed into a solution of calcium hydroxide, the carbonate is precipitated as a white powder which, in suspension, gives to the water a 'milky' appearance. When the current of carbon dioxide is continued, the white precipitate redissolves.

When this solution is boiled, the carbonate, and with it the turbidity, reappears and the excess carbon dioxide is expelled from the solution.

One litre of water saturated with carbon dioxide dissolves about 0·7 gram of calcium carbonate.

The carbonates of barium, magnesium, manganese and iron (ferrous) are, in like manner, slightly dissolved in water

containing dissolved carbonic acid. None of the compounds formed can be isolated, for they are dissociated by heating. If this behaviour is compared with that of solutions of hydrogen potassium carbonate, it will be found to differ only in the solubility of the various compounds; one therefore concludes that here also hydrogen carbonates are formed.

$$CaCO_3 + H_2CO_3 = Ca(HCO_3)_2.$$

The hydrogen carbonates of these metals differ in one important respect from the hydrogen carbonates of potassium and sodium: they are *more* soluble than their normal salts.

$$Ca(HCO_3)_2 = CaCO_3 + H_2O + CO_2.$$
(dissolved)

Hardness of Water.

Water which contains soluble salts of calcium and magnesium is said to be '**hard.**' When soap is added to it, a curdy solid is formed by the action of the soap with salts of calcium and magnesium, and continues to be formed as long as any salts of these metals remain in solution; all the soap so used is worthless as a cleanser.

The amount of soap which must be added before a permanent 'lather' is formed gives a rough measure of the hardness of the water. Soap is a mixture of the sodium salts of two acids (palmitic and stearic) whose glycerine salts are contained in fat; these sodium salts are soluble in water whereas the calcium and magnesium salts are insoluble, hence the first quantity of soap added yields, by double decomposition, the insoluble salts.

$$MgCl_2 + 2Na\ (palmitate) = 2NaCl + Mg\ (palmitate).$$

Water which has been thus treated is said to be 'softened.' To soften water by sacrificing soap is a costly process, and other methods are employed. The hardness of water due to the presence of hydrogen carbonates of calcium and magnesium can be destroyed by the decomposition of these compounds on boiling; the normal and insoluble salts are precipitated (furr in boilers and kettles).

$$Mg(HCO_3)_2 = MgCO_3 + H_2O + CO_2.$$

The cost of fuel is so serious, however, that the commoner custom is to add the calculated quantity (not more) of slaked lime.

$$Ca(HCO_3)_2 + Ca(OH)_2 = 2CaCO_3 + 2H_2O.$$

Water which has been softened by boiling, or by addition of slaked lime, may still contain soluble sulphates and chlorides of calcium and magnesium, which will still form the insoluble curd with soap. Hardness due to such soluble salts can be removed by the addition of 'washing soda,'

$$CaCl_2 + Na_2CO_3 = 2NaCl + CaCO_3,$$

or by the waste of soap. It is called 'permanent hardness,' that which may be removed by boiling is called 'temporary hardness.' Permanent hardness is not removed from drinking waters. In laundries the washing soda not only removes the hardness but any excess aids the cleansing operations.

Basic salts.

When dissolved sodium carbonate is added to a solution of a soluble salt of magnesium a white precipitate forms, which is *not* the normal carbonate but corresponds to the complex formula $3MgCO_3Mg(OH)_2 2H_2O$, that is, the magnesium carbonate has suffered partial hydrolysis.

$$MgCO_3 + 2HOH = Mg(OH)_2 + H_2CO_3,$$
$$3MgCO_3 + Mg(OH)_2 + 2H_2O = 3MgCO_3,\ Mg(OH)_2 2H_2O.$$

Such a partially hydrolysed salt is called a **basic** salt.

The normal magnesium carbonate occurs in nature and can be prepared by adding to the solution of magnesium chloride, a solution of hydrogen sodium carbonate and then warming; the slight tendency to hydrolyse is opposed by the liberated carbonic acid.

$$MgCl_2 + 2NaHCO_3 = MgCO_3 + 2NaCl + H_2CO_3.$$

The basic carbonates of zinc and lead are precipitated from solutions of their soluble salts by normal sodium carbonate. but the normal carbonates are precipitated when hydrogen sodium carbonate is used. From copper salt solutions, only the basic carbonate is precipitated whichever sodium salt is employed. The normal carbonate of copper (and of bismuth) is unknown.

To sum up, when the weak carbonic acid reacts with stronger bases, stable normal carbonates are formed, which when soluble are alkaline to litmus. The hydrogen carbonates of the strong bases are fairly stable, but are neutral to phenol-phthalein. With the still strong bases, calcium and barium

hydroxides, stable normal salts are formed which, however, are insoluble, their hydrogen carbonates are soluble but unstable.

Of the weaker base magnesium hydroxide, although an unstable hydrogen salt exists, the normal salt is easily hydrolysed to produce the basic salt. Zinc hydroxide, a base weaker than magnesium hydroxide, forms no hydrogen carbonate, and copper and bismuth do not possess simple normal carbonates. Hence it will be seen that hydrolysis becomes more and more complete as weaker bases are combined with the weak carbonic acid.

When a solution of sodium carbonate is added to solutions of soluble salts either of aluminium or of (ferric) iron, there is an immediate and considerable effervescence, the whole of the carbon dioxide escapes, and the gelatinous *hydroxides* of these metals are precipitated.

$$Al_2(SO_4)_3 + 3Na_2CO_3 + 3H_2O = 2Al(OH)_3 + 3Na_2SO_4 + 3CO_2.$$

A similar reaction occurs with tin salts. Hence not even the basic carbonates of these three very weak bases are formed, or they are immediately and completely hydrolysed.

The formation of basic salts is characteristic of the combination of weak base and weak acid, although it is not entirely confined to them. Thus when white mercuric sulphate is treated with hot water, the yellow basic mercuric sulphate is formed.

$$3HgSO_4 + 2H_2O = HgSO_4 2HgO + 2H_2SO_4.$$

This hydrolysis can be prevented by the presence of sulphuric acid, and if one wishes to prepare the normal salt, the latter must be crystallised from a solution containing sufficient *excess* of sulphuric acid to prevent hydrolysis. The reaction is reversible

$$3HgSO_4 + 2H_2O \underset{\text{with excess acid.}}{\overset{\text{with excess of water}}{\rightleftharpoons}} HgSO_4 2HgO + 2H_2SO_4$$

And this applies to all salts which tend to hydrolyse. The excess acid remains in solution and does not combine with the salt, for metals whose normal salts with strong acids suffer some hydrolysis do not tend to form hydrogen salts.

Another very interesting instance of hydrolysis of the salt of a strong acid is afforded by bismuth chloride ($BiCl_3$). When this is brought into water, the basic chloride (oxychloride) is precipitated.

$$BiCl_3 + HOH = Bi\,O\,Cl\,[Bi(OH)_2Cl{-}H_2O] + 2HCl.$$

The basic salt may be transformed into the normal chloride by the addition of hydrochloric acid

$$BiOCl + 2HCl = BiCl_3 + H_2O.$$

The solution of the chloride can be so adjusted that the addition of a little water causes a little oxychloride to appear, this basic salt may then be redissolved by the addition of a little more acid, and so on as often as one pleases. The reaction, in common with all reversible reactions, is also **balanced**. Such reactions are often written

$$BiCl_3 + H_2O \rightleftharpoons BiOCl + 2HCl.$$

Basic salts by oxidation.

We have in earlier chapters mentioned two other basic salts formed, not by hydrolysis, but by oxidation. Cupr*ous* chloride (CuCl) on exposure to the air (Chapter VI.) is oxidised to cupr*ic* oxychloride, whose composition appears to correspond to the formula

$$2CuO,CuCl_2 + 4H_2O.$$

Similarly ferr*ous* sulphate crystals (green vitriol), or the solution, on exposure to air is oxidised to insoluble basic ferr*ic* sulphate.

$$A.\quad 2FeSO_4H_2O,\ 6H_2O + O = 2FeSO_4OH + 13H_2O.$$

In both cases, the lower normal salt is oxidised to a higher basic salt.

When a solution of ferrous sulphate containing an excess of sulphuric acid is warmed in contact with air, the soluble *normal* higher salt is formed.

$$B.\quad 2FeSO_4OH + H_2SO_4 = Fe_2(SO_4)_3 + 2H_2O.$$

Hence the necessity of keeping air from a solution of ferrous sulphate.

Basic salts occur in nature, such are Malachite $CuCO_3Cu(OH)_2$ and Azurite $2CuCO_3$, $Cu(OH)_2$. Basic aluminium sulphate $Al_2(SO_4)(OH)_4$ occurs in alumstone (alunite).

Heating the carbonates.

The effect of heat upon the carbonates is not less important than the effect of water. All the carbonates of the heavy metals are completely dissociated at moderate temperatures.

$$PbCO_3 = PbO + CO_2,$$

$$2PbCO_3, Pb(OH)_2 = 3PbO + 2CO_2 + H_2O.$$

('White Lead')

This dry method of forming oxides is one of the most convenient we know. The carbonate of magnesium is not quite so readily decomposed as those of the heavy metals. Calcium carbonate begins to decompose at about 100° C., but the reaction is not completed below 1000° C., while to decompose barium carbonate the temperature must reach 1600° C. Potassium and sodium carbonates are only very slightly decomposed by heat.

The oxides of potassium, sodium, barium and calcium absorb carbon dioxide from the air to reform their carbonates, wherefore when calcium carbonate is 'burnt' in limekilns (L. *culina* = oven) to form quicklime, a good current of air is necessary to carry away the carbon dioxide, as soon as it is expelled from the limestone.

$$CaCO_3 \longrightarrow CaO + CO_2.$$

Limekilns differ in construction in different localities. In some, the limestone ($CaCO_3$) is mixed with coal and the coal is ignited. The heat of the gases produced decomposes the limestone, and the carbon dioxide is carried away in the draught. Continuous furnaces also are used. In some of these the coal is burnt on a hearth, the quicklime is withdrawn below, and more limestone constantly added above (Fig. 77).

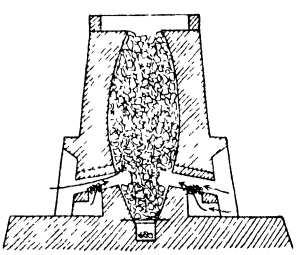


Fig. 77.

The solid hydrogen carbonates of potassium and sodium are readily decomposed by heat,

$$2KHCO_3 = K_2CO_3 + H_2O + CO_2,$$

and as these salts are obtained pure commercially more easily than the normal carbonates, it is usual, when a pure sample of the latter is required, to prepare the hydrogen carbonate

and to heat this strongly until no further loss of weight occurs.

Titrations with carbonate

The pure normal carbonate thus obtained is often used for preparing standard solutions of acids. The dry solid is accurately weighed, introduced into a graduated flask, dissolved, and then water added (with continual shaking) to the mark.

The result of a titration of acid with the standard carbonate gives the concentration of the former; and a simple calculation shows to what volume it must be diluted.

$$Na_2CO_3 + 2HCl = 2NaCl + H_2O + CO_2.$$

Although the titration with sodium carbonate is carried out exactly as if it were a base, the two reactions must not be confused. An acid and a base neutralise each other, but the carbonate is not neutralised, it is *decomposed* by the acid. One often speaks of it loosely as a neutralisation, but it must be borne in mind that the reaction is essentially similar to the preparation of hydrochloric acid, yet in consequence of the weakly acid property and the instability of carbonic acid, as well as of the volatility of carbonic anhydride, sodium carbonate may be used in titration

$$2NaCl + H_2SO_4 = Na_2SO_4 + 2HCl,$$
$$Na_2CO_3 + H_2SO_4 = Na_2SO_4 + H_2O + CO_2.$$

For the titration in the cold methyl orange is used as indicator; the free sodium hydroxide formed by the hydrolysis of the salt keeps the indicator yellow, the free carbonic acid having no action on this indicator (pink in acid solution). But the more sensitive litmus will not give a sharp end point unless the carbonic acid is expelled, therefore if litmus is used the titration solution must be kept nearly boiling. Methyl orange gives a sharp end point only when the least quantity of the indicator is used.

Estimations.

The ease with which carbonates are decomposed by acids enables one to determine simply their percentage of 'fixed' carbon dioxide.

A weighed quantity of solid carbonate may be placed in a tube which is suspended in a flask containing acid. The solid is dropped into the acid, and the gas evolved is either collected over mercury or, better, collected in weighed absorption apparatus, or the loss of weight may be found directly.

For the latter method one uses a very small Erlenmeyer flask with a well-fitting cork, through which passes a tube bearing a calcium chloride tube (Fig. 78). A small open vessel is suspended in the flask by a thread kept in position by the cork. A weighed quantity of carbonate is introduced into the tube, and the whole apparatus containing acid weighed. The carbonate is lowered into the acid, and the expelled carbon dioxide escapes; traces of moisture which would also be lost are retained by the calcium chloride. Finally, the carbon dioxide still remaining in the flask may be replaced by dry air, and the apparatus weighed again. A more accurate apparatus of the same type is specially made for use in analytical laboratories.

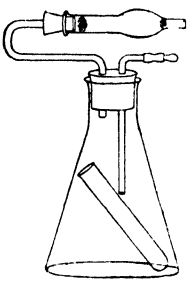


Fig. 78.

A similar method is sometimes used to find the equivalent mass of a metal, the metal of course is used instead of carbonate; hydrogen is evolved.

If the formula of a normal carbonate is known, the atomic weight of the metal may be accurately determined by decomposing a weighed quantity of the carbonate and weighing the residual oxide. $XCO_3 = XO + CO_2$. The value of X may be calculated. By this method, the atomic weight of calcium was shown to be 40·1.

B. *The Natural Carbonates.*

Carbonates occur in enormous quantities in nature: whole mountain ranges may consist almost entirely of limestone, (or dolomite).

Influence of atmospheric carbon dioxide.

There is no doubt that many of the native carbonates are formed directly by the action upon rocks of the carbon dioxide of the air. This gas now occurs only in the small proportion of one-twentieth per cent. by weight, yet the total quantity in the atmosphere attains to millions of tons; and although its work may appear to us slow, in the course of time its influence upon the surface of the earth has been prodigious.

Oxides often occur with a covering of carbonate. Where sulphides are exposed to the air, carbonates occur together with the oxides and sulphates; thus at Leadhills, cerussite ($PbCO_3$) is found with minium, and calamine ($ZnCO_3$) is frequently found encrusting blende.

The disintegration of mineral silicates, wherein the action of the carbon dioxide is most marked, will be discussed at

a later stage; it is sufficient now to say that carbonates do not occur amongst the older rocks except as obvious decomposition products, and many chemists and geologists believe that ages ago the atmosphere contained vastly more carbon dioxide than it does now; the diminution is due to gradual 'fixation' by the rocks to form carbonates.

Influence of living beings.

Carbonates or hydrogen carbonates so formed have been swept into the streams and borne to the oceans. In the rivers, lakes and seas, much of the calcium hydrogen carbonate is withdrawn by animals in order to make their protective shells. Such is the origin, for instance, of the bivalve shells of oysters, mussels, scallops and their kind; of the shells of whelks and snails, sea urchins and their kind, as well as the cuttlebone of sepia, the hard casing of lobsters, &c.

When these creatures are killed by their enemies or die naturally, the untenanted shells are left to accumulate; the sediment covered by clays and compressed into compact rock may, centuries later, involved in some great earth movement, form part of an upheaved land surface, even of a whole mountain range.

The histories of many limestones have been revealed by their fossils.

If the scrapings of a piece of chalk are vigorously agitated with water in a test tube, the sediment, studied with the aid of a microscope, will be found to consist largely of the minute testae of the Foraminifera. These animals are usually microscopic, and yet some chalks, which in many places are hundreds of feet thick, consist largely of their remains.

Limestone is also found as **marble**, a crystalline form. Artificial marble has been prepared by subjecting ordinary limestone to high temperatures; it is believed that marble is formed by the metamorphosis (change of form) of limestone in the hotter depths of the earth's crust.

Limestone occurs massive as fossil coral (Purbeck marble), which for its beauty is often used for decorating interiors of buildings. The formation of **coral** can be studied to-day. The coral animals (which are not related to insects) secrete calcium carbonate to form a common platform. The corals can grow only within certain limits of depth and temperature,

and as they depend for their food upon other inhabitants of the sea, they cannot thrive above high water mark; they flourish best upon the outskirts of the reef. Immense areas of limestone are thus added every year in tropical and sub-tropical waters.

Calcium carbonate frequently occurs massive with magnesium carbonate, as magnesium limestone and as dolomite.

The streams flowing through limestone districts always contain considerable quantities of calcium hydrogen carbonate in solution, and where carbon dioxide is lost into the air, calcium carbonate is deposited as 'travertine.' This is particularly the case when subterranean springs come to the surface. When water charged with calcium hydrogen carbonate percolates through the rock into caves, the drops of water as they hang from the roof evaporate, and, losing carbon dioxide, deposit a film of calcium carbonate; the rest of the drop falls to the floor and, evaporating completely, deposits the remainder of the carbonate. More drops appear where the old ones were suspended, and in course of ages masses of calcium carbonate project from the roof. These are called **stalactites**. On the floor, hillocks are formed called **stalagmites** (σταλάσσειν = to drip). Sometimes they meet and, fusing, look like massive columns supporting the roofs.

The massive forms of calcium carbonate are largely used for decorative or building purposes; thus the 'oolitic' (ᾠόν = egg or roe, λίθος = stone) limestone of central England can be traced by many beautiful domestic and ecclesiastical buildings from Somerset to Lincolnshire.

Besides the massive forms of calcium carbonate which may be crystalline, but are almost invariably impure, the substance exists in two forms, as Calc spar (Iceland spar) or Calcite, and as Arragonite, which occur in large crystals. Each belongs to a different crystal system. Hence calcium carbonate is dimorphous. When the carbonate is precipitated by sodium carbonate from a warm solution, it appears as minute crystals of Arragonite, but from a cold solution minute crystals of calcite appear.

Besides Limestone, the more important natural Carbonates are Witherite ($BaCO_3$); Strontianite ($SrCO_3$), the chief source

of strontium compounds; Magnesite ($MgCO_3$) magnesium carbonate, which also occurs as a basic salt; Iron (ferrous) carbonate, as bog iron ore and spathic iron ore; and Malachite (green) and Azurite (blue), the basic carbonates of copper

PROBLEMS. XIII.

1. What volume of carbon dioxide could be obtained by treating 1 gram of anhydrous sodium carbonate with dilute acid?

2. What percentage loss is sustained by potassium hydrogen carbonate when heated?

3. Add sodium carbonate and sodium hydrogen carbonate to different solutions of mercuric chloride (corrosive sublimate—CARE), and investigate the precipitates.

4. How much quicklime should be obtained from a ton of marble?

5. What volume of air is denuded of carbon dioxide to transform 1 cwt. of slaked lime into carbonate?

6. Determine the simplest formula for azurite, given that when 4 grams of it were heated, the total loss of weight was 1·23 grams, of which 1·02 grams was carbon dioxide and the remainder water. The residue is copper oxide.

7. A villager had a well of very hard water; the local surveyor told him to soften it by throwing down a cartload of lime. Discuss the advice.

8. 100 c.c. of $\frac{E}{100}$ $Ba(OH)_2$ were shaken up with 1 litre of air at S.T.P. After the carbonate had settled, the remainder of the solution needed 97·3 c.c. of $\frac{E}{100}$ acid for neutralisation. Find the volume of carbon dioxide in 10 litres of air.

9. ·3 gram of a mixture of barium and calcium carbonates was dissolved in 10 c c. of E.HCl, and the solution made up to 100 c.c. 10 c.c. of this solution needed 5·97 c.c. $\frac{E}{10}$ NaOH for neutralisation. Find the percentage composition of the mixture.

10. Treat egg-shells and powdered bones with dilute hydrochloric acid. Suggest an explanation of the reactions.

11. Suggest a method of obtaining palmitic and stearic acids from soap, given that they are insoluble in brine. Try your method. Wash them thoroughly, dissolve them in alcohol, and test their action on phenolphthalein.

12. Find the percentage composition of strontianite (strontium and calcium carbonates).

A. 1·487 grams gave 1·68183 grams of strontium sulphate and ·07933 gram of calcium oxide.

B. 56925 gram of strontianite was dissolved in 100 c.c. $\frac{N}{5}$ HCl.

This solution was neutralised by 122·4 $\frac{N}{10}$ NaOH.

13. Hinrichsen found that on prolonged heating 100 grams of pure calcium carbonate gave 56·062 grams of quicklime. Find the percentage purity of a piece of calcium metal ·401 gram of which displaces 200 c.c. of hydrogen from water.

14. 10 c.c. of a solution known to contain sodium hydroxide and normal sodium carbonate were 'neutralised' by the addition of $\frac{E}{10}$ HCl. Phenolphthalein was first added; when the pink colour was discharged, methyl orange was added. As a mean of three experiments, it was found that the first indicator changed when 7 c.c., and the second when 11 c.c. of acid had been added. Calculate the concentration of hydroxide and of carbonate.

15. Mix solutions which contain equivalent proportions of copper sulphate and caustic soda. Filter and wash precipitate. Add it to a second equal quantity of copper sulphate solution. Explain the reaction.

16. Prepare the basic salt $Pb(NO_3)_2Pb(OH)_2H_2O$ by interaction of the nitrate and hydroxide. Recrystallise it from hot water (soluble 1 in 500). Analyse it as well as you can.

CHAPTER XVI.

REACTIONS WITH CARBON. THE HYDROCARBONS.

Preparation of Metals.

In Chapter X. the various modifications of carbon were described: in this chapter, coal and the two varieties of amorphous carbon—coke and charcoal—will be more fully studied.

Origin of the carbon of coal.

The manner in which coal occurs in nature has led to the belief that it is the remains of former vegetation. If the carbon dioxide and the water resulting from burning wood are collected and weighed, it can be shown that together they contain more oxygen than has been supplied for the combustion; hence wood not only contains carbon and hydrogen, but oxygen also. From what sources are these three elements derived?

When we consider that a large tree, such as a sycamore, begins its separate existence as a small seed, it is evident that chemical processes on a large scale must take place during the growth. At one time, common belief held that plants obtain all their nourishment from the soil in a condition ready for use. At the beginning of the seventeenth century, Van Helmont believed he had proved that plants are nourished entirely on water.

"He placed in a pot a certain quantity of earth, which when highly dried weighed 100 lbs.; a willow branch weighing 5 lbs. was set in this pot, which was protected by a cover from dust, and daily watered with rain water. In five years' time the willow had grown to be large and strong, and had

increased in weight by 164 lbs. though the earth in the pot, when once more dried, only showed a loss of two ounces. Van Helmont concluded from this experiment that the considerable increase of weight in the plant had been gained entirely at the cost of the water, and consequently that all the materials in the plant, though distinct from water, nevertheless come from it[1]."

The perception of the true nature of plant nutrition followed the discoveries of oxygen (1775) and of the composition of water (1781) and air (1784). In 1796, Ingen Houss, a Dutch physician practising in London, showed that the carbon dioxide of the atmosphere is the main source of carbon in plants. Eight years afterwards, this conclusion was confirmed by de Saussure, a Genevan professor, who proved in addition, that simultaneously with the absorption of carbon dioxide, the elements hydrogen and oxygen are obtained from the water drawn by the plant from the soil, and further, that for every volume of carbon dioxide absorbed an equal volume of free **oxygen** is evolved.

The carbon dioxide is decomposed only in the green parts of plants, and then only when these are illuminated. Sachs, later on, showed that from the carbon, hydrogen and oxygen, are formed sugar and starch. These two complex substances are stages in the synthesis of the still more complex wood.

When wood is burnt in air, the carbon and hydrogen combine with oxygen and return to their original condition of water and carbon dioxide, but when no extra oxygen is supplied the excess carbon is left as charcoal.

Charcoal is prepared in immense quantities as a fuel, and for chemical purposes.

Carbonization.

Wood is heaped up into stacks and covered with clay, draught holes being left for the admission of air. The air intake is regulated so that some of the wood is burnt, and by the heat of combustion the rest is charred. When wood is heated in closed retorts ('destructive distillation') decomposition occurs; gaseous bodies are driven off which may be collected. These do not consist entirely of carbon dioxide and water; for part will condense to a tarry liquid,

[1] Sach's *History of Botany*.

part is found to be ammonia, while yet another part is composed of inflammable gases. Amongst the last products is found a gas which also occurs in coal mines, and is called by the miners 'fire damp[1].' This same inflammable gas escapes in large quantities from the decomposing plants of marshes, and is therefore also known as 'marsh gas.'

The process by which carbon is obtained from wood, whether carried on naturally or artificially, is called 'carbonisation': coal may therefore be considered as partially carbonised wood.

There is found on the earth a series of natural substances in progressive stages of carbonisation, namely peat, lignite, and the different kinds of coal, cannel, bituminous and anthracite.

Peat, occurring in bogs, is credited with several origins; vegetable and animal matter have been partially oxidised in the air with the fermentative aid of bacteria: it contains about 60 per cent. carbon as compared with the 50 per cent. of carbon contained in wood. **Lignite**, which according to its origin and locality differs in compactness, may contain as much as 67 per cent. carbon. More highly carbonised are the coals. Specimens of **cannel** coal contain from 66 to 84 per cent. carbon, **bituminous** (bitumen = tar) coal contains 70 to 90 per cent. carbon, and **anthracite** coal (steam coal) contains from 87 to 94 per cent. of carbon.

At one time it was generally believed that anthracite has arrived at its present condition through the intermediate stages—peat, lignite and bituminous coal. Recently, however, rival hypotheses have been advanced. One of these maintains that fragments of vegetation brought by running water accumulated in marshes and swamps, where it became peat. It was then covered over by incursions of mud, and, according to the degree of oxidation it had already undergone, it was converted, in the deeper and hotter parts of the earth's crust, into the several varieties of coal, of which one is anthracite. Coal consists mainly of Hydrocarbons (p. 191).

Coal—especially bituminous coal—is often further carbonised to **coke** by heating either in retorts or in open heaps. Coke varies in texture according to the conditions of its formation.

[1] Germ. *dampf* = steam, vapour.

Carbon as a reducing agent.

Coal and amorphous carbon, charcoal and coke, are the cheapest of reducing agents, and therefore are extensively employed in commerce.

Many oxides when mixed and heated with carbon are reduced to the metal, oxides of carbon being formed at the same time.

Advantage is taken of these reactions in analysis.

A small hole is made in a block of compressed carbon, and the oxide placed in it. A small flame is projected upon the oxide by means of a mouth blowpipe. By this simple method, the oxides of lead and bismuth are reduced to the metals. These metals are similar in appearance, but the former is grey, soft, malleable, and marks paper; the latter is brittle, has a pinkish lustre and when clean will not mark paper. In both cases the metal collects into a molten bead. To promote the reduction, the oxides may be mixed with powdered carbon. When the *salts* of the heavy metals are to be analysed by this method, dry sodium carbonate should be mixed with them. (Why?)

In addition to lead and bismuth, antimony (brittle and white), tin (malleable and white) and silver are also obtained as beads when their compounds are treated in this way. Iron remains as a black powder, and copper in red flakes, the temperature attained being insufficient to melt either of these two metals.

Zinc, cadmium and arsenic compounds are also reduced in the same circumstances, but the metals are vapourised and burn in the air; the colour of the fumes or of the deposited oxides, leads to their detection.

Other oxides—those of calcium, barium, manganese and chromium—are not reduced by this means.

Several of the metals are produced for the market by reduction of their oxides: as the oxides are not reduced with equal facility, and the metals themselves differ in temperature of fusion and degree of volatility, the furnaces employed are varied to suit these conditions. To illustrate the main types of furnaces, the reduction of the oxides of zinc, tin and iron will be shortly described. Of the three, iron oxide is most difficult to reduce, and the metal is the last to fuse. Both zinc and tin oxides are readily reduced, but whilst at the temperature of the reduction tin only melts, zinc is vapourised.

Zinc. Zinc oxide (obtained from calamine or blende) is mixed with coal and the mixture placed in clay retorts, arranged together in a furnace chamber so that the flames of the fuel coal may raise them to the temperature of reduction. The liberated zinc escapes from the retort by the clay delivery pipe as vapour, and is condensed in an iron tube leading to a closed recess (Fig. 79).

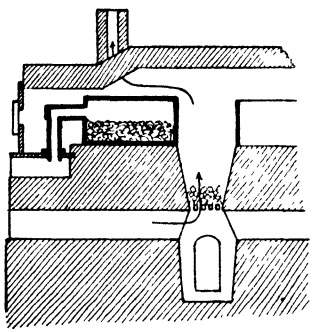


Fig. 79.

It is to be noticed that the furnace coal burning in the draught supplies the heat whereby the coal in the retorts (muffles) reduces the oxides. The fuel and reducing coal are quite separate.

Tin. For the reduction of tin oxide, the temperature necessary for reduction is such that there is no danger of loss of tin as vapour. Instead of a 'muffle,' a **reverberatory** furnace is used[1]. This furnace is specially constructed for the fuel to burn at one end and for the hot products of

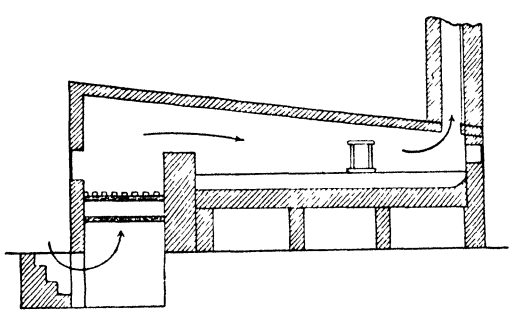


Fig. 80.

combustion to traverse the whole length of the furnace before they leave it at the opposite end. During their passage they pass just above a raised bed, so near the roof that the heat

[1] *reverbero* = beat back.

of the furnace gases is reflected down upon it. Upon the bed is placed the mixture of anthracite and washed ore (tin stone, SnO_2). The molten tin is run off through a hole not given in the figure (Fig. 80).

Iron. For the reduction of iron oxide, a special upright furnace (the blast furnace, Fig. 81) of considerable height and lined with brick work is used. As iron is so difficult to melt no escape of heat is permissible, consequently the carbon (usually coke) both for the fuel and for the reduction

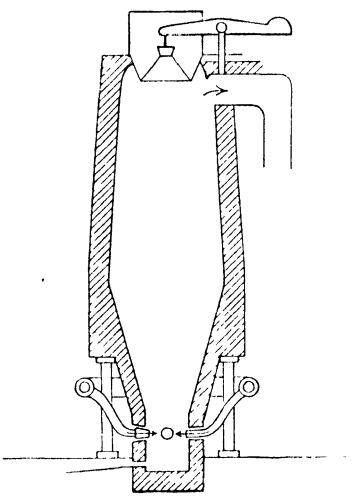


Fig. 81.

is mixed with the ore. A blast of air supplies oxygen for combustion of part of the coke; the heat thus evolved is sufficient to enable the remaining coke to reduce the oxide of iron, both reactions occurring side by side. The quantity of ore directly reduced by the coke is slight. The main part of the reduction is accomplished in the middle regions of the furnace by carbon monoxide formed from air and coke in the lower hotter parts. The iron is melted and the remainder of the ore is reduced in the lower region. Before introduction into the furnace the ores are calcined (roasted in air) to expel water and carbon dioxide, &c., and to render them porous. Some impurities, such as silicates, still remain. To

assist in removing these, calcium carbonate is mixed with the ore; in the furnace the carbonate is dissociated, and the quicklime formed reacts with the silicate to form calcium silicate. This product, fusing at a lower temperature than iron and having a lesser specific gravity, is eventually found floating above the molten metal, whence, as it accumulates, it is drawn off and solidifies as 'basic slag.'

In modern furnaces, the mouth is effectually closed by a cup and counterpoised cone arrangement which allows the introduction of the *charge* when required, but prevents the escape of gas. The air for the combustion of the fuel coke is supplied at a high temperature (800° C.), and at a considerable pressure through pipes (twyers).

The gases evolved with the nitrogen consist chiefly of carbon monoxide—not the dioxide—and this, escaping at the side draught, is burnt in 'stoves' to help heat the blast air. The molten iron is run out into moulds where it solidifies, forming 'pig iron.' The purer samples of iron are obtained from pig iron by various processes of 'refining.'

The Electric Furnace. Several oxides resist reduction, or the metals remain infusible, even at the temperature of the blast furnace where 1400° C. may be reached; few, however, remain unchanged in the Electric Furnace. This furnace consists essentially of a small chamber cut in lime or magnesia blocks; heat is supplied by a powerful electric arc. The best form was devised by M. Moissan, who succeeded in producing a furnace in which the electrolytic effects of the electric current are completely avoided, and only the heating effects employed.

The arc is produced between two stout carbon rods, placed well above the mixture to be heated. M. Moissan frequently employed a current of 1200 ampères at 110 volts, and so obtained temperatures up to 3500° C.: at this point most substances are decomposed or volatilised. For the preparation of chromium and manganese, a lower temperature is employed (600 ampères at 60 volts). In order that the reduction may be continuous, and at the same time to protect the metals produced from the action of the gases expelled from the furnace blocks, Moissan passed the mixture of oxide and carbon through a graphite tube traversing the furnace chamber (Fig. 82).

This tube is inclined, and as the molten metal falls from the lower end, the tube is replenished with the mixture at the upper end.

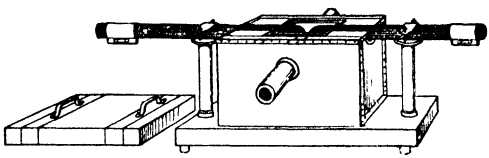


Fig. 82.

In this manner, he obtained not only chromium and manganese, but also silicon, aluminium, titanium, molybdenum, tungsten, uranium and other rarer elements.

Other methods of obtaining elements.

Electrolysis. Calcium and barium cannot be obtained by the reduction of their oxides, consequently they must be prepared by the electrolytic decomposition of their fused chlorides. The electrolytic method of obtaining metals finds a large and increasing field of usefulness.

Sodium and potassium are obtained electrolytically from their fused hydroxides or chlorides; calcium, barium and magnesium from their fused chlorides; and aluminium is obtained in great quantity by the electrolysis of the pure oxide (alumina) fused with cryolite, a naturally occurring compound of aluminium.

Displacement by metals. The methods cited above do not exhaust our resources for the preparation of metals. When sodium was cheapened, it was commonly used for heating with the chlorides of other metals, sodium chloride and the metal being formed. By that means magnesium was, and still is, largely obtained. Magnesium itself is similarly used to displace boron and silicon from their oxides, a reaction which may easily be imitated on a small scale in a hard glass tube. The reaction is dangerous if the substances are not perfectly dry. By a similar method (Goldschmidt's reaction), chromium and manganese are to-day cheaply prepared by heating their oxides with aluminium powder.

All the materials must be dry. The oxide is mixed with excess of aluminium and the reaction started at one spot by means of a fuse, a piece

of magnesium ribbon, leading to a pill of aluminium powder and barium peroxide (or potassium chlorate), imbedded in the reduction mixture. The ribbon, when fired, initiates in the pill the combustion of the aluminium powder at the expense of the peroxide (or chlorate).

The oxidation of aluminium is accompanied with so great an evolution of heat that the reaction spreads from the pill to the mixture, and there the aluminium burns at the expense of the chromium oxide. To such a height does the temperature rise (3000° C.) that, provided the mixture is constantly renewed, not only is the oxide reduced, but the chromium is melted and can be cast as an ingot. The experiment may easily be carried out in a magnesia crucible placed on an asbestos board.

This reaction finds application for the welding of iron rails in the streets or on the railroad; iron oxide is used instead of chromium oxide. The method is called **aluminothermy**, and the reduction mixture thermite.'

Other reducing actions by carbon.

Preparation of some chlorides. Some oxides, which are not reduced by carbon alone, are decomposed when the heated mixture is submitted to a current of chlorine; in this case, the metal combines with the chlorine and the carbon with the oxygen. The method was at one time important for the production of anhydrous chlorides of silicon and aluminium.

$$3Cl_2 + Al_2O_3 + 3C = 2AlCl_3 + 3CO.$$

Carbonates. Carbon reduces carbonates, either to the metal or to the oxide. The method is employed for obtaining barium oxide from witherite ($BaCO_3$), which is not easily decomposed by heat alone.

$$BaCO_3 + C = BaO + 2CO.$$

The alkali metals (potassium and sodium) were also prepared from their carbonates by reduction, before the electrolytic method was introduced.

Sulphates. Carbon is useful for reducing sulphates and sulphites to sulphides.

$$CaSO_4 + 2C = CaS + 2CO_2.$$

This reaction affords an effective test for the presence of compounds containing sulphur.

If some of the residue obtained by heating a salt mixed with carbon and sodium carbonate, as mentioned above, is placed upon a silver coin and there moistened, an immediate blackening indicates the presence of a compound of sulphur in the original salt. A sulphate is reduced by the carbon to sulphide, which interacts with sodium carbonate to produce soluble sodium sulphide. When this is placed on silver, black silver sulphide is formed. The test can be rapidly performed with a charred match. A piece of washing soda ($Na_2CO_3 10H_2O$) is melted by holding it in a flame, and the fused salt is rubbed well into the match. The latter is then charred in the flame and loaded with a little of the powder to be tested. It is now heated again in the flame, and a piece of it is placed on a coin and moistened.

One of the methods for manufacturing washing soda (Le Blanc process) is based upon analogous reactions. Sodium chloride is first of all converted into sodium sulphate by treatment with oil of vitriol.

$$2NaCl + H_2SO_4 = Na_2SO_4 + 2HCl.$$

The sulphate is then mixed with carbon and excess of chalk, and heated in a reverberatory furnace. The sulphate is reduced to the sulphide which, by double decomposition with the calcium carbonate, forms sodium carbonate (more stable than chalk at the temperature) and calcium sulphide.

$$Na_2SO_4 + 2C = Na_2S + 2CO_2,$$
$$Na_2S + CaCO_3 = CaS + Na_2CO_3.$$

The above reaction explains why, when barium sulphate is ignited in a filter paper, a slight loss of weight occurs. By the use of an oxidising agent (Chapter XVIII.), the sulphide formed may be reconverted into sulphate.

$$BaSO_4 \longrightarrow BaS \longrightarrow BaSO_4.$$

The carbides and the hydrocarbons.

When certain oxides mixed with sufficient carbon are heated to a high temperature in the electric furnace, the reduced metal combines with the excess of carbon to form crystalline carbides, which are stable even at the highest temperatures obtainable.

Of these carbides some are unattacked by water, such as the carbides of iron, chromium and silicon; others react with water to produce the hydroxide of the metal and a gaseous compound of carbon and hydrogen—a 'hydrocarbon.' Thus the carbides of lithium, barium and calcium all yield acety-

lene. Aluminium carbide reacts slowly with water to produce pure methane (marsh gas, fire damp). Manganese carbide gives rise under the same conditions to a mixture of methane and hydrogen. When uranium carbide is treated with cold water, chiefly methane and hydrogen are evolved, but there is also a third gaseous hydrocarbon, ethylene, besides some liquid and solid hydrocarbons.

Acetylene, methane and ethylene must be studied at some length. Their densities (H = 1), percentage composition and formulae are tabulated below.

	VD	Molecular weight	% Comp.	Formula
			C. H.	
Methane ...	8	16	75 : 25	CH_4
Ethylene ...	14	28	85·7 : 14·3	C_2H_4
Acetylene ...	13	26	92·3 : 7·7	C_2H_2

All are combustible in air, methane burns with non-luminous flame, the other two with intensely luminous flames; all three are present in coal gas.

Methane is colourless and odourless, and rather insoluble in water. It is exothermic. As we have mentioned above, it is abundantly formed during the carbonisation of plants. It is evolved in marshes, and in large quantities in coal mines where, mixed with air, it forms a dangerous explosive. Its products of combustion are carbon dioxide and water—the former is known to miners as 'Black or Choke-damp' and is greatly feared by them. Methane is prepared pure by reactions whose description is outside the scope of this chapter.

Ethylene has a sweet odour. It has the same specific gravity as nitrogen and carbon monoxide, but is otherwise *different* in physical properties. It is generally formed by heating a mixture of concentrated sulphuric acid and alcohol (C_2H_5OH) to 180° C. The elements of water are abstracted from alcohol, ethylene is evolved and may be collected over water in which it is insoluble.

$$C_2H_5OH - H_2O = C_2H_4.$$

Acetylene is a colourless, poisonous gas, of objectionable smell, soluble in its own volume of water. It is formed (1) when hydrogen is passed slowly through a globe in which an electric arc passes between two carbon poles (Fig. 83). (2) When a bunsen burner 'strikes back.'

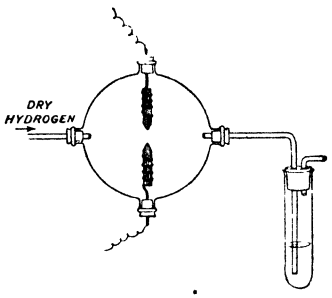


Fig. 83.

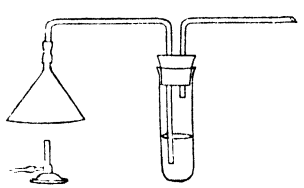
At one time the pure gas was usually obtained from copper carbide, a red compound (dangerous when dry) precipitated when acetylene is passed into a solution of cuprous chloride in ammonia. The solid damp copper carbide is treated with a dilute acid, when acetylene is again evolved.

$C_2H_2 + 2CuCl = Cu_2C_2 + 2HCl$ (attacked by ammonia)

$Cu_2C_2 + 2HCl = 2CuCl + C_2H_2$.

By the formation of this copper compound we can prove the formation of acetylene in a bunsen that has struck back. A glass funnel is inverted over a burner in that condition and the escaping gases are aspirated through the ammoniacal solution of cuprous chloride (Fig. 84).

It will be noticed that in the above two reactions the acetylene behaves like an acid, and indeed copper carbide is also called copper acetylide; but its other reactions do not entitle it to a place amongst true acids.


Fig. 84.

Acetylene burns with an intensely luminous and very hot flame, and in spite of the disadvantage of being poisonous, it is widely used as an illuminant in localities where coal is dear because it may be simply and cheaply produced from calcium carbide. Whole towns in South America are lighted by acetylene.

$$CaC_2 + 2H_2O = Ca(OH)_2 + C_2H_2.$$

For the manufacture of the gas, calcium carbide is prepared on a very large scale by heating lime with carbon in electric furnaces.

Acetylene is an **endothermic** substance, that is, it is formed from its elements with absorption of heat. This fact is determined indirectly as follows.

When the carbon and hydrogen of acetylene part company, the heat of combination is set free, consequently when acetylene is burnt in air the heat liberated is greater than would be evolved by the combustion of the same masses of its constituents in the free state. The heat of formation of carbon dioxide from its elements is 96,960 calories (for 44 grams) and we already know that for 18 grams of **water** formed, 68,400 calories are evolved, hence when 24 grams of carbon and 2 grams of hydrogen burn $(96{,}960 \times 2) + 68{,}400 = 262{,}300$ calories would be set free. But when 26 grams of acetylene are burned 309,900 calories are evolved, hence the difference, 47,600 calories, represents the heat liberated by the decomposition of the acetylene, and therefore also the energy which must be supplied for the union of the elements to form 26 grams of acetylene.

$$C_2H_2 + 5O = 2CO_2 + H_2O + 309{,}900 \text{ calories}$$

193,9 calories 0 68,400 calories

When acetylene is heated to red heat in a tube (Fig. 85), it *contracts* in volume with the formation of a substance which at ordinary temperatures is an oily liquid. It is called **Benzene**; it has the same percentage composition as acetylene but its vapour density is three times as great. Its formula is therefore C_6H_6,

$$3C_2H_2 = C_6H_6.$$

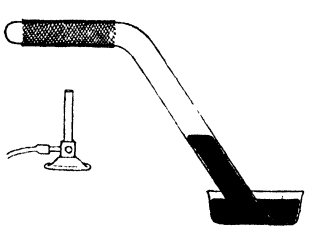


Fig. 85.

Benzene is said to be formed from acetylene by 'polymerisation[1]'; its properties generally differ widely from those of acetylene. It burns with a luminous and very sooty flame.

Methane, ethylene, acetylene and benzene are representatives of four series of Hydrocarbons, of which there are many members. Hydrocarbons with a comparatively low percentage of carbon are gases, the higher members are

[1] πολύς = many, μέρος = a part.

liquids and solids. The lowest and highest are very soluble in the liquid members, forming mixtures most difficult to separate.

Petroleum is such a mixture of hydrocarbons. Its name, 'Rock Oil,' indicates its origin. It is also called mineral oil to distinguish it from oils of vegetable and animal origin (which are not hydrocarbons), such as linseed oil and cod liver oil. Petroleum is generally obtained by tapping subterranean reservoirs; in these the oil generally occurs, together with brackish water, under a considerable pressure of gaseous members such as methane. When the reservoirs are tapped the liquid may be ejected with considerable force, but usually it must be pumped out. Sometimes shales (ancient muds), as at Burntisland, contain so much petroleum that they are worth distilling.

When crude petroleum is heated, gaseous hydrocarbons, largely methane, are first evolved, followed by a successive series of mixtures of liquids having boiling points within certain limits of temperature. These are petroleum ether (40°—70°), petrol (70°—90°), benzine (99°—120°). The liquid fraction boiling above 150° C. is called kerosene or paraffin oil. Upon further distillation, paraffin wax, a mixture of solid hydrocarbons, is left. Candles are often made from paraffin wax, but palmitic and stearic acids obtained from fat are used for the same purpose. With special treatment petroleum yields a jelly called 'vaseline.' Petroleum burns to carbon dioxide and water with a very luminous and hot flame —hence it is used in immense quantities both as an illuminant and as a fuel.

There are several views as to the origin of petroleum, according to one it is due to the decomposition of animal (fish) and vegetable remains; Moissan suggested that it may have been formed by the action of water under pressure upon metallic carbides. Asphalt and manjak, found in the West Indies, seem to stand midway between petroleum and coal.

Coal gas is another illuminant and fuel of great importance. For its manufacture certain kinds of bituminous coals are destructively distilled in fire-clay retorts. If the temperature is comparatively low, the vapours evolved are of

the nature of petroleum, at higher temperatures methane and hydrogen are formed more abundantly. The vapours are first cooled,—this leads to the deposition of tar,—then washed and purified from ammonia, hydrogen sulphide, and carbon dioxide. Finally the gas is stored in the gasometers whence it enters the mains.

A fair sample of coal gas consisted of

50 per cent. hydrogen
33 „ „ methane
13 „ „ carbon monoxide
4 „ „ ethylene, acetylene, benzene, &c.

The illuminating power of the gas depends upon the 4 per cent. of ethylene &c., its heating power upon the other constituents.

Another illuminant.

Another fuel of some importance is made by passing superheated steam over heated anthracite. The reaction varies with the temperature; above 1000° C., carbon monoxide and hydrogen are formed, below 600° C., carbon dioxide and hydrogen result.

$$C + H_2O \xrightarrow{\text{above } 1000^\circ \text{ C.}} CO + H_2$$

$$C + 2H_2O \xrightarrow{\text{below } 600^\circ \text{ C.}} CO_2 + 2H_2.$$

Commercially the heating is carried out at a high temperature. This is an important instance of the **influence of temperature** upon the course of a reaction. The mixture of carbon monoxide and hydrogen is known as 'Water gas,' a term which should have been reserved for steam[1].

Flame.

The flames produced when petroleum and coal gas burn in air are very naturally more complex than the flames of the simpler bodies.

Thus when hydrogen or carbon monoxide burns at a jet, the flame is a hollow cone; the former a pale blue almost colourless, the latter a pronounced blue. The simplicity of the flames is due to the simplicity of the chemical reactions

$$2H_2 + O_2 = 2H_2O$$

$$2CO + O_2 = 2CO_2.$$

When hydrogen sulphide burns, more than one substance is formed, and the blue flame consists of inner and outer mantles about the inside cone of unburnt gas.

[1] Germ., steam = Wasserdampf.

The more complex flames of candles, petroleum, and coal gas (Fig. 87, right), are due to more complex chemical changes taking place in the different parts of the flame which at present are not perfectly understood. In the candle the solid hydrocarbons (or fatty acids) are melted by the heat and ascend in the wick where they are volatilised. The vapour passes through the cone of non-burning gas and undergoes changes to form new gaseous hydrocarbons. These substances meet the air in the inner mantle and burn with a brilliant yellowish-white flame. The brilliance of the flame is due partly to incomplete combustion—for there is still not sufficient air—some carbon particles are liberated and are heated to incandescence. Beyond the bright mantle the partly oxidised gas meets with more air and burns completely to carbon dioxide and water in the transparent and (compared with inner sheath) colourless outer mantle. In addition to the inner and outer mantles of the flame, there is at the base a blue region due apparently to a comparatively greater supply of air.

That the hollow portion within the flame contains unburnt gas, can be proved by placing one end of an upwardly inclined tube in it and lighting the escaping gas at the top end, or by rapidly depressing paper into the middle of the flame when a sectional diagram of the flame will be formed in soot.

The ordinary coal gas flame has the same appearance as the candle flame. If air is admitted with the gas before it reaches the jet, the luminosity of the flame is destroyed; its size is diminished but the average temperature is increased; at the same time the flame itself is simpler. This is the principle of the **Bunsen** (Fig. 87, left). It consists of two flame mantles surrounding the hollow portion; the inner sheath of flame is pale blue and the outer, which might easily escape notice, is still paler blue. Although the flame is so hot the unburnt gas is quite cool; if a match be fixed head upwards in the netting at the mouth of a bench bunsen, the gas may be lit and will continue to burn all day without igniting the match within. The bunsen flame is used for the 'incandescent' gas light. The colourless but very hot flame impinges upon the 'mantle' and raises it to incandescence.

The 'mantle' itself is made by immersing a woven framework in the 'milk' of certain earths (mainly thorium oxide with a little cerium oxide). When dry the cotton model is burnt away leaving the infusible earth as the mantle.

If too much air is drawn in, the flame roars, the inner cone becomes green and the flame may strike back down the tube and burn at the lower jet. Here soot is set free and acetylene formed. But if the air supply is gradually cut off, a luminous portion is developed at the top of the inner sheath and the flame gradually assumes the form of an ordinary gas flame. If now the gas supply also is gradually diminished, the luminous portion gradually disappears but the blue region

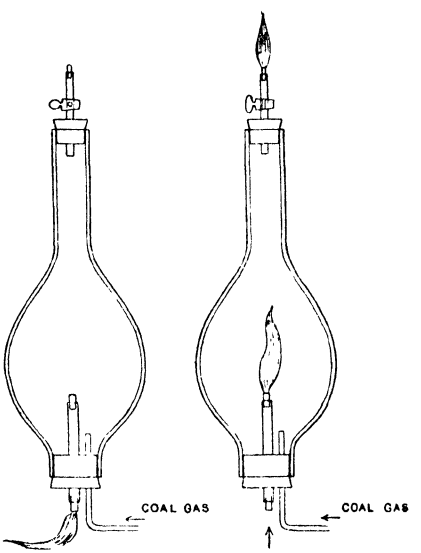


Fig. 86.

at the base proportionally increases until, when the flame just exists, the blue portion forms a continuous cone. In this flame the blue portion is believed to correspond to the inner mantle of the bunsen and the outer portion to the outer portion of the bunsen.

As a flame is produced by the combination of gaseous substances it follows that air can burn at a jet in an atmosphere of coal (or other combustible) gas. Combustion is

said to be reciprocal. In this case the relative position of the combustion mantles will be reversed.

A lamp chimney is corked top and bottom. Through the lower cork pass a short glass tube open at both ends and another tube to carry the coal gas just inside the cork. The upper stopper bears one short tube which can be closed. Coal gas is passed into the chamber and a light applied to the open tube below. When the top tube is closed the gas burns below, but if the upper tube is open, air burns in gas inside the vessel. The excess gas may be lit at the upper stopper (Fig. 86).

When a piece of copper wire is thrust into the bunsen flame so that it pierces both mantles, it will be found that black oxide of copper is formed in the outer mantle, whilst no change takes place in the inner sheath. If now the oxidised portion of the wire is moved into the inner sheath,

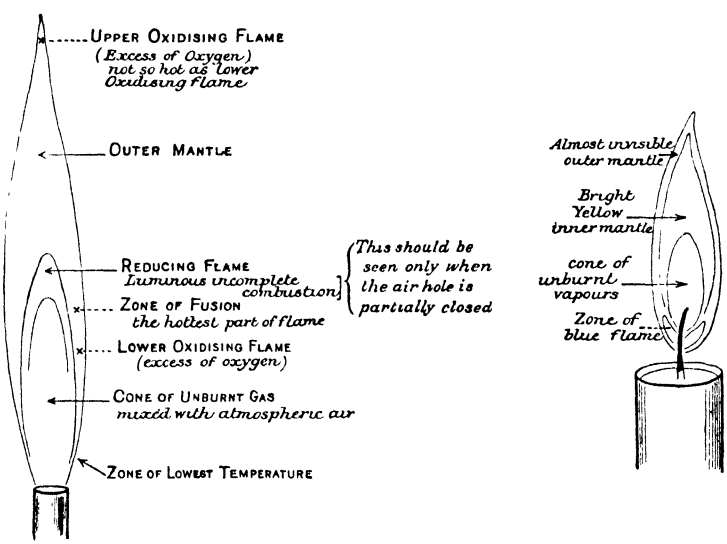


Fig. 87.

it is reduced again to copper. In the hot inner sheath, therefore, is a deficiency of oxygen, in the outer mantle an excess. For dry methods of analysis advantage is taken of this condition. Appended is a diagram of the ordinary bunsen flame with the different regions marked.

The compounds of many metals when placed in the flame give characteristic colours. A little of the salt or oxide is

taken up on the end of a writing pencil (graphite)[1], moistened in concentrated hydrochloric acid and heated in both parts of the flame.

Sodium	compounds	colour	the	flame	yellow
Ammonium	„	often „	„	„	yellowish
Calcium	„	„	„	„	orange red
Strontium	„	„	„	„	crimson
Potassium	„	„	„	„	violet
Barium	„	„	„	„	apple green
Copper	„	„	„	„	blue green.

PROBLEMS. XIV.

1. How much heat will be evolved by burning 10 grams of alcohol? The heat of formation of alcohol (mol. wt. = 46) is +71,100 calories (that is the energy which would be absorbed if 46 grams of alcohol were transformed into free elements).

2. The **heat of combustion** of methane is 213,500 calories (that is the quantity of heat liberated when 16 grams of methane (mol. wt. = 16) are completely burnt to carbon dioxide and water). What is the heat of **formation** of methane?

3. 100 c.c. of a mixture of methane and hydrogen were mixed with oxygen and burnt completely to carbon dioxide and water. The increase in weight of the potash bulbs was ·02 gram. Find the percentage composition of the mixture.

4. The **Law of Hess** says that the total quantity of heat evolved by the change of one system into another is independent of the intermediate stages.

Find the heat of formation of carbon monoxide, given that the heat of formation of carbon dioxide is 96,960 calories and the heat of combustion of carbon monoxide is 68,200 calories.

[1] The pencil (HB) should be sharpened flat and broad, and a new surface exposed for each experiment. This is quicker than cleaning a platinum wire.

For further particulars concerning the origin and nature of coal see Newell Arber's "*Natural History of Coal*," 1*s.* and for a summary of "the results of the principal researches upon the chemical aspects of gaseous combustion" see Dr W. A. Bone's *Report on Gaseous Combustion* to the British Association 1910 (Sheffield). Especially Section V.

CHAPTER XVII.

AMMONIA.

AMMONIA, a pungent gas, is removed as a bye product from coal gas by the washing process. Its saturated solution (S.G. = ·880) is sent into the market; from this solution gaseous ammonia can be entirely expelled by boiling.

Ammonia is formed by the destructive distillation not only of coal, but of almost any substance of animal or vegetable origin; from the fact that it was formerly obtained in this way from hoofs and horns of cattle and like substances, it acquired the name of 'spirit of hartshorn.' The gas is absorbed by oil of vitriol and by calcium chloride, but can be dried by passing it over quicklime or dry caustic potash. It is easily liquefied, and the liquid is largely used in refrigerating machines, but in laboratories its solution is almost invariably used. The gas is very soluble in water at 0° C.; its great solubility can be demonstrated in the same manner as that of hydrochloric acid gas, which is only half as soluble as ammonia.

Composition.

Although ammonia does not burn in air, when warmed before it reaches the jet it may just be lit, and it burns readily in oxygen. The inner and outer mantles of the flame are yellow ochre and faint green respectively. The chief products of combustion are nitrogen and water: ammonia contains nitrogen and hydrogen.

In order to show that ammonia contains *only* nitrogen and hydrogen, the two elementary gases mixed together are exposed to the influence of the silent electric discharge in an ozone tube (Fig. 32), the smell of ammonia is soon evident. When ammonia gas is submitted to the electric arc, it is slowly

decomposed into free nitrogen and hydrogen. This is the reverse action of the formation of ammonia by the influence of the silent discharge upon a mixture of nitrogen and hydrogen. In the synthetic reaction, only a very small proportion of the two gases combines. It may be shown that in the analytic reaction, a small proportion of the ammonia resists decomposition. When ammonia gas, confined in a eudiometer over mercury, is subjected to the electric arc, decomposition proceeds until the volume of the mixed gases is very nearly twice that of the original ammonia. Upon the admission of a few drops of oil of vitriol, a slight contraction takes place due to the absorption of the undecomposed ammonia. If the contraction is subtracted from the volumes, both of the original ammonia and of the final mixture, it will be shown that one volume of ammonia is decomposed into exactly two volumes of a mixture of nitrogen and hydrogen.

The reaction is balanced when about 2 per cent. ammonia is present.

Ammonia $\rightleftarrows$ Nitrogen and Hydrogen.

The mixture now contains no ammonia. If, with the vitriol present, the sparking is recommenced, *contraction* again occurs and *proceeds to completion*, and the mercury and vitriol ascend to the top of the eudiometer. Hence in the presence of the oil of vitriol, which absorbs the ammonia as soon as it is formed, the action is no longer balanced.

Nitrogen and Hydrogen ——→ Ammonia.

Advantage is taken of the combustion and decomposition of ammonia to deduce its composition and formula. When a known volume of ammonia is 'sparked' with a known volume of oxygen (but little in excess), water is formed and free nitrogen together with the excess of oxygen remains. The oxygen is absorbed by special reagents (such as pyrogallic acid or ferrous hydroxide), and the volume of the residual nitrogen is measured. This is found to be one half that of the ammonia from which it was set free. Now we know that 1 volume of ammonia yields 2 volumes of mixed gases, hence it yields $\frac{1}{2}$ volume of nitrogen and $1\frac{1}{2}$ volumes of hydrogen. Therefore 2 volumes of ammonia yield

1 volume of nitrogen and 3 volumes hydrogen,

and, by Avogadro's Theory, $2x$ molecules of ammonia yield

x molecules of nitrogen and $3x$ molecules hydrogen,

or $$2N_xH_y = N_2 + 3H_2.$$

Hence the formula of ammonia must be NH_3.

This conclusion agrees with the observed density of ammonia $\frac{17}{2}$ (H = 1). Equations of the above reactions are

$$2NH_3 = N_2 + 3H_2 \text{ and } 4NH_3 + 3O_2 = 2N_2 + 6H_2O.$$

The combustibility of ammonia enables one to obtain pure nitrogen very readily. Oxygen or air is aspirated through a solution of ammonia, and the mixture drawn through a heated glass tube. The mixed ammonia and oxygen react to produce nitrogen and water. The nitrogen is collected over a dilute solution of sulphuric acid, which absorbs any excess of ammonia. When oxygen is used the nitrogen comes only from the ammonia, when air is used the nitrogen is chiefly atmospheric.

The gravimetric analysis of ammonia may be achieved by combustion. A current of dried ammonia is passed over a weighed quantity of heated copper oxide, and the nitrogen liberated is collected over dilute sulphuric acid to absorb unoxidised ammonia. The loss of weight of the copper oxide gives by calculation (8 : 1) the weight of hydrogen originally combined with the liberated nitrogen.

The composition of ammonia may be partially determined by two other methods.

(1) A mixture of nitrogen and hydrogen in volume proportion 1 : 3 is exposed to the electric arc in the presence of dilute sulphuric acid. The whole of the mixture combines, and the gas is absorbed by the acid.

(2) When chlorine is introduced into an atmosphere of ammonia, reaction takes place with evolution of light. Hydrochloric acid is formed, and nitrogen is liberated.

For the experiment, a long tube (shown in Fig. 88) is filled with dry chlorine gas and a little concentrated *solution* of ammonia is admitted. Action occurs immediately. Ammonia solution in small quantities is allowed to enter the tube until the action ceases. When the tube is opened under water (the hydrochloric acid formed having already dissolved in the water of the ammonia solution), water rises two-thirds of the

way up the tube. As one volume of chlorine combines with one volume of hydrogen ($H_2 + Cl_2 = 2HCl$), it follows that three volumes of chlorine have combined with a quantity of hydrogen which, when free, would also occupy three volumes. One-third of that volume (one volume) of nitrogen has been displaced from the ammonia. Hence ammonia consists of nitrogen and hydrogen in the proportion of (1×3) grams of hydrogen to (14×1) grams of nitrogen.

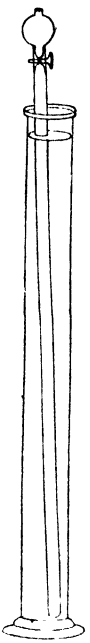


Fig. 88.

It will be noticed that neither the synthetic nor the analytic method just described affords information as to the *volume* of ammonia formed or decomposed. This can easily be obtained from a knowledge of the density of the gas.

The expulsion of nitrogen from ammonia by chlorine affords a simple method of preparing nitrogen. A slow current of chlorine is led into a large volume of ammonia solution. The nitrogen liberated is collected over water (Fig. 89). It is absolutely essential that the ammonia be in large excess, otherwise nitrogen chloride (NCl_3), one of the most dangerously explosive substances known, will be formed.

Salt formation.

It has been repeatedly mentioned above that ammonia is absorbed by acids; like caustic bases, its solution turns litmus blue. When ammonia

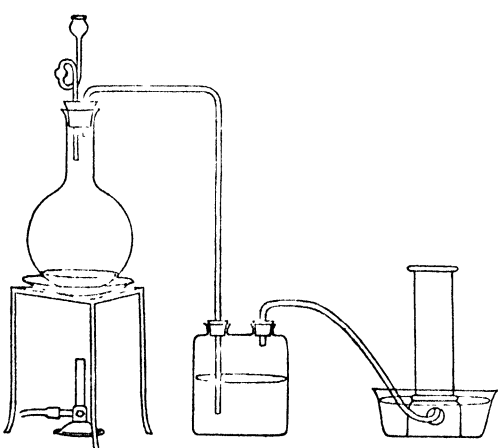


Fig. 89.

solution is added to hydrochloric acid solution the latter may be exactly neutralised and, from solution, crystals may be obtained which resemble in appearance potassium chloride. When these crystals are heated with concentrated sulphuric acid, hydrochloric acid gas is evolved just as it would be if potassium chloride were used. When sulphuric acid is neutralised by a solution of ammonia, crystals can be obtained which have exactly the same appearance as potassium sulphate. It appears therefore, at first thought, that ammonia reacts with acids to produce salts in which ammonia plays the part of a metal in much the same way as potassium.

When ammonia *gas* and hydrogen chloride *gas* are passed into the same vessel, dense white fumes are formed which, on settling, are seen as minute crystals. They are identical with the crystals formed by the neutralisation of the solutions of the two substances. Gay Lussac showed that *equal volumes* of gaseous ammonia and gaseous hydrogen chloride combine to produce this salt. Hence its simplest formula is NH_3, HCl. By neutralising standard solutions of ammonia and sulphuric acid, the composition of the sulphate may be shown to correspond to the formula H_2SO_4, $2NH_3$.

The radicle ammonium.

Comparing the above formulae with those of the potassium salts (which they resemble), we see that one molecule of ammonia (NH_3) + one hydrogen atom correspond to one atom of potassium. In potassium salts 39 grams of potassium *replace* one gram of acid hydrogen, but in these 17 grams of ammonia are *added* for every gram of acid hydrogen.

$$\begin{array}{rcl} K & | & Cl \\ NH_3H & | & Cl \end{array} \qquad \begin{array}{rcl} K_2 & | & SO_4, \\ 2(NH_3),\ H_2 & | & SO_4. \end{array}$$

Hence it is usual to write the formulae of the above salts NH_4Cl and $(NH_4)_2SO_4$. They should not be termed the salts of *ammonia* but of the hypothetical group (NH_4). Because this group assumes the functions of an atom of metal, it is called the electro-positive radicle **ammonium**. The hypothetical radicle ammonium—in common with the hypothetical electro-positive radicle 'ethyl' (C_2H_5) and the hypothetical electro-negative radicles (SO_4), (CO_3), &c.—has never been isolated.

Possible evidence of its existence is found in the formation of ammonium 'amalgam.' This body is formed by electrolysing a solution of an ammonium salt, using mercury as kathode. The mercury swells up, forming a body which is thought to be analogous to potassium amalgam[1]. On heating this, ammonia and hydrogen are evolved, and the mercury regains its original volume. (*See also Problems* xv. No. 5, p. 212.)

We have seen that a solution of ammonia acts like a base, both in its propensity to salt-formation and its effect on litmus. If we accept the view that the caustic bases are hydroxides, we might expect a solution of ammonia to contain at least some ammonium hydroxide (from $NH_3 + HOH$). We should write the equation for the formation of its chloride in solution

$$NH_4OH + HCl = NH_4Cl + H_2O \text{ analogous to}$$
$$KOH \quad + HCl = KCl + H_2O.$$

All attempts to isolate the hydroxide of ammonium end in obtaining ammonia gas, just as attempts to obtain carbonic acid fail to give anything but carbon dioxide gas: if it exists, ammonium hydroxide is very unstable.

Although there is no direct evidence of the existence of ammonium hydroxide, there is good indirect evidence. This evidence depends upon a series of actions in which an element resembling chlorine plays the part assigned below to the latter; the change in no way renders the argument invalid. The element is Iodine.

When alcohol is saturated with hydrogen chloride gas, 'ethyl' chloride is formed.

$$C_2H_5OH + HCl = C_2H_5Cl + H_2O.$$

When ethyl chloride is heated in a sealed tube with ammonia, amongst others, a substance is formed having the following formula, $NH_3(C_2H_5)Cl$. Upon treatment with caustic potash, potassium chloride and a gas of the composition $(C_2H_5)NH_2$ are obtained. The gas is soluble in water, and deports itself so much like ammonia that it is regarded as ammonia in whose molecule one atom of hydrogen is replaced by the radicle ethyl (C_2H_5). It is called ethylammine, one of the class of 'ammines' or substituted ammonias. Its solution is not only basic but even more strongly basic than that of ammonia, and indeed (although both are volatile) it will expel ammonia from ammonium salts to form ethyl-ammonium chloride.

$$NH_4Cl + NH_2(C_2H_5) \text{ dissolved} = NH_2(C_2H_5)H.Cl + NH_3.$$

The substitution of the radicle ethyl for an atom of hydrogen leads to an *increase* in basic properties.

[1] Amalgam is the name given to alloys containing mercury (from μάλαγμα = a soft mass).

When ethylammine, in its turn, is heated with ethyl chloride, combination again takes place, $NH_2(C_2H_5)+(C_2H_5)Cl=NH_2(C_2H_5)_2Cl$, and the new salt with potash yields the gas *di*-ethyl-ammine.

$$NH_2(C_2H_5)_2Cl+KOH=KCl+H_2O+NH(C_2H_5)_2.$$

A solution of di-ethyl-ammine is more pronouncedly basic even than ethyl-ammine, and expels the latter from its salts

$$NH_3(C_2H_5)Cl+NH(C_2H_5)_2=\underset{\text{(di-ethyl-ammonium chloride)}}{NH_2(C_2H_5)_2Cl}+NH_2(C_2H_5).$$

Similarly, di-ethylammine combining with ethyl chloride forms *tri*-ethyl-ammonium chloride $[NH(C_2H_5)_3Cl]$.

In tri-ethylammine $N(C_2H_5)_3$, which is still more basic than di-ethyl-ammine, all the hydrogen atoms of ammonia have been substituted by the radicle 'ethyl.' Tri-ethylammine also combines with ethyl chloride to form *tetra*-ethyl-ammonium chloride,

$$N(C_2H_5)_3+C_2H_5Cl=N(C_2H_5)_4Cl$$

a salt in which all four hydrogen atoms of the hypothetical radicle ammonium have been severally replaced by the radicle 'ethyl.'

The result of the total substitution is striking, for whilst ammonia and the three substituted ammonias could be displaced from the respective salts by potassium hydroxide, this strongest of bases has no effect upon tetra-ethyl-ammonium chloride. When, however, the latter is treated in solution with silver 'hydroxide,' silver chloride is precipitated, leaving a very caustic solution from which, by evaporation, may be obtained a deliquescent solid whose composition corresponds to tetra-ethyl-ammonium hydroxide,

$$N(C_2H_5)_4Cl+AgOH=AgCl+N(C_2H_5)_4OH$$

which is substituted ammonium hydroxide.

In review we learn that as each atom of hydrogen in ammonium is successively replaced by the radicle ethyl, the basic properties and the stability of the substances formed are augmented until tetra-ethyl-ammonium hydroxide is reached, which is known as a stable solid.

Retracing the steps of the argument, we conclude that the existence of at least some ammonium hydroxide in a solution of ammonia is highly probable.

Preparation.

Ammonia is most conveniently obtained in the laboratory by heating ammonium salts with caustic bases. Slaked lime is generally employed.

$$(NH_4)_2SO_4+Ca(OH)_2=CaSO_4+2H_2O+2NH_3.$$

Since the gas combines with sulphuric acid, it is dried by passing it up towers containing quicklime or soda-lime (a prepared mixture of caustic soda and quicklime). It can be collected over mercury or by 'upward' displacement of air (S.G. $=8\frac{1}{2}$, $H=1$). (Fig. 90.)

If a solution of ammonia is to be prepared, care must be taken to prevent the back flow of water, by fixing an inverted funnel at the end of the delivery tube. The apparatus of Fig. 92 *a* is much more convenient.

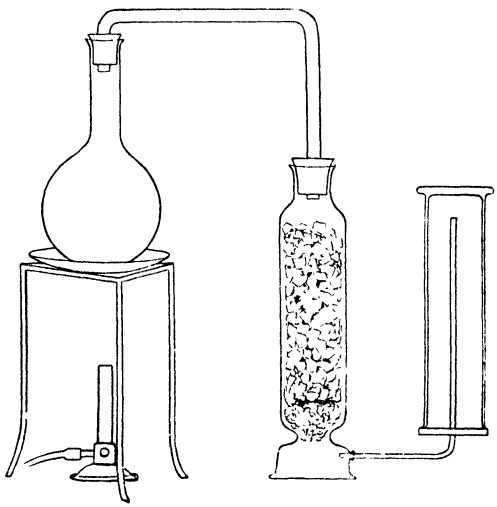


Fig. 90.

[The quicklime lasts longer when the gas is passed up the tower.]

The salts.

Of ammonium salts, the normal and hydrogen carbonates, the sulphate and chloride are found in nature, but the chief source of ammonia is the sulphate produced in gas works. The chloride has long been known as 'sal ammoniac,' whence the name ammonia.

When the solid chloride is heated, it is vapourised; its vapour density (reduced to S.T.P.) is just half of what one would expect from its formula. For that reason it was said to have an 'abnormal' vapour density. To account for this peculiarity, it was suggested that the supposed vapour of ammonium chloride is a mixture of gaseous ammonia and gaseous hydrogen chloride; that the solid, when heated, decomposes into the gaseous substances which, on cooling, recombine to form solid ammonium chloride. That this assumption adequately accounts for the lower vapour density is evident, for instead of x molecules of ammonium chloride, there would be x molecules of ammonia and x molecules of hydrogen chloride; the same mass would occupy twice the volume. The trustworthiness of the view could

be established by separating the two constituents; this should not be difficult seeing that the densities of ammonia and hydrogen chloride are as 17 to 36·5, and therefore their rates of diffusion roughly as 6 to 4. The following experiment shows how this may be done (Fig. 91). A clay-pipe stem (porous) is fitted into a hard glass tube by corks, and arranged so that a current of air may be passed through it into a beaker of water very slightly acidulated and reddened with litmus. The annular space is also provided with a short glass tube for exit. Near this is placed a piece of blue litmus paper. Near the opposite end of the jacket tube is placed some solid ammonium chloride. Whilst air is being passed through the porous tube, the salt is heated and vapourised. The litmus paper will turn red and the litmus solution blue. Hence excess of the lighter ammonia has diffused through the pipe stem and left an excess of hydrogen chloride gas in the annular space.

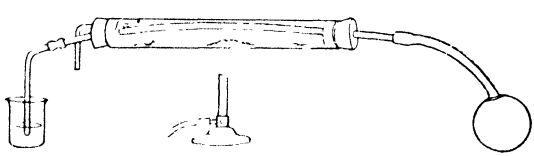


Fig. 91.

A body is said to '**dissociate**' when, on rise of temperature, it decomposes into constituents which recombine on a fall of temperature.

The truth of the hypothesis stated above has been placed beyond dispute by the discovery that when the ammonium chloride is absolutely dry, it vapourises without dissociation and its vapour density conforms with Avogadro's Theory. On the other hand, when absolutely dry ammonia and hydrogen chloride are brought together, they will not combine. The least trace of water is sufficient to allow the combination or dissociation[1]. This remarkable catalytic property of moisture

[1] The above is a simple and exquisite example of scientific method, and the student is urged to study it carefully. A fact is discovered which is in conflict with an accepted theory (Molecular Theory). An assumption is made which reconciles the new fact and the accepted theory. That is not enough. A crucial experiment is devised which supports the assumption, and the latter becomes an hypothesis. Finally, new discoveries establish the hypothesis as a theory.

is by no means uncommon; for instance, hydrogen and chlorine when absolutely dry will not combine even in bright sunlight, nor will even hydrogen and oxygen combine to form water unless there is a trace of moisture already present; many other similar cases are known.

It is characteristic of all ammonium salts to dissociate or decompose upon moderate heating. The carbonate when warmed yields ammonia, carbon dioxide and water.

$$(NH_4)_2CO_3 = 2NH_3 + H_2O + CO_2.$$

The sulphate first yields the hydrogen salt

$$(NH_4)_2SO_4 \longrightarrow NH_4H.SO_4 + NH_3$$

and afterwards complex acid salts.

In the next chapter, some peculiar decompositions of ammonium salts will be studied.

The ease with which salts of ammonium can be volatilised by heating gives them an extensive use in the laboratory for the preparation of pure substances. For instance, whenever possible, ammonium hydroxide replaces caustic potash and soda for the preparation of oxides by the wet method (see Chapter XIII.).

$$FeCl_3 + 3NH_4OH = Fe(OH)_3 + 3NH_4Cl.$$

When the washed precipitate is heated, any ammonium chloride still remaining is driven off, leaving the pure oxide. Similarly in the preparation of pure calcium carbonate, the latter is precipitated from the solution of a calcium salt by means of ammonium carbonate

$$CaCl_2 + (NH_4)_2CO_3 = CaCO_3 + 2NH_4Cl,$$

and the last traces of ammonium chloride are expelled when the precipitate is dried. For the same reason, the hydroxide, carbonate, chloride, sulphide, acetate and oxalate of ammonium are used in qualitative analysis of salts, both as precipitants and solvents, and many complications are thereby avoided.

But ammonium salts cannot be used for all cases: for instance, a solution of ammonia does not precipitate copper hydroxide from copper sulphate solution; instead, a beautiful blue solution is formed from which, by crystallisation, a purple solid may be obtained of the formula $CuSO_4 4NH_3 H_2O$. Ammonia also reacts with salts of silver and of mercury

to form complex compounds. When passed over calcium chloride, it is absorbed to form the substance $CaCl_2 8NH_3$; hence the anhydrous chloride cannot be used for drying ammonia gas.

The proportion of 'ammonia' in ammonium salts may be estimated by heating them with caustic bases.

Estimations.

Method I. A weighed quantity of the salt to be analysed is heated with a known volume of *standard* caustic soda in excess. Ammonia escapes, and the *excess* of standard alkali is determined by titration with standard acid solution.

Method II. A weighed quantity of the salt to be analysed is heated with some solution of caustic soda in a flask, and the whole of the expelled ammonia is absorbed by a known volume of standard acid in excess. The excess of standard acid is determined by titration with standard base.

The apparatus of Fig. 92 is convenient for the experiment A small flask has a wide delivery tube joined to a 50 c.c. pipette just dipping into a portion of the standard acid. The trap contains broken glass moistened with a little of the standard acid. When all the ammonia has been expelled from the salt by boiling, the flask and delivery tube are disconnected.

The remainder of the standard acid is poured down the pipette and trap, and then washed into the main quantity with distilled water. Finally, the

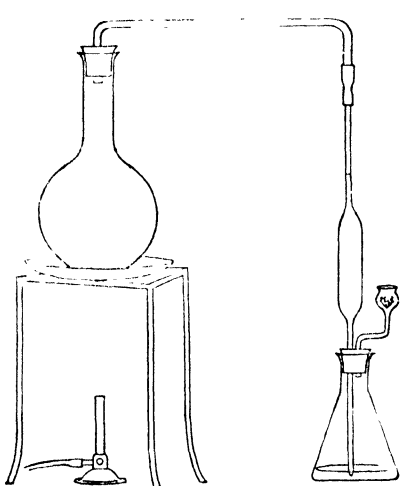


Fig. 92.

acid is titrated to determine the quantity not neutralised by the absorbed ammonia.

Instead of the pipette and trap, a wide inclined tube, drawn out to a fine point, may be used. This is simpler and quite efficient (Fig. 92*a*).

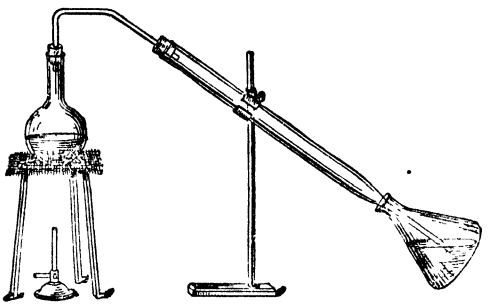


Fig. 92*a*.

(This method may be used instead of that of Fig. 66 for the preparation of solutions of very soluble gases. For still others see Figs. 111 and 125.)

PROBLEMS. XV.

1. When a solution of silver sulphate is added to a solution of ammonium chloride, silver chloride is precipitated and ammonium sulphate may be obtained by evaporation. Does this action affect your views regarding the radicle ammonium?

2. Find the purity of a sample of sal ammoniac. One gram was heated with 20 c.c. *E*. KOH, excess potash was neutralised by 14 c.c. *E*/10 HCl.

3. The ammonia expelled from 1 gram of a specimen of ammonium sulphate was absorbed by 25 c.c. of *E*. H_2SO_4. The solution was then neutralised by 100 c.c. of *N*/10 KOH. Find the purity of the sample.

4. Mix saturated solutions of brine and ammonia in a gas-jar. Cork securely, and pass into the jar carbon dioxide direct from a good Kipp apparatus until no more will be absorbed under the pressure attainable. Wash crystals in small quantities of cold water, and identify them. Explain the Solvay Process for obtaining sodium carbonates. Draw curves for the solubilities of the following:

100 parts of water dissolve 11·9 parts $AmHCO_3$ at 0°, 13·35 parts at 4°, 15·58 parts at 10°, 18·3 parts at 15°, 21 parts at 20°.

100 parts of water dissolve 8 parts $NaHCO_3$ at 0°, 9 8 parts at 20°, 12·7 parts at 50°.

5. Prepare a little sodium amalgam by adding one by one a few small pieces of sodium (impaled on a long glass rod drawn out to a point) very cautiously, to slightly warmed mercury (contained in a high crucible and placed behind the screen of a draught chamber). When the amalgam is cold pour on to it some ammonium chloride solution. Examine the product and show that it soon begins to yield ammonia *and hydrogen*.

CHAPTER XVIII.

THE OXIDES AND OXYACIDS OF NITROGEN.

The 'sparking' of air.

WHEN air is submitted to the influence of the electric arc, reddish-brown strongly smelling fumes appear. These fumes are absorbed by water to form an acidic solution and, therefore, they may be removed from gaseous mixtures by absorption with a caustic base.

To demonstrate the formation of the brown gas, air is slowly aspirated through a globe in which an electric arc is passing between two platinum terminals, the brown fumes are drawn with the excess of air through a solution of caustic soda (Fig. 93).

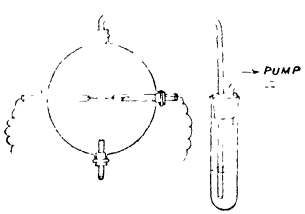


Fig. 93.

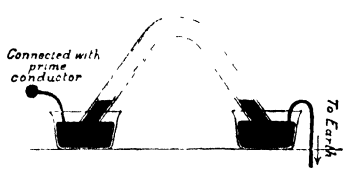


Fig. 94.

Cavendish in 1784 'sparked' air confined over mercury in a syphon tube (Fig. 94). The legs of the syphon tube rested in two cups, the mercury of one cup was 'earthed,' that of the other connected with a ball placed near the prime conductor of an electric machine. Cavendish found that, upon admitting a little potash solution into the gas space, there was a diminution of volume, and nitrogen alone remained. He subsequently showed that a further contraction took place when extra oxygen was added to the residual nitrogen and

the current again passed, and finally that when five parts of oxygen were mixed with three parts of air, all but a small fraction of the whole could be absorbed after electric action. This result—not a perfect one—indicates that the brown soluble gas is formed by combination of nitrogen and oxygen, in the volume proportion of about 3 : 7. This brown gas is now called **nitric peroxide.** When the solution formed by absorbing it with potash was evaporated, a salt was recovered identical with the well-known substance nitre or 'saltpetre.' Saltpetre, therefore, is the potassium salt of an oxyacid of nitrogen. The acid is called nitric acid, and nitrogen itself was renamed after the reaction described above. Nitre, which crystallises well and is very soluble in water, is neutral to litmus, hence we may presume that nitric acid is a strong acid.

Nitric acid.

To obtain the acid, a mixture of nitre and (an excess of) concentrated sulphuric acid is cautiously distilled from a retort. At first red fumes are evolved, but soon a colourless vapour comes over, which may be condensed as a yellowish liquid in a glass receiver kept cool either by immersion in ice water or by a constant current of tap water (Fig. 95). Hydrogen potassium sulphate is left in

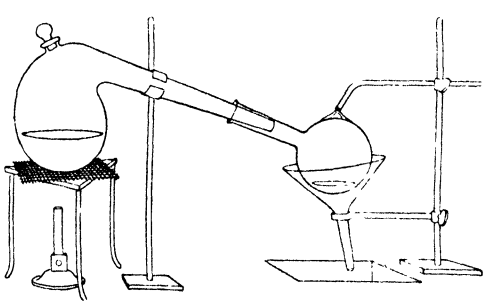


Fig. 95.

the retort. The yellow distillate contains some water from which it may be freed almost entirely by redistillation, after mixing it with more concentrated sulphuric acid. If the new distillate is yellow it contains some dissolved brown oxide, this impurity may be expelled by a current of dry air; what remains is almost pure nitric acid.

Even at ordinary temperatures, nitric acid is unstable. The decomposition, which is accompanied by evolution of brown fumes, is accelerated by light, and especially by heating. At about 78° C. boiling begins, but the decomposition proceeds so rapidly that eventually a solution remains containing only 68 per cent. of acid. This distils at 120·5° C. (760 mm.) without further decomposition. A dilute solution when boiled loses water until a solution containing 68 per cent. of acid is left (compare solution of hydrogen chloride).

When the purest nitric acid was mixed with phosphoric oxide at a low temperature and the mixture gently warmed, a colourless crystalline solid was obtained (Berthelot). This solid dissolves in water with evolution of heat to form nitric acid. On standing, and explosively when heated, it decomposes into nitrogen peroxide and oxygen. Hence this substance is the **anhydride of nitric acid**, and the peroxide is a lower oxide. We will postpone the inquiry into the production of nitric acid by the solution of the peroxide.

The composition of the anhydride has been directly determined by heating a weighed quantity with copper filings, which reduce the oxide completely to nitrogen. The nitrogen was collected and its weight deduced. The anhydride was found to consist of 25·9 per cent. nitrogen and 74·1 per cent. oxygen. Dividing these numbers by the atomic weights of the respective elements, we obtain the atomic proportion $1 : 2\frac{1}{2}$, hence the simplest formula is N_2O_5—nitrogen pentoxide.

The simplest reaction that could occur when the anhydride reacts to form nitric acid is represented by the following equation

$$H_2O + N_2O_5 = H_2N_2O_6.$$

But as nitric acid is monobasic, its probable formula is HNO_3.

Pure nitric acid is a very dangerous substance and all experiments with it, and still more those with the hot acid, must be performed with the greatest care.

When nitric acid is heated it decomposes into water, oxygen and the brown fumes. That oxygen is produced in the decomposition of nitric acid may be shown in a simple but unpleasant manner with a 'churchwarden' clay pipe. The pipe is clamped with the mouthpiece so arranged that

after air is displaced, oxygen escaping at that end is collected in an inverted test tube containing water. The stem is strongly heated in the middle and then nitric acid poured into the bulb; as it falls through the pipe it is decomposed in the heated part, but the weight of the nitric acid above forces the decomposition products downwards. The oxides of nitrogen dissolve and the oxygen is collected.

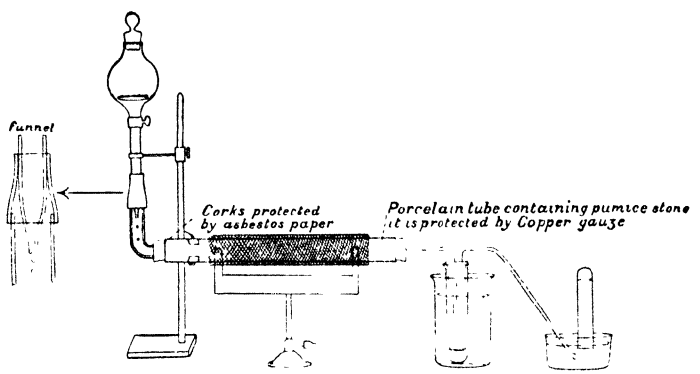


Fig. 96.

Nitrogen peroxide.

The brown substance has been isolated by heating nitric acid in a platinum flask and passing the gases evolved through a U-tube immersed in a freezing mixture. There the brown fumes condense to a pale yellow liquid and the oxygen simultaneously formed passes on. This experiment may be imitated with the apparatus of Fig. 96.

The yellowish liquid when cooled to $-10°$ C. solidifies to form colourless crystals. With gradual rise of temperature they melt to form a *colourless* liquid which becomes yellow and progressively darker as the liquid assumes the ordinary temperature. It boils at 22° C. forming the reddish-brown vapour. When this vapour is heated it becomes increasingly darker and finally opaque. With fall of temperature the changes are reversed.

The percentage composition of nitric peroxide has been determined by reducing it to nitrogen by means of copper in the following manner. A hard glass tube is drawn out and sealed at one end. Copper filings are placed at the sealed end, and then, nearly half way, a sealed thin-walled bulb is

placed containing a known weight of nitric peroxide, the rest of the tube contains copper powder and turnings. The charged tube is put in a furnace and closed at the open end by a stopper carrying a delivery tube which leads to a mercury trough (Fig. 97).

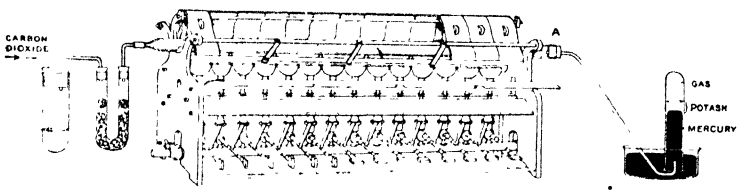


Fig. 97.

The drawn out end of the combustion tube is broken and the air swept out by a current of carbon dioxide. Then a graduated tube containing mercury is placed over the end of the delivery tube and a few c.c. of saturated caustic potash solution are introduced. The combustion tube is now heated, starting at the ends and moving gradually along so that the bulb shall be heated last. The bulb bursts, the escaping gaseous oxide is reduced by the copper, and the free nitrogen is swept into the collecting tube by the current of carbon dioxide. The latter is absorbed by the caustic potash.

The composition of the oxide is found to be

Nitrogen	30·43	which ÷ 14 = 2·16	and this ÷ 2·16 = 1
Oxygen	69·57	which ÷ 16 = 4·35	and this ÷ 2·16 = 2
	100·00		

The simplest formula is NO_2. The vapour density of the *gas* has been determined at different temperatures. When allowance is made for expansion according to Charles' Law the results do not approximate to a constant number. From 2° C. to 140° C. the density decreases from 37·4 to 23 (H = 1). Above 140° C. (afterwards see question 13) the gas expands regularly according to Charles' Law, that is, the (corrected) density is a constant number, 23, corresponding to the molecular weight 46 and to the formula NO_2. Below 140° C. the density gradually increases with fall of temperature, hence, according to Avogadro's Theory, the molecular weight increases *gradually* also—an inconsistency.

To account for the anomalous behaviour it is suggested that as the temperature falls there is a **gradual** association of dark NO_2 molecules to form colourless N_2O_4 molecules, and further that the quite colourless liquid consists entirely of the **tetroxide** molecules.

This supposition is not without support (Chap. XXVI.) but the student should compare this case of 'dissociation' with that of ammonium chloride.

We can represent the system at any temperature below 140° as balanced, $2NO_2 \rightleftarrows N_2O_4$.

Now that the formula of the peroxide is established the decomposition of nitric acid can be represented by an equation

$$4HNO_3 = 2H_2O + 4NO_2 + O_2.$$

The nitrates of the heavy metals decompose in a perfectly analogous way, thus lead nitrate (which is formed by dissolving litharge in nitric acid and crystallising out the salt) when heated yields nitric peroxide, oxygen, and litharge. This reaction is important historically and analytically, and is useful for the preparation of nitrogen peroxide

$$2Pb(NO_3)_2 = 2PbO + 4NO_2 + O_2.$$

Powdered lead nitrate is heated strongly in a retort and the gases evolved are passed through a U-tube immersed in a freezing mixture (Fig. 98). The open limb of the U-tube is drawn out to a fine nozzle, through which the oxygen escapes, carrying with it a considerable part of the nitric peroxide as well, some of the latter however is liquefied.

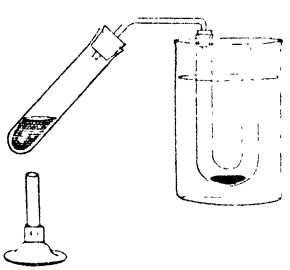


Fig. 98.

Another method of finding the formula of nitric acid.

When a *weighed* quantity of lead nitrate is heated strongly and the residual litharge weighed, the nitrate is found to lose 32·6 per cent. of its weight. This loss represents the percentage of nitric anhydride, and from this result we may confirm our previous surmise of the composition of nitric acid. For litharge in the lead salt takes the place of water in the acid, that is, every 223 grams of litharge in the salt represent 18 grams of water in the acid. It is found that 223 grams of litharge are combined with 108 grams of nitrogen and oxygen, hence 18 grams of water are combined with 108 grams of nitrogen and oxygen (representing the anhydride) in nitric acid, and the acid being monobasic its molecular weight is $\frac{18+108}{2} = 64$ ($HNO_3 = 63$).

The molecular weight and formula of nitric acid were determined before those of the anhydride were known. The method employed was similar to that for finding the composition of the peroxide. Instead of the phial of peroxide, a boat containing a weighed quantity of lead nitrate is placed near the sealed end of the combustion tube. The rest of the tube is filled with copper and the heating managed as before. The free nitrogen is collected, the litharge remaining in the boat is weighed and the oxygen combined with the copper found by difference. From the known percentage composition of litharge (Chapter II.), and by substituting 1 gram of hydrogen for the equivalent of lead (103·5), the percentage composition of the acid follows.

Oxygen	76·28		50·85 ÷ 16 = 3·17
Nitrogen	22·22	or	14·81 ÷ 14 = 1·06
Hydrogen	1·5		1·00 ÷ 1 = 1
	100·00		66·66

corresponding roughly to HNO_3. The accuracy of this formula was proved by the synthesis of silver nitrate.

All the metallic nitrates are soluble in water. They can be prepared (1) by the solution of the hydroxides and oxides in the acid, or by the action of the acid on carbonates, and (2) by the corrosion of the metals themselves.

Nitric oxide.

In Method 2 brown fumes of nitric peroxide are formed in the air, but if the gases evolved are collected over water, in which the brown fumes are dissolved, colourless gases collect according to the conditions of the experiment and the reacting metal. Only in special and rare circumstances is hydrogen evolved.

Thus when copper is attacked by the nearly concentrated acid, a colourless gas is evolved which is not hydrogen, for, on exposure to the air, brown fumes of the peroxide are immediately formed. When oxygen is admitted slowly to the gas contained in a jar inverted over a little icecold potash, combination takes place to form peroxide which is all absorbed, and, when about half its volume of oxygen has entered, the gas is completely transformed into peroxide which dissolves and the potash solution fills nearly the whole space.

The colourless gas is called **nitric oxide.**

Before the composition of the atmosphere was properly understood use was made of this reaction to test the 'goodness' (that is the proportion of oxygen) of the air. The vessel used was through a misconception called the eudio-

meter[1]. Nitric oxide was admitted to the air confined over potash until no further diminution of volume took place. The method is unsuitable for estimating the composition of air, but Cavendish, the most accurate of experimenters, obtained the following result by means of it,

Nitrogen 79·16
Oxygen 20·84 by difference.

When nitric oxide is obtained by the action of nitric acid on copper, it is contaminated with another lower oxide of nitrogen and also with nitrogen. Hence pure nitric oxide cannot be obtained by this reaction.

To prepare the pure gas, advantage is taken of its solubility in a cold saturated solution of ferrous sulphate, to form a brown compound. Nitrogen and the lower oxide are not absorbed by ferrous sulphate, and any peroxide formed is first reduced to nitric oxide which dissolves. From the brown solution nitric oxide is expelled by boiling. It is unnecessary to prepare the pure gas by this method however, for it is obtained more easily by dropping nitric acid slowly (stoppered funnel) into a boiling solution of ferrous sulphate.

Nitric oxide is a colourless gas, nearly insoluble in water, its liquid boils at $-150°$ C. The gas is slightly heavier than air and about 15 times as heavy as hydrogen: its molecular weight is therefore 30.

This number indicates a formula NO, as we might anticipate since it combines with half its volume of oxygen to produce nitric peroxide $2NO + O_2 = 2NO_2$ (dissolved). Its composition may be determined directly by causing it to oxidise barium sulphide. In a bent hard glass tube (Fig. 85) some sulphide is placed, the tube is filled with mercury and then inverted over mercury. Pure dry nitric oxide is admitted to the tube and the sulphide, heated in the horizontal part, reduces the oxide to nitrogen. When the original temperature is established, the nitrogen is seen to occupy one half the original gaseous space. Hence 30 grams of nitric oxide (V.D. = 15) contain 14 grams of nitrogen (V.D. = 14) and, by difference, 16 grams of oxygen, $2NO \longrightarrow N_2$.

[1] εὔδιος = fine weather, μέτρον = measure.

Given the formula of nitric oxide we can supply an equation to represent the reaction in which it is formed. The oxide is a reduction product of nitric acid, hence we may proceed as for the preparation of sulphurous oxide

$$\begin{array}{l} 3[Cu + 2HNO_3 = Cu(NO_3)_2 + H_2] \\ 3H_2 + 2HNO_3 = 4H_2O + 2NO \\ \hline 3Cu + 8HNO_3 = 3Cu(NO_3)_2 + 4H_2O + 2NO \end{array}$$

A convenient way of arriving at the equations which express reactions in which nitric acid suffers reduction is to regard the acid **anhydride** as the body reduced,

$$(N_2O_5)\,H_2O = H_2O + 2NO + 3O.$$

Hence 3 atoms of oxygen must have needed 6 atoms of hydrogen. These must have been supplied by 6 molecules of nitric acid, from which they were displaced by 3 atoms of copper. Therefore,

$$3Cu + (6+2)\,HNO_3 = 3Cu(NO_3)_2 + (3+1)\,H_2O + 2NO.$$

Nitrous acid.

We have mentioned above that when the nitrates of the heavy metals are heated, nitric peroxide and oxygen are evolved and the metallic oxide remains, but when potassium nitrate (nitre) is heated strongly only oxygen is lost, and there remains a deliquescent white substance, very soluble and not easily crystallised. Its solution is neutral to litmus, and slowly takes up oxygen from the air to reform potassium nitrate. The loss of weight of the nitrate on heating gives the formula of this deliquescent body as KNO_2. In accordance with the usual system of nomenclature it is called potassium **nitrite.**

It is usually obtained by causing potassium nitrate to oxidise lead, by heating the substances in an iron tray.

If one attempts to prepare the corresponding **Nitrous Acid** by the action of concentrated sulphuric acid upon the nitrite, its decomposition products alone are obtained, namely nitric oxide and peroxide. Its pure dilute solution is formed by adding the right quantity of dilute sulphuric acid to the barium salt.

$$Ba(NO_2)_2 + H_2SO_4 = BaSO_4 + 2HNO_2.$$

This cannot be concentrated without decomposition, and on exposure to the air it is oxidised.

An oxide corresponding to **nitrous anhydride** (N_2O_3) may be obtained by reducing nitric acid (s.g. = 1·3) with arsenous oxide. It is collected in the same way as liquid peroxide.

$$(H_2O)\,N_2O_5 \longrightarrow N_2O_3.$$

It is a dark blue-green liquid which, when warmed, decomposes into the higher and lower oxides $N_2O_3 = NO + NO_2$. It dissolves in icecold water to form nitrous acid: at ordinary temperatures this solution can be kept only when greatly diluted. [See Probs. XVI. 20.]

The nitrites of the other metals are obtained by double decomposition with sodium nitrite; most are soluble, but silver nitrite is rather insoluble.

The solution of nitrogen peroxide.

We are now in a position to explain why nitric peroxide —a lower oxide than nitric anhydride—can, on solution in water, form nitric acid. When the peroxide (solid or liquid) is dropped into a cylinder of cold water (about 4° C. say), it changes to dark green the instant it enters the water and then falls in drops to the bottom of the cylinder. *Colourless* bubbles ascend from it through the water and, reaching the air, break into brown fumes; at the same time the drops of peroxide disappear leaving a colourless solution of nitric acid. If the ascending bubbles are caught in an inverted tube full of water they remain colourless, and, by the admission of air or oxygen, can be shown to be nitric oxide. Hence the formation of the nitric acid may be represented by

$$3NO_2 + H_2O = 2HNO_3 + NO.$$

Should the nitric oxide so formed come into contact with oxygen more peroxide is formed; this may redissolve and the reaction is repeated, and so on until either the nitric oxide or the oxygen is used up.

But when nitric peroxide is dissolved in a little icecold water, or when dissolved in cold caustic potash solution, there is no effervescence.

Now when silver nitrate solution is added to the solution formed by the absorption of nitrogen peroxide in cold caustic potash (the excess potash having been neutralised by nitric acid to prevent precipitation of silver oxide), silver nitrite is precipitated. Hence, *both nitric and nitrous acids are*

formed when nitric peroxide dissolves *in icecold water* without evolution of nitric oxide.

$$H_2O + 2NO_2 = HNO_2 + HNO_3$$
$$2KOH + 2NO_2 = KNO_2 + KNO_3 + H_2O.$$

Decomposition of ammonium nitrate.

Ammonium nitrate, when heated, decomposes in a manner altogether different from the other nitrates: water and a colourless gas are formed. The latter differs entirely from nitric oxide; it does not react with oxygen and it dissolves in its own volume of water at ordinary temperatures. As a supporter of combustion it stands second only to oxygen; a glowing splinter is rekindled when thrust into it. It may easily be distinguished from oxygen because it does not react with nitric oxide. Its density differs entirely from that of oxygen; it is 22 times as heavy as hydrogen, hence its molecular weight is the same as that of carbon dioxide, (44). When it supports combustion it is reduced to nitrogen, and therefore its formula is found by the method adopted for nitric oxide (page 220).

In this case the tube may be filled with gas before it is inverted over mercury, and some gas withdrawn afterwards.

After reduction the volume is found unchanged. Hence 22 grams of this oxide (V.D. = 22) contain 14 grams of nitrogen (V.D. = 14) and, by subtraction, 8 grams of oxygen. Its simplest and true formula is N_2O. It is called nitr*ous* oxide.

$$NH_4NO_3 = 2H_2O + N_2O.$$

It is to be noticed that nitrous oxide is not the anhydride of nitrous acid, nor is nitric oxide the anhydride of nitric acid.

Nitrous oxide (nitrogen monoxide) is easily liquefied and boils at $-90°$; it has a sweet taste. When inhaled it has the physiological property of producing insensibility and is, therefore, used in dentistry as an anaesthetic; when taken in large doses it proves fatal. Davy, who discovered it, called it 'Laughing Gas.'

It is most conveniently prepared by cautiously heating a mixture of dry ammonium nitrate and dry sand, passing the gas through a solution of ferrous sulphate to free it from any nitric oxide which may be formed at the same time.

It will be noticed that the equation represents only one of several reactions which take place: the reaction is not peculiar on that account.

Whilst potassium and sodium nitrites are stable towards heat, the nitrites of the heavy metals decompose into the metallic oxides and oxides of nitrogen. Again the ammonium salt differs in its method of decomposition, water and nitrogen being formed,

Decomposition of nitrites.

$$NH_4NO_2 = 2H_2O + N_2.$$

A concentrated solution of the nitrite may be heated in a flask; the ammonium nitrite need not be used directly; a mixture of the saturated solutions of ammonium sulphate and potassium nitrite in molecular proportions answers the purpose just as well.

The oxides of nitrogen afford the finest example of the Law of Multiple proportions to be found in inorganic chemistry.

Example of Law III.

Oxide.	Proportion by parts.	Formula.	Other name.
Nitrous oxide	28 : 16	N_2O	monoxide
Nitric oxide	28 : 32	NO	(sometimes dioxide)
Nitrogen trioxide	28 : 48	N_2O_3	nitrous anhydride
Nitrogen peroxide	28 : 64	NO_2	tetroxide
Nitrogen pentoxide	28 : 80	N_2O_5	nitric anhydride

In addition, there is evidence of a sixth oxide, the true Nitrogen trioxide 28 : 96 NO_3.

The ratio of oxygen to a fixed quantity of nitrogen (or vice versa) is 1 : 2 : 3 : 4 : 5 (and perhaps 6).

Nitric acid and the nitrates.

Nitric acid ranks in importance with hydrochloric and sulphuric acids. Like the former it is monobasic and volatile, like the latter it is an oxyacid and an oxidising agent. We have seen that the properties of hydrochloric acid, in ordinary circumstances, are those of an acid uncomplicated; sulphuric acid when concentrated has, in addition, powerful desiccating and considerable oxidising properties. Nitric acid has oxidising properties so fully developed that probably it finds more extensive use as an oxidiser than as an acid.

Its efficiency as an oxidising agent depends upon its large percentage of oxygen and its ready decomposibility, by which not only is free oxygen

Oxidising properties.

directly furnished, but the oxides of nitrogen, which are capable of catalytically accelerating processes of oxidation, are produced also.

Nitric acid which contains dissolved oxides of nitrogen—called fuming nitric acid—is even more powerful as an oxidiser than pure nitric acid.

It not infrequently happens that the oxidising reactions of nitric acid bar its use as an acid.

The danger attending the use of nitric acid is due mainly to its oxidising action on flesh, partly to inhalation of poisonous fumes. Many instances of the use of nitric acid for oxidation will arise in Part II.; a few only, which refer to substances already studied, will be mentioned here. Thus sulphur, sulphur dioxide, and hydrogen sulphide are oxidised to sulphuric acid, and the sulphides to sulphates.

Before heating, a drop of concentrated nitric acid is added to the filter ash containing barium sulphide (see pages 98 and 191).

Charcoal is oxidised to carbon dioxide. Nitric acid (with the aid of potassium chlorate) oxidises graphite to a white solid called graphitic acid.

There seem to be many varieties of graphite, whose only common property is this formation of graphitic acid. Neither charcoal nor diamond yields this substance.

Organic substances containing carbon, hydrogen, and oxygen, are completely oxidised to carbon dioxide and water, or (by the diluted acid) to oxalic acid—one stage short of complete oxidation. Thus sugar and starch, warmed with the slightly diluted acid, after a somewhat violent action, yield oxalic acid, but if the reaction is not properly managed, complete oxidation ensues.

The progress of oxidation is shown below:

	Sugar $\longrightarrow$ $(C_{12}H_{22}O_{11})$	Oxalic acid $\longrightarrow$ $(C_2O_4H_2)$	Complete oxidation $(2CO_2 + H_2O)$
Carbon	42·1	26·7	22·6
Oxygen	51·7	71·1	75·5
Hydrogen	6·2	2·2	1·8

Ferrous salts are oxidised to ferric salts. Thus for the conversion of ferrous sulphate into ferric sulphate,

$$2FeSO_4 \longrightarrow Fe_2(SO_4)_3$$

(that is, from the ferrous oxide condition to the ferric oxide condition $2FeO \longrightarrow Fe_2O_3$), nitric acid must supply one oxygen atom to every two molecules of ferrous sulphate. In order to convert the whole of the ferrous sulphate into ferric sulphate, sulphuric acid must be present.

We may regard the oxidation as in two stages:

A. $2FeSO_4$ (ferrous sulphate) $+ H_2O + O$ (from nitric acid) $= 2FeSO_4OH$ (basic ferric-sulphate).

B. $2FeSO_4(OH) + H_2SO_4 = Fe_2(SO_4)_3 + 2H_2O$

A + B. $2FeSO_4 + H_2SO_4 + O = Fe_2(SO_4)_3 + H_2O$

The equation takes account only of the oxygen supplied by the nitric acid. If we *assume* that the acid is reduced to nitric oxide

$$(H_2O)\,N_2O_5 = (H_2O) + 2NO + 3O,$$

the complete equation reads

$$6FeSO_4 + 3H_2SO_4 + 2HNO_3 = 3Fe_2(SO_4)_3 + 2NO + 4H_2O.$$

Nitric acid was at one time largely used in Grove's and Bunsen's batteries to prevent the polarisation by hydrogen of the platinum or carbon poles.

Nitric acid was known to the alchemists who, because it will corrode all metals known to them save only gold, called it **aqua fortis.** The mixture of nitric acid and hydrochloric acid, which will corrode even gold, the king of metals (forming gold *chloride*), they called **aqua regia.**

Corrosion of metals.

That nitric acid is so powerful a corrosive agent is due partly to the general solubility of nitrates, but chiefly to its great oxidising power.

There are two views regarding this oxidising action. According to one, the immediate object of the oxidation is the metal, but according to the other it is the hydrogen. Thus, according to the first view, we should represent the corrosion of copper by the following series of equations:

$$3Cu + 2HNO_3 = H_2O + 2NO + 3CuO$$
$$3CuO + 6HNO_3 = 3H_2O + 3Cu(NO_3)_2$$
$$3Cu + 8HNO_3 = 4H_2O + 2NO + 3Cu(NO_3)_2$$

The second view is certainly the more interesting, and the one in present favour.

Nascence

It is well known that hydrogen is more reactive at the instant of its liberation than in its ordinary condition as a gas. To the former condition, to which oxygen and other elements also are subject, the name '**Nascent**[1]' has been applied.

Several explanations of this extra activity have been advanced: the most favoured amongst them holds that upon liberation the element is in the free atomic state and, therefore, more at liberty to form compounds than afterwards, when the atoms have combined together to form diatomic molecules. Another view, which does not invoke the aid of the molecular theory, attributes the greater reactivity to greater concentration. Thus silver is deposited from silver nitrate in the presence of nascent hydrogen, and some deposition also occurs when gaseous hydrogen is dissolved under pressure in a solution of silver nitrate. Whatever may be the cause of the properties of 'nascent' hydrogen, the divers reactions which take place when metals are corroded by nitric acid, may be imputed to it.

Hydrochloric acid is slow to corrode copper under ordinary conditions. As soon as some action took place, nascent hydrogen would be liberated, and would tend to replace the dissolved copper. The deposition of the dissolved copper may be prevented by oxidising the nascent hydrogen. Thus copper is slowly dissolved by hot concentrated hydrochloric acid if air is passed into it. Copper is corroded by sulphuric acid, provided the latter is hot and concentrated, but nitric acid, even when cold and to some degree diluted, corrodes it with ease.

A. $3Cu + 6HNO_3 = 3Cu(NO_3)_2 + 6H$

B. $6H + 2HNO_3 = 4H_2O + 2NO$

$$3Cu + 8HNO_3 = 3Cu(NO_3)_2 + 4H_2O + 2NO$$

In addition to nitric oxide, some nitrous oxide and nitrogen are evolved in the reaction.

$$(H_2O)N_2O_5 \longrightarrow 2NO + 3O$$
$$\downarrow \qquad \searrow N_2O + 4O$$
$$N_2 + 5O$$

The more dilute the acid, the more complete the reduction.

[1] *Nasci* = to be born.

Generally, the products of reduction of nitric acid vary

(1) with the concentration of the acid,
(2) with the temperature of the reaction,
(3) with the metal employed.

When zinc is attacked by concentrated nitric acid, nitric oxide is formed; with the diluted acid, the chief products are nitrous oxide and nitrogen and a lesser proportion of **ammonia**, which combines with nitric acid to form dissolved ammonium nitrate. More or less ammonia is formed when cadmium, tin, or iron is used. Magnesium (and manganese) liberates some hydrogen from dilute solutions of nitric acid.

Some metals, for instance aluminium and chromium, are scarcely attacked by nitric acid. This seems to be due to a protecting film of oxide. When clean sheet iron is placed in the concentrated acid, it too becomes 'passive.' This condition is for iron easily destroyed by rough treatment.

The Nitrates.

The nitrates are likewise used for oxidising purposes. When potassium nitrate is heated alone oxygen and the nitrite are formed; when heated with lead the same decomposition takes place more readily, the lead being oxidised to litharge. $KNO_3 + Pb = KNO_2 + PbO$.

Heated with charcoal, potassium carbonate is formed

$$4KNO_3 + 5C = 2K_2CO_3 + 3CO_2 + 2N_2,$$

and with sulphur, the sulphate is produced

$$2KNO_3 + 2S = K_2SO_4 + SO_2 + N_2.$$

Gunpowder consists of an intimate mixture of saltpetre, carbon, and sulphur: when fired, the substances formed do not entirely conform to the above equations. The gaseous products include both the oxides of carbon, some free nitrogen, hydrogen, sulphur dioxide, hydrogen sulphide. The solid products contain not only potassium carbonate and sulphate, but also a considerable percentage of a potassium salt, corresponding to the sodium salt, 'hypo,' and a less proportion of potassium sulphide.

Potassium and sodium nitrates are both found native. The latter is found in Chili as 'caliche' or Chili saltpetre, and finds its chief application as a fertiliser for crops. It is useless for gunpowder, because it is hygroscopic.

Potassium nitrate is less abundant, but is in greater demand. It comes chiefly from India. It is sometimes pre-

pared by double decomposition between sodium nitrate and potassium chloride.

$$KCl + NaNO_3 = KNO_3 + NaCl.$$

All four salts are soluble in water, and at ordinary temperatures there is no change on the mixing of the solutions. If the accompanying diagram is studied, it will be seen

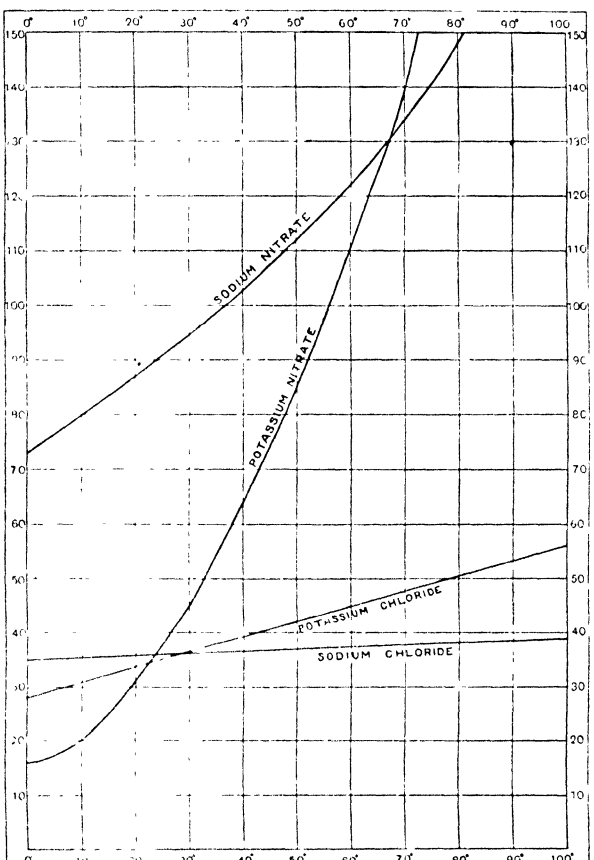


Fig. 99.

that for high temperatures the curves diverge widely. Hence when hot saturated solutions of potassium chloride and sodium nitrate are mixed in molecular proportions, and the mixture

is maintained at a high temperature, the least soluble sodium chloride is precipitated, leaving the very soluble potassium nitrate in solution. The sodium chloride may be separated by filtration in the hot water funnel. On allowing the filtrate to cool, the potassium nitrate crystallises out.

This important experiment illustrates a process very frequently employed in laboratories and technical works.

Ammonium nitrate, mixed with aluminium powder, is used as a blasting explosive.

Most nitrates decompose, when heated, into nitrogen peroxide and oxygen. This reaction is one of the most convenient for obtaining the oxides. Thus baryta is most easily prepared by heating barium nitrate (obtained by dissolving witherite in nitric acid)

Preparation of oxides.

$$2Ba(NO_3)_2 = 2BaO + 4NO_2 + O_2.$$

Copper oxide is best prepared in this manner.

If the formula of a nitrate is known, the atomic weight of the metal may be determined by the method; if the formula is unknown, the equivalent of the metal may still be determined.

The equivalents of metals may be very easily and exactly determined by oxidising the metal with pure nitric acid. For this purpose place a weighed quantity of pure metal in a weighed crucible and then add the concentrated acid drop by drop, waiting each time for the violence of the action to diminish. When all the metal is oxidised, heat the crucible strongly to drive away the excess of acid, and to leave the oxide pure and dry. Allow the crucible to cool in a desiccator, and weigh again.

Some of the substance may be lost with the red fumes. Such loss may be avoided by using a crucible higher and narrower than the ordinary form, or one with a specially designed lid.

Tin is oxidised by nitric acid to the white dioxide SnO_2, hence the equivalent of tin found by this method will be half that found when hydrogen is displaced from hydrochloric acid (Probs. V. 17, page 72).

$$Sn + 2HCl = SnCl_2 + H_2 \qquad \text{Equiv.} = 59{\cdot}5$$
$$Sn + O_2 = SnO_2 \qquad \text{Equiv.} = 29{\cdot}75$$

Cadmium oxide (CdO) obtained by this method is the grey crystalline variety, quite different in appearance from

the brown amorphous variety formed when cadmium burns in air.

A lower nitrate of a metal when heated yields the higher oxide, and the oxygen is retained.

$$Hg(NO_3)_2 = HgO + 2NO_2 + O$$
$$HgNO_3 = HgO + NO_2$$

When the nitrates of mercury are heated, some of the oxide formed is decomposed into metal and oxygen. Silver nitrate yields the metal at once.

Silver nitrate.

Silver nitrate is of special importance for analytical purposes. It is the most soluble of silver salts, and is therefore used for the precipitation of insoluble silver chloride. The formation of a white precipitate —insoluble in hot water but soluble in ammonia—when silver nitrate is added to any solution containing free nitric acid proves therein the occurrence of a chloride, and, conversely, the same substance formed when a soluble chloride is added to any solution containing free nitric acid indicates the presence of a silver salt.

As silver chloride is soluble in pure water to the extent of 2 milligrammes per litre only, silver nitrate is used in volumetric and gravimetric analysis for the estimation of chlorides

$$AgNO_3 + NaCl = AgCl + NaNO_3.$$

Volumetric. Decinormal silver nitrate solution is run into the solution of chloride until the precipitation is complete. In the most accurate work the end point is determined by waiting for the precipitate to settle after each drop. When the titration is carried out in the yellow sodium light, the end point (no turbidity) is very accurately observed. For ordinary rapid work in neutral solution, a drop of a solution of a salt called potassium chromate (yellow) is added as an indicator, and the solution continually stirred; the titration is completed when a permanent brick-red precipitate is formed.

Gravimetrically. A known weight of the chloride is dissolved and a slight excess of silver nitrate solution added. The precipitated silver chloride is washed, filtered, and dried, by the methods described for barium sulphate (pages 8 and 98).

The precipitate should be shielded as much as possible from the light. During the burning of the filter paper, some of the adhering silver chloride is reduced to silver, and must be transformed into the chloride by the addition of a drop of aqua regia. The chloride is perfectly dried in a porcelain crucible heated gradually over a small flame until the fusion point is just reached.

Some of the most famous exact determinations of atomic weights were based upon these methods. Stas, a great Belgian chemist, determined very accurately the atomic weights of chlorine, potassium, sodium, silver, and some other elements. He weighed out a quantity of potassium chlorate —the purest he could prepare—and found the loss of weight on heating. This gave him the ratio

$$KCl : 3O$$

and direct comparison with oxygen.

He dissolved a weighed quantity of the purest silver in dilute nitric acid, and precipitated the whole of the silver again as chloride, using both volumetric and gravimetric methods.

This gave him the ratio

$$Ag : Cl.$$

He then precipitated as silver chloride the whole of the chlorine in a weighed quantity of potassium chloride. The ratio Ag : Cl being known, he thereby obtained the ratio

$$K : Cl$$

and all the data necessary for the determination of the atomic weights of potassium, chlorine, and silver. His numbers will probably be altered slightly in a short time because, in spite of extraordinary precautions, potassium chlorate cannot be obtained absolutely pure.

PROBLEMS. XVI.

1. What was the percentage error of Cavendish's result with the sparking of air, assuming that the whole of the nitrogen peroxide formed was transformed into nitric acid?

2. Mix, in a test tube, cold solutions of ferrous sulphate and of nitre. Add cautiously down the side of the test tube oil of vitriol, until it forms a $\frac{1}{2}$" layer below the solution. Leave it to stand, and observe it from time to time. Can you explain what happens?

3. What percentage of NO_2 and N_2O_4 molecules respectively has a sample of peroxide gas of density 2·52? (Air = 1.)

4. Write equations to represent the liberation (1) of nitrous oxide, (2) of nitrogen, when copper is corroded by nitric acid.

5. Distinguish between rock salt and saltpetre.

6. Compare the effects of adding dilute and concentrated nitric acid to cuprous and cupric oxides respectively.

7. A process has been started for obtaining nitrates for fertilising purposes. A current of air is exposed to the electric arc, and then drawn over milk of lime. Find the volume of air which must be 'fixed' in order to prepare 1 kilogram of calcium nitrate.

8. 150 grams of a certain nitrate were heated, and 87·536 grams of oxide remained (Morse). Find the equivalent mass of the metal.

9. Find the atomic weight of barium from the following: 112·06 grams of nitrate gave 100·03 grams of sulphate. (Given S = 32, O = 16, N = 14, and the formulae.)

10. Find the equivalent mass of tin oxidised by nitric acid.

Weight of crucible		49·101 grams
"	+ tin	50·020 "
"	+ oxide	50·267 "

11. Baryta for Brin's process is made by heating the nitrate obtained from the carbonate. What are the least quantities of witherite and nitric acid that can be used for obtaining 1 kilo of baryta?

12. One gram of metal was found to give 1·886 grams of a stable oxide when dissolved in nitric acid and ignited. If the metal is capable of dissolving in dilute sulphuric acid with evolution of hydrogen, calculate the probable volume of hydrogen (at S.T.P.) which would be evolved in this operation, and explain carefully where and why uncertainty presents itself in the calculation. (Sidney Sussex Scholarships, 1901.)

13. On heating nitrogen peroxide gas above 158° C. the chocolate colour gradually fades until at about 600° C. the gas is colourless. At the same time the density of the gas falls to about 15 (H = 1). On the fall of temperature, the changes occur in reverse order. Suggest an explanation of the phenomena, and state whether you could test your assumption experimentally.

14. Nitrous acid can act either as oxidising or reducing agent. Suggest reasons for this. Test the oxidising action of the acid upon ferrous sulphate and sulphur dioxide. How could you distinguish between solutions of nitrites and nitrates?

15. When a mixture of air and ammonia gas is passed over a glowing spiral of platinum, the platinum continues to glow without further heating. (Some flour is now bleached by the products of a similar reaction.) Using the apparatus of Fig. 100, or some modification of it, attempt to discover the cause of the continued glowing. (Ammonia solution in flask to left, water or caustic potash to right.) Use platinised asbestos in a tube (starting the glowing by a little heating) and make a rough comparison of its efficiency with that of the spiral.

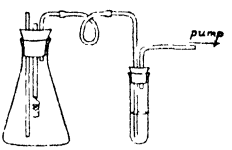


Fig. 100

16. Compare the solubilities, at ordinary temperature, of the nitrates and nitrites of sodium and potassium respectively.

17. Write equations to represent the oxidation by nitric acid of sulphur to sulphur dioxide and sulphuric acid, after doing the experiment.

18. Immerse pieces of copper shavings in (*a*) air-free solution of hydrochloric acid; (*b*) in air-free atmosphere of damp hydrogen chloride; (*c*) in a space containing both air and the acid gas; and half immerse shavings in the acid solution contained in a dish. Compare the results.

19. Immerse thin copper shavings in very dilute solutions of nitric acid. After several days investigate the changes.

20. Dr H. B. Baker has recently shown that perfectly dry nitrogen trioxide (N_2O_3) may be vapourised without decomposition. The vapour density (corrected) varies from 38 to 62. Can you suggest an explanation? (See *Proceedings Chem. Soc.* 16/11/07 or *Journal C. S.* Nov. 07.)

21. 'When iron is placed in *very* dilute cold nitric acid, ferr*ous* nitrate and ammonium nitrate are formed.' Prove this, and write an equation to express the reaction.

22. Examine the statement that 'possibly the atmospheric nitrogen is the source of all the ammonia and ammonium compounds in nature' when you have read pp. 239 and 240 and Chapter XXXI.

23. Stas found

(1) that 498·6355 grams of potassium chlorate ($KClO_3$) gave, on ignition, 303·3870 grams of potassium chloride (KCl)

(2) that 145·70775 grams of potassium chloride reacted with a solution of silver nitrate made with 210·85488 grams of silver.

(3) that 969·35485 grams of silver dissolved in nitric acid and treated with ammonium chloride gave 1287·7420 grams of silver chloride.

Given O = 16, find the atomic weights of the other elements.

CHAPTER XIX.

THE ATMOSPHERE.

A. Constituents of the Atmosphere.

The atmosphere consists chiefly of nitrogen and oxygen. In addition there is a small fairly constant proportion of carbon dioxide, a varying proportion of water vapour, and almost negligible proportions of ammonia, and the oxides of nitrogen. The two last owe their presence to chemical processes, and are found chiefly in the atmosphere near towns.

Estimation of atmospheric carbon dioxide.

The proportion of carbon dioxide in the air is very small —about 3 volumes per 10,000. It may be estimated gravimetrically or volumetrically, the latter method is the more accurate.

Gravimetrically. Air is aspirated through a series of U-tubes containing desiccators which remove ammonia as well as moisture, and then through a U-tube containing moist pieces of potash, followed by another U-tube containing phosphoric oxide to retain any moisture lost by the potash. The increase in weight of these two tubes is the weight of carbon dioxide absorbed. The volume of the air from which the carbon dioxide was absorbed, is the capacity of the aspirator itself.

Volumetrically. A known volume of air is shaken with a known volume of standard base, and the excess determined by titration with standard acid. The greatest care must be taken to avoid contact with outside air, and burettes are specially designed to that end.

When standard baryta is used, barium carbonate is precipitated; the standard acid used must be too feeble to redissolve this precipitate. When caustic potash is used, the excess is titrated with standard sulphuric acid, and phenol phthalein is used as indicator; the end point is reached when the solution contains K_2SO_4 and $KHCO_3$ (see Chapter XIV.).

Inert elements.

In addition to carbon dioxide and the other substances which occur in almost negligible proportions, the atmosphere normally contains as much as 1·2 per cent. of certain gaseous elements, undistinguished from the nitrogen, until their discovery by Lord Rayleigh and Sir William Ramsay.

When Cavendish analysed air, he sought to show that purified air contains only nitrogen and oxygen, but he always failed to account for a certain amount, which he estimated as 0·9 per cent. The result was not regarded as significant, until Lord Rayleigh found that atmospheric 'nitrogen' had a slightly greater density than nitrogen obtained from chemical compounds. Many explanations of the discrepancy were offered, such as the possible occurrence of a condensed (ozonic) form of nitrogen. Efforts to form such a substance failed, and in 1895 Professor Ramsay isolated a new element which he called Argon. VD = 20 (H = 1).

He took advantage of the combination of nitrogen and magnesium, when heated, to form magnesium nitride. Air was first deprived of oxygen by heating with copper, and then of nitrogen by heating strongly the residue with magnesium. See his *Gases of the Atmosphere.*

Sometime afterwards, Sir William Ramsay showed that his residual gas was really a mixture of argon with other gases in much smaller proportions. They all resemble argon in containing only one atom in the free molecule, and in having so far resisted all efforts to cause them to form compounds. These gases—the inert elements—are called Argon (Gk. = idle), Xenon (Gk. = strange), Neon (Gk. = new), Krypton (Gk. = hidden).

When searching for Argon in the emanations from certain minerals (cleveite) Ramsay discovered Helium (VD = 2), an inert gas which also occurs in air. Lockyer had discovered its presence in the sun (ἥλιος) by the spectroscope (1868). Onnes obtained 60 c.c. liquid Helium (BP = 4·3° absolute) July '08, see *The Times*, 20/7/08.

B. Chemical Actions in the Atmosphere.

Oxidation and hydration.

Many instances of chemical reaction between the solid minerals and atmospheric oxygen and carbon dioxide have been mentioned in the preceding chapters of this book; such are the formation of oxides and

sulphates from exposed sulphides, and the transformation of oxides and silicates into carbonates. To these may be added a few familiar instances of oxidation and hydration.

Iron hydroxide is deposited as a brown stain when chalybeate[1] springs come to the surface; the ferrous hydrogen carbonate is oxidised or a ferric salt is hydrolysed. Ferrous and manganous silicates—frequent constituents in minerals—are decomposed and oxidised to ferric and manganese oxides when exposed to the air. The change is accompanied by darkening in colour, as may be seen when the light green mineral Olivine is weathered to Serpentine, a mineral which owes its beauty largely to the streaks of red ferric and manganic oxides.

Substances which readily oxidise in contact with air, are often spoken of as 'unstable,' whereas they are usually quite stable in an atmosphere containing no oxygen; thus ferrous salts are quite stable in an atmosphere of nitrogen. It is a common practice to perform, in artificial atmosphere, experiments which involve the use of easily oxidised bodies.

Similarly, substances which are easily hydrated, are usually unstable in moist air, but quite stable in dry air. Lime, which may be kept indefinitely in dry air deprived of carbon dioxide, is unstable in air under ordinary conditions.

When applied to chemical substances, the terms stable and unstable must be suitably qualified.

The rusting of metallic iron affords an interesting problem in instability, and one upon which much attention has been bestowed recently. The conditions which favour the oxidation may be studied in a few simple experiments. Equal weights of thin piano wire, well scoured from rust, are separately placed

(1) in air confined in a cylinder over water,
(2) in carefully dried air over mercury,
(3) in a jar of oxygen over water,
(4) in a jar of dry oxygen over mercury,
(5) in tap water (immersed),
(6) in a corked flask full of boiled distilled water,
(7) exposed to air in a saucer ('control' experiment for comparison).

[1] $\chi\acute{\alpha}\lambda\upsilon\psi$ = iron.

Record should be made each day of the appearance of the several specimens. After a suitable time each piece is re-weighed, heated, and weighed a third time.

Experiment 8.

Put into a 500 c.c. flask, 100 c.c. of 15 per cent. caustic potash solution. Fit it with a partially-bored sound cork, and shake occasionally for two days. Boil a bright long nail in distilled water and then push it, to within 1 inch of the head, through the thin place in the cork. Observe from day to day. (See Mr Watson's letter to *Nature*, Sept. 5th, 1907.)

It will be found that not only oxygen, but also moisture and carbon dioxide are necessary for rusting to take place.

Dr G. T. Moody first proved the necessity for the presence of carbon dioxide. A full account of the experiment will be found in the *School World*, January, 1907. Dr Moody showed that the oxygen and carbonic acid act on the metal to produce (dissolved) ferrous hydrogen carbonate (Chapter XV.). And this is oxidised further by oxygen to the ferric compound which yields ferric hydroxide by hydrolysis (Chapter XV.). Dr Moody has since published an account of a simple and elegant experiment whereby 'the exact mechanism of the production of rust' is 'visualised.'

'In the bottom of a glass cylinder are placed some rods of bright iron, such as French nails. These are only loosely packed, for the most part heads upward, and are so arranged that some of them remain vertical whilst others occupy inclined positions.

Recently boiled distilled water is then poured into the cylinder, until it stands about one and a half inches above the heads of the nails. The mouth of the cylinder is loosely closed with a sheet of paper so as to exclude dust, and at the same time to allow free access of air to the water, whereby carbon dioxide and oxygen are absorbed. In the course of twenty-four hours the water shows signs of becoming turbid, and shortly afterwards a copious separation of brown particles from solution is distinctly observed. These brown particles are continuously formed, and gradually settle on the heads of the nails, and on the upper parts only of those nails which are inclined. The vertical nails and the under parts of the inclined nails remain bright, no general corrosion of the surfaces being observable. At the end of seven days a thick layer of hydrated ferric oxide has collected on the upper surfaces of the nails, and also on the bottom of the cylinder. If a sheet of hardened filter paper, or some other material which allows of diffusion, be placed in a horizontal position immediately over the nails at the beginning of the experiment, the rust which separates from the solution above it gradually collects on its upper surface, and eventually forms a thick layer. The separation of the rust from the water, and its non-formation on the surface of the iron, can be explained only as an oxidation of ferrous iron actually in solution.' (*Proceedings of the Chemical Society*, 28/3/07.)

Bacterial action.

Oxidations of far reaching importance occur when dead animals and vegetables lie exposed. Under the influence of bacteria and other fungi putrefaction sets in, an oxidising process in which soluble and gaseous substances are formed, which either escape into the air or are washed into the soil.

Warmth and moisture are most favourable to bacteria, by whose aid not only the bodies of dead animals and plants, but the excretions of living ones, are changed into substances fit for re-absorption by plants. Upon such action the efficiency of manuring depends (see Chapter XXXI.). By the putrefaction complex compounds are broken down into simpler ones, much of the organic carbon is liberated as carbon dioxide, and the nitrogen eventually goes to form ammonium carbonate, which is washed into the soil. There the ammonia, in the presence of sodium, potassium, and calcium carbonates, is oxidised to nitric acid to form nitrates. In hot countries, such as India, saltpetre is actually prepared for the market by men who supply potassium carbonate (wood ashes) in places near villages, where their experience tells them putrefaction is taking place. Crystals of calcium nitrate may frequently be seen on the walls of cowsheds and stables, the vaporised ammonia being oxidised in the presence of the mortar.

Large deposits of alkali-nitrates, especially sodium nitrate, occur in the nitrate beds of Chili and Peru. Their situation and the nature of some other salts found with them, favour the view that these nitrates were formed by the putrefaction of marine animal and plant remains left exposed to the air. The accumulation of such vast stores is attributed to the dryness of the climate, otherwise they would have been washed away.

The formation of nitrates in the soil has been closely studied. Amongst the animal excretions is a substance called **urea**, whose composition is represented by the formula CON_2H_4. Under the influence of certain bacteria, one of which has been named *micro-coccus ureæ*; the urea combines with water to produce ammonium carbonate,

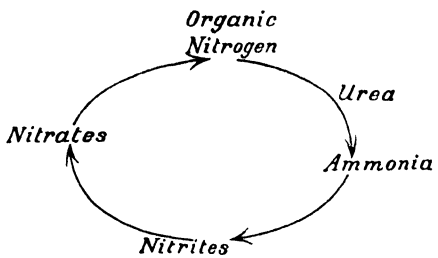
$$CON_2H_4 + 2H_2O = (NH_4)_2CO_3.$$

The ammonium carbonate then becomes oxidised to nitrous acid under the attack of **nitromonas**, the **nitrous ferment**,

which has been isolated from the soil and cultivated by M. Winogradsky.

By this step, called 'Nitrosation,' nitrites are formed in the soil. By the next—'Nitration'—the nitrites are oxidised to nitrates, the bacillus in this case being the **nitric ferment,** likewise isolated by M. Winogradsky.

The nitrogen thus returned to the soil as nitrates is absorbed by plants again, in time to suffer the same transformation. This series of changes has therefore been called **the cycle of nitrogen.**



In addition to those mentioned above, certain bacteria, as well as certain species of green **algae,** by their power of oxidising, or 'fixing,' atmospheric nitrogen itself, are constantly enriching the soil in nitrates.

Another instance of the oxidation of free nitrogen will be given in Chapter XXXI.

Many other fermentations[1] are due to the activity of fungi, for instance, the preparation of alcohol from sugar by the action of **yeast**; and the souring of wine, that is, the oxidation of alcohol to acetic acid under the influence of **mycoderma aceti,** a bacterium which can further oxidise acetic acid to carbon dioxide and water.

	Alcohol ⟶ (C_2H_6O)	Acetic acid ($C_2H_4O_2$)
Carbon	52·2	40·0
Hydrogen ...	13·0	6·6
Oxygen	34·8	53·3
	100	100

In its dilute form vinegar, acetic[2] was the first known acid[3].

[1] *fermentare* = to swell up.
[2] *acetum* = vinegar.
[3] *acidus* = sour.

C. THEORIES OF COMBUSTION.

Some of the most important experiments in the history of chemistry were contrived to elucidate the true nature of combustion, and the part played in the action by the atmosphere. These experiments led, ultimately, to the complete overthrow of the theory of phlogiston, and established in its stead the oxygen theory of combustion, which changed entirely the language and, not a little, the methods of thought pursued by chemists.

Until the compositions of air and of water were known, the true perception of combustion was impossible. Flame was then believed to be a material substance endowed with mass, and distinction was seldom made between ordinary air and other gases, all being regarded as one substance capable of endless modifications and, save to a rare few, too elusive and mysterious to warrant investigation.

Doctrine of phlogiston.

In the latter part of the 17th century, the doctrine of phlogiston was developed, and for over a hundred years was the medium by which all chemical phenomena were interpreted. Briefly, the doctrine maintained that all combustible substances contain 'phlogiston[1],' which they lose during combustion. Substances which, like sulphur and charcoal, leave but little ash when burnt, consist chiefly of 'phlogiston,' or are mere varieties of it. A metal which lost lustre, or burnt in air, was held to have lost phlogiston, and the residual 'calx'[2] was therefore simpler than the metal; when a calx is heated with any substance, such as carbon, rich in phlogiston, the metal appears because phlogiston has been returned to the calx. In the corrosion of a metal by an acid, phlogiston is lost, and the calx formed dissolves in the acid; the 'inflammable air' often evolved was by some identified with phlogiston itself.

To explain the fact that burning is strictly limited in closed vessels, the phlogistonists endowed the air with a limited capacity for absorbing phlogiston, so that when air is saturated with phlogiston—being phlogisticated—combustion cannot continue in it. Thus 'fixed air' (carbon dioxide) rediscovered by Black in 1752, and 'mephitic[3] air' (nitrogen)

[1] φλογιστός = burnt. [2] *calx* = lime; the term was extensive.
[3] *mephitis* = a noxious exhalation.

discovered by Rutherford in 1772, are both phlogisticated airs.

In 1775 Priestley discovered oxygen by heating mercuric oxide—then called mercury precipitate. In this air substances were found to burn more readily than in ordinary air, hence it was held to differ from ordinary air in being totally deprived of phlogiston, and Priestley named it 'dephlogisticated' air.

From the discovery of oxygen the theory of phlogiston began to wane, and, before another twenty years had passed, was supplanted by Lavoisier's oxygen theory of combustion, which survives almost unchanged to the present day.

Reactions seemingly contradictory to the phlogistic theory were known even before its birth, and many more acccumulated during its life. Such was the well established rule that metals, on becoming calces, increase in mass although they lose phlogiston. Explanations of a kind were offered to account for this—that phlogiston had negative 'weight'—but the discrepancy was by many held to be unimportant compared with the real advantage gained by having a theory which explained and unified many phenomena. One very serious difficulty arose when it was shown that mercury calx (mercuric oxide) could be transformed into metal in a closed vessel where no 'phlogiston' could possibly have reached it.

Lavoisier's earlier work had admirably prepared him to challenge the truth of the theory. In 1770 he had exposed the prevalent fallacy that water could be changed into earth; a not unnatural conclusion from repeated observations that earthy matter was left in vessels in which even the purest water had been heated.

Lavoisier's work.

Lavoisier achieved success in this, as in all his experiments, because, following Black, he had one arbiter—the balance.

Lavoisier placed a weighed quantity of rain water in a weighed closed vessel called a **pelican** (Fig. 101), and heated it on a furnace

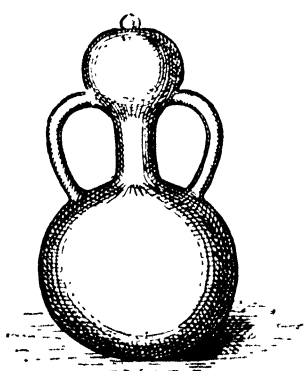


Fig. 101.

for a hundred days. No change in weight had occurred, although an earthy substance was visible in the pelican. He collected the earthy substance and weighed both it and the vessel, with the result that their united weights equalled the original weight of the pelican.

Oxygen theory of combustion.

In 1772 he repeated some experiments a fellow countryman named Jean Rey had performed, in 1630, **upon the calcination of tin.** Lavoisier introduced a weighed quantity of tin into a weighed retort, and sealed it up. The vessel was heated until the tin seemed to undergo no further change, whereupon he weighed the closed retort again. No change had occurred. On opening the vessel air was heard to rush in, and now, on reweighing, the retort was heavier. The calcined tin was separated and weighed, and was found to have increased in weight by an amount practically equal to the increase of weight due to the inrush of air. Hence Lavoisier proved that the calx of tin was formed by the absorption of air.

In 1775 Lavoisier showed that the gas recently discovered by Priestley is the portion of the air fixed by metals for the formation of their calces, and that 'fixed air' consists of a compound of the same gas and carbon. He was then enabled to prove that the formation of metals from their calces by heating them with charcoal was due to the abstraction from the calces of this gas by carbon to form 'fixed air.'

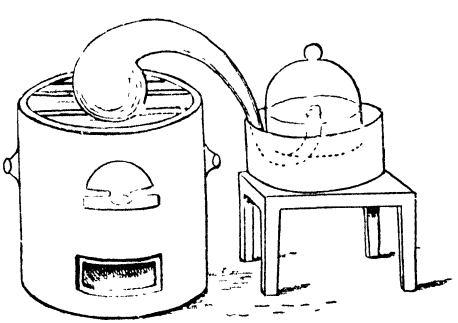


Fig. 102.

In 1782 Lavoisier published the results of one of his most important researches. He placed a weighed quantity of pure mercury in a small retort, the end of which communi-

cated with air confined in a bell jar over water (Fig. 102). For twelve days he heated the mercury to a temperature just short of boiling; as red specks were formed on the mercury, water gradually rose in the jar. The air which remained was irrespirable. The contraction of the air was estimated, and from its known density its weight was determined. The calcined mercury was then weighed, and the increase of weight was found equal to that estimated for the absorbed air. Not content with the completeness of the proof, Lavoisier confirmed it by collecting and heating the red calx: it yielded the same volume of air as the mercury had previously absorbed, and, when this gas was mixed with the residual irrespirable air of the first experiment, ordinary air resulted.

By such experiments Lavoisier established the true cause of combustion. Incidentally they led him to state the Law of Conservation of Mass.

The oxygen theory of acids.

Lavoisier showed that when Priestley's gas combines with some substances like sulphur, carbon, phosphorus, and nitrogen, bodies are produced, which, in water, give acid solutions, and react with the metallic calces to form salts. He therefore argued that all acids contain the gas, and perpetuated his theory by renaming it oxygen. He regarded these oxides as the acids themselves. According to this theory, hydrochloric acid—then called marine acid air or muriatic acid—contains oxygen and chlorine; the gas obtained by oxidation of muriatic[1] acid was called oxymuriatic acid because, it was argued, it must contain even more oxygen than muriatic acid.

To the phlogistonists chlorine was 'dephlogisticated' muriatic acid.

It was not until 1810, sixteen years after Lavoisier was guillotined, that Davy showed that neither muriatic nor oxymuriatic acid contains oxygen, and in doing so gave the death blow to the oxygen theory of acids.

Lavoisier was so convinced of the truth of his theory concerning acids, that he had repeatedly attempted to obtain an acid by burning 'inflammable air' (hydrogen) whose individuality was recognised by Cavendish in 1766.

[1] *muria* = salt.

The triumph.

In 1781 Cavendish showed that when a mixture of inflammable air (hydrogen) and dephlogisticated air (oxygen) is submitted to the electric discharge, pure water is formed, and water until then had been regarded as the type of element.

Cavendish, who like Priestley, never wavered in his wholehearted support of the phlogistic theory, interpreted the formation of water according to his faith.

But for Lavoisier the result brought victory. He could at last explain satisfactorily what happens when acids corrode metals with liberation of hydrogen. The metal liberates hydrogen from the water to form its oxide, which then combines with the dissolved acid to produce a salt. This hypothesis be supported by his experience that iron calx is formed and hydrogen is liberated when the heated metal is treated with steam.

ANSWERS TO PROBLEMS.

Problems I (page 29).

(4) 0·1184 gram. (5) 95·65 c.c.; 89·97 c.c.; 0·1163 gram. (6) 3·954 litres. (7) 11·124 litres. (8) 22 and 1·53. (9) 15·88. (10) nearly 7 c.c.

Problems II (page 40).

(3) 3 c.c. excess oxygen, 24 c.c. steam. (4) 100 : 208. (6) 9·8° C. (7) 2 : 3, V.D. = 24. (8) No.

Problems III (page 49).

(2) Nitrogen to Oxygen = 4 : 1. (3) 96·4 °/₀ silver. (4) 92·83 °/₀ and 90·65 °/₀ lead. (5) 32·7 grams. (6) 9·65 grams. (7) A. 79·93 °/₀ copper. B. 79·88 °/₀. (10) 92·6 °/₀ mercury. (11) A. 1 : 7·94. B. 1 : 8. C. 1 : 2 nearly. (12) A. 20·94 : 79·06 by vol. B. 22·96 : 77·04 by weight.

Problems IV (page 59).

(3) 11·12 litres; 22·25 litres. (4) At least 16 c.c. (5) 39·4 °/₀ sodium. (6) 47·26 °/₀ copper.

Problems V (page 71).

(1) 48 °/₀ zinc. (2) 15·4; 1 gram. (3) No. (4) (*a*) 62·57 tin. (*b*) 47·98 °/₀ zinc. (5) 32·74 grams. (6) 65 °/₀. (7) 4 grams. (8) 10·32 °/₀ oxygen. (9) 45·42 °/₀ cobalt. (10) 69·64. (11) Zinc 32·7, Tin 59·5, Aluminium 9, Cobalt 29·5, Sodium 23. (12) 75·28 °/₀ silver; 107·9. (13) 39·138. (14) 108 grams. (15) 9·34 caustic potash, 7·84 oxide. (16) 63·2 °/₀ metal.

Problems VI (page 83).

(4) ·00142 gram per c.c. (5) Chlorine 28·91 %, Potassium 31·93 %, Oxygen 39·15 %.

Problems VII (page 101).

(3) 695 c.c. (5) 23·3. (7) 1·9 litres; 10·256 grams. (8) 5·632 grams. (9) 7·426 grams per litre. (10) 34·3 % acid. (11) 56. (12) 101 Sulphuric, 62 Hydrochloric. (13) 9·017.

Problems VIII (page 109).

(2) 1 litre (nearly), 2·86 grams. (3) 4·31 grams. (4) 97·9. (5) 465 c.c.; 232 c.c. (6) Hydrogen 1, Sulphur 15·98, Oxygen 31·99.

Problems IX (page 114).

(1) Copper 78·1, Nickel 21·4, Iron 0·5. (2) 28·9 grams (too much hydrogen). (3) 1 : 3·4. (4) 12·1. (5) 100. (6) 65·24. (7) 31·8 copper; 32·64 zinc.

Problems X (page 123).

(1) Carbon 3·001. (2) 1·87 litres. (5) 42·857 % carbon. (7) Hydrogen 3·226 %, Carbon 19·355, Oxygen 77·420. (8) 13·93 kilos.

Problems XI (page 147).

(2) X_2SO_4; X_2SO_3; X_2S; XCl. (3) X_3QO_4; $Y_3(QO_4)_2$; ZQO_4.
YSO_4; YSO_3; YS; YCl_2. (6) About 253. (7) 120.
$Z_2(SO_4)_3$; $Z_2(SO_3)_3$; Z_2S_3; ZCl_3. (8) 12.

(9) 35·5 (H.C.F. of 71 and 106·5).

(10)

		ratio by mass	ratio by atoms
52·17	$\frac{52·17}{12} = 4·35$		$\frac{4·35}{2·17} = 2$
13·04	$\frac{13·04}{1} = 13·04 \rightarrow$		$\frac{13·04}{2·17} = 6$
34·8	$\frac{34·8}{16} = 2·17$		$\frac{2·17}{2·17} = 1$

Approx. M. Wt. = 46 ∴ formula C_2H_6O.

(11) CO_2H simplest; $C_2O_4H_2$ as it must have at least 2 atoms of hydrogen.

(12)

		ratio by mass	ratio by atoms
Carbon	·12627	1·09	12
Hydrogen	·01933	2 →	22
O (by difference)	·15440	1	11

(13) $C_2H_3O_3$.

(14) Atomic weights 238; 119; 59·5. (15) Gold 197·2; AuCl; $AuCl_3$; Specific heats ·027; ·054; ·108. Platinum 194·8; $PtCl_2$; $PtCl_4$.

(16) 75; $AsCl_3$. (17) SrCl; $SrCl_2$; $SrCl_3$; $SrCl_4$.
43·8; 87·6; 131·4; 175·2.

Problems XII (page 160).

(1) A. 7; B. 6; C. 1; D. 0. (2) 2. (3) 5.
(4) $X(OH)$; $X(OH)_2$; $X(OH)_3$; $X(OH)_4$; $X(OH)_5$; $X(OH)_6$
$XO(OH)$; $XO(OH)_2$; $XO(OH)_3$; $XO(OH)_4$
$XO_2(OH)$; $XO_2(OH)_2$

Problems XIII (page 180).

(1) 210 c.c. (2) 31 %. (4) ·56 ton. (5) 1,800,000 c. ft.
(6) $Cu(OH)_2$, $2CuCO_3$. (8) 3 c.c. (9) 62·3 $BaCO_3$.
(12) Strontia 63·8, Lime 5·33, Carbonic anhydride 30·83. (13) 86·6 %.
(14) 4·24 Carbonate; 1·2 Hydroxide.

Problems XIV (page 200).

(1) 71,300 calories. (2) 20,260 calories. (3) 90 c.c. hydrogen, 10 c.c. methane. (4) 28,760 calories.

Problems XV (page 212).

(2) 99·5. (3) 99·0.

Problems XVI (page 233).

(1) $\frac{2}{3} : \frac{2}{7} = 100 : 107$, hence +7 % error. (3) 100 molecules become $(100-x)+2x = 100+x$ molecules. $100 : 100+x = 36·4 : 46$. Ans. 23·6 %.
(7) 136½ litres nitrogen, 410 (nearly) litres oxygen. (8) 56·2.
(9) 137·4. (10) 29·8. (11) 1287 grams Witherite, 822 grams Nitric acid. (12) 1·23 litres.

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INORGANIC CHEMISTRY

BY

E. I. LEWIS, B.A. (CANTAB.), B.Sc. (LOND.)

ASSISTANT MASTER AT OUNDLE SCHOOL

PART II.

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PREFACE TO THE COMPLETE WORK.

THIS volume is the outcome of an attempt to provide a chemistry course for a class of boys of whom some had been promoted from a lower science set, and the rest had come over from the classical side. The course had therefore to be both a revision and an introduction.

In preparing the course an endeavour was made to follow the strictly logical method; hence no compound of unknown composition could be employed for chemical purposes except with the object of determining its composition. Acids, for instance, could not be used to supply hydrogen, nor potassium chlorate to supply oxygen. This imposed a somewhat unusual order and the introduction of some discussions not generally included in an elementary course. It demanded also the postponement of the convenient methods of preparing gases. Although at first sight these restrictions may appear fatal to efficiency, I found them in the event altogether advantageous. As soon as the student has obtained a little of a given substance and has recognised it by its properties, it is both quicker and less wasteful to supply him with sufficient for his experiments. Take, for instance, sulphur dioxide. As soon as he has obtained some of the gas by burning sulphur, the student can use a supply from a syphon for further experiments, and he may prepare it for himself by the usual method when he has sufficient knowledge to suggest the explanation

of the reaction. It is then not merely the 'Preparation of Sulphurous Oxide' but the 'Reduction of Sulphuric Acid.'

Nearly every lesson begins with the study of a simple reaction. This is followed by a discussion involving the suggestion of further experiments, as far as possible such as are suitable for the laboratory. Each lesson was carefully prepared beforehand, but the boys, in class, by their own reasoning, questioning, and suggestion, led me to alter radically the plans of many chapters. The changes were justified by the experience that other forms followed very much the same line of reasoning.

The notes of these discussions taken by the classes were not always sufficient for evening revision; for the more successful the lessons, the fewer were the notes taken, and, even after a few hours, the clearest impressions were likely to become obscured by subsequent work in other subjects. For this and other reasons it seemed desirable to incorporate the subject matter of the lessons in a logical order.

The encouragement I have received during the preparation of the book has led me to hope that it will supply a want felt by other teachers.

The book is meant to be used for the revision of lessons, chapter by chapter. A lasting impression of the important points of each lesson is most easily insured by setting a few problems each evening. These should be graduated. At the end of most chapters in Part I. some exercises and problems have been collected; these are supplementary to the text, and are more particularly suitable for a second revision; many of them are of scholarship standard.

The Atomic Theory has been offered later than usual, and is then studied thoroughly. There is perhaps no more insidious enemy to sound thinking than an undigested formula, and with the formulae the nomenclature based upon them must be postponed also. The experience of many teachers emphasises the advantage of this order of treatment.

I have endeavoured to avoid everything savouring of dogmatism. It is not always easy to recognise, and, but for Mr Neville's interest, many more instances would have survived.

In Part II. I have endeavoured to apply to senior forms a method which has promised well with junior boys. In this part there is a greater abundance of information; this is introduced not for committing to memory, but as material to support the arguments. The Arsenic family is not discussed systematically as it provides an excellent opportunity for the exercise of discretion in the use of reference books: it follows as an exercise on Chapter XXIII. As all the salts of importance are mentioned in the body of the book, there seems no advantage in devoting a special part to 'Metallic' Chemistry, especially as this branch can be learned most intelligently with the aid of reference books during the study of the Periodic Classification. Chapter XXVIII. is devoted mainly to the 'non-metallic' compounds of the elements concerned.

It will be noticed that greater prominence than usual has been given to 'out-of-doors' chemistry. More than any other, this part of chemistry secures the sympathetic interest of beginners.

In order to make the book more complete an Introductory Chapter has been added. This is mainly for reference. No experiments have been given in proof of the Gas Laws, or the other physical laws of almost equal importance. To treat these subjects adequately is possible in a physical text-book only; they are discussed briefly, but, I hope, sufficiently.

The examinations of the Oxford and Cambridge Joint Board (L. C., S. C., and H. C.), the University Local Examinations (senior and junior), and the London Matriculation Examination are fully covered. The Army Examination syllabus is sufficiently provided for by Part I.

I have to thank Messrs Longmans for the loan of Figures 44

and 105 from Mr Newth's text-book; the Cambridge University Press for Figures 101, 102, 103, and Lothar Meyer's Curve from Miss Freund's book, from which I have also derived the data for many of the problems; and Mr E. T. Bucknell and the Editors of the *School World* for Figure 52, and for permission to include the methods for obtaining the equivalent masses of sodium and of aluminium, &c. (pages 63 and 66).

Throughout the preparation of the book I have received unstinted help from my colleagues Mr H. O. Hale and Mr H. M. King; and Mr W. E. Cross of the Whitgift School has helped me with the proofs. I am greatly indebted to Dr H. O. Jones for much invaluable criticism in Part I., and to Mr F. H. Neville for both criticism and advice throughout the book. I have endeavoured to take full advantage of these. For the first part of Chapter XXXI. I have to thank Dr F. F. Blackman. I must also thank the University Press for the generous manner in which they have met my wishes.

E. I. L.

OUNDLE,
September, 1907.

The issue of the second edition of this book has enabled me to correct many oversights due to hasty reading of the proofs of the first edition. Advantage has been taken to bring it up to date (pp. 234 and 236). I should like to add that the diagrams are in most cases given to illustrate the more difficult experiments, and some few commercial processes. A large number of important experiments need no description. Many of these are only referred to in the text. Thus, although Chapter XIII. is entirely practical, the estimations alone are specially described.

E. I. L.

July, 1908.

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CHAPTER XX.

OXYGEN AND OZONE. THE OXIDES. BALANCED ACTIONS.

OXYGEN was discovered by Scheele in 1774, and independently by Priestley in 1775. The latter had priority in publishing. Scheele, who discovered the gas by heating nitre, called it **fire air**; Priestley discovered it by heating mercuric oxide. The properties of oxygen have been studied in Part I.; we have only to add the critical temperature, $-118°$ C., the critical pressure, 50 atmospheres, and the boiling point under atmospheric pressure, $-183°$ C.

Morley's work.

The exact specific gravity of oxygen, as determined by several experimenters, is 15·88 (H = 1). This suggests for the atomic weight of oxygen 15·88, a number departing considerably from the value 15·96 found by Dumas and Stas by the gravimetric synthesis of water. Morley (1895) obtained results consistent with the specific gravity. Pure dry hydrogen, obtained by the electrolysis of water, was absorbed by palladium metal in a weighed tube; pure dry oxygen, obtained by electrolysis or by heating pure potassium chlorate, was collected in a weighed globe. These gases were allowed to enter the apparatus of Fig. 103 by the two upper tubes *c*, *d*, and were made to combine as they met in the middle chamber, at *a*, by the heat of an electric arc. The water formed condensed, and, when sufficient had collected, the taps were closed and the hydrogen tube and oxygen globe were reweighed. The small volume of uncombined oxygen and

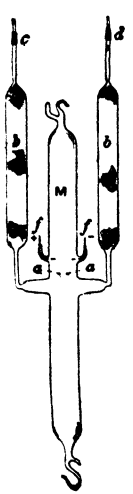


Fig. 103.

hydrogen still remaining in the apparatus was pumped out and analysed. In order to prevent loss of water vapour, the parts *b*, *b* were filled with phosphoric oxide. He reweighed the apparatus and, by difference, found the mass of water produced. The ratio of the weights of hydrogen and oxygen was 1 to 7·94. The atomic weight of oxygen, as calculated from this result, is 15·88 (H = 1) or, if O = 16, then H = 1·008.

Oxygen is prepared commercially by the decomposition of barium peroxide (Brin's process). Baryta is heated to dull redness in air deprived of moisture and carbon dioxide: the baryta combines with oxygen to form peroxide, $2BaO + O_2 = 2BaO_2$. The reaction is reversible, for at a bright red heat the peroxide is dissociated,

Preparation of oxygen.

$$2BaO_2 = 2BaO + O_2.$$

The decomposition also takes place at a red heat when the pressure is diminished (see Physical Chemistry at the end of this chapter). Advantage is now taken of this circumstance in the technical preparation, for it is found cheaper to vary the pressure by means of pumps than to vary the temperature.

The operation is carried out in specially designed retorts; the air, carefully purified and dried by passing over lime, is pumped in at a pressure of 15 lbs. per square inch, and is absorbed by the baryta kept at 700° C. The retorts are then exhausted, the nitrogen which comes first is allowed to escape into the air, and the oxygen which follows is passed on and compressed into iron cylinders.

Oxygen may also be obtained from liquid air; the nitrogen (B.P. – 195° C.) evaporates far more rapidly than the oxygen. The blue liquid left after liquid air has stood for some time is nearly pure oxygen.

The oxides are classified into two main groups, **Acidic** and **Basic**. These may be considered as the anhydrides of corresponding hydroxides (Chapter XIII.). In addition to the oxides which fall into these two series, some are known, which, like carbon monoxide and nitric oxide, are apparently related to no acid or base. There are also a few oxides which, when dissolved, can give rise to a mixture of **two** acids, such is nitrogen peroxide (Part I., Chapter XVIII.).

Oxides.

Certain basic oxides can give rise to two series of salts, such is triferric tetroxide, Fe_3O_4, which on solution in acids

yields a mixture of ferrous and ferric salts, as if it were a compound of the two oxides (FeO, Fe_2O_3). For that reason it is also called ferroso-ferric oxide,

$$Fe_3O_4 + 8HCl = FeCl_2 + 2FeCl_3 + 4H_2O.$$

Minium, Pb_3O_4, reacts with dilute nitric acid to form a solution of lead nitrate, $Pb(NO_3)_2$, and solid lead peroxide. Hence it would seem that minium is a compound of both oxides, possibly 2PbO, PbO_2,

$$Pb_3O_4 + 4HNO_3 = PbO_2 + 2Pb(NO_3)_2 + 2H_2O.$$

When dissolved in acids lead peroxide, like manganese peroxide, yields salts corresponding to a lower oxide, and, either oxygen, or its equivalent, is evolved.

$$2MnO_2 + 2H_2SO_4 = O_2 + 2MnSO_4 + 2H_2O,$$
$$MnO_2 + 4HCl = Cl_2 + MnCl_2 + 2H_2O.$$

For oxides of this type the term 'peroxide' is often specially retained; to some of them corresponding salts are known which, however, are unstable under the conditions of the experiments given above. Thus lead tetrachloride ($PbCl_4$), a liquid obtained by passing chlorine over lead, is unstable in solution, being hydrolised to hydrochloric acid and the peroxide.

Elements which form basic oxides are called **metals**, the rest are called **non-metals**. As we mentioned in Chapter XIV., the distinction is vague, and there are elements like arsenic and antimony which have the appearance, but not the properties, of metals. Even tin, which is always regarded as a metal, resembles antimony in some of its compounds.

In recognition of their properties, these elements are sometimes placed in a third group, the **metalloids**, with the result that there are three ill-defined groups instead of two. There are certain elements, always included amongst the metals, which have several oxides, of which the lower are uncompromisingly basic, and the higher are as uncompromisingly acidic. We shall study the two most important of these elements in Chapter XXVIII. Argon and the inert gases form no oxides[1].

Ozone. (See Chapter I.)

Ozone, the odorous modification of oxygen, is, at ordinary temperatures, a gas. In the liquid condition it maintains its individuality; liquid ozone is blue-black in colour, and boils

[1] It should be noticed that the non-metals are usually distinguished from the metals by positive properties. The non-metals also include hydrogen, which is more electro-positive than many metals, as well as the inert gases which apparently have no active chemical properties.

at − 119° C. Its special properties are attributed partly to the composition of its molecule, which is said to consist of three atoms, O_3. As the pure gas is very unstable, the ordinary method of finding its specific density cannot be used. Its density was established by two independent experiments; the one, to compare the rates of diffusion of ozone and chlorine (Soret); the other, to prove that ozone occupies just two-thirds the volume of the oxygen from which it is formed, $3O_2 = 2O_3$ (Brodie and Soret).

The latter experiment may be repeated with the apparatus of Fig. 104 (see also page 37). Turpentine, a liquid which has been shown to dissolve ozone without decomposing it, is contained in a thin glass vessel. The latter is suspended in the gas space by means of glass pegs in such a manner that it may be broken by turning slightly the inner tube. After the oxygen is subjected to the silent electric discharge, the contraction in volume is observed; the turpentine is liberated and a second contraction takes place which—when allowance is made for the vapour pressure of the turpentine—is found to be double that of the first. Hence two volumes (second contraction) of ozone were formed from 3 volumes (total contraction) of oxygen. The density of ozone, 24 (H = 1), its molecular weight, 48, and its formula, O_3, follow.

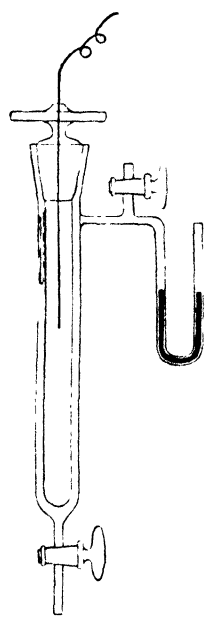


Fig. 104.

One indication of the presence of ozone is its smell; its active oxidising properties afford many others of a chemical nature. This activity is attributed to the ease with which the extra atom of oxygen is liberated.

Ozone is decomposed by heating; by contact with finely divided platinum, the peroxides of lead and manganese, or copper oxide, it is decomposed catalytically at ordinary temperatures. The decomposition of ozone is accompanied by liberation of energy.

$$2O_3 = 3O_2 + 61{,}400 \text{ calories.}$$

Its power as an oxidiser is shown by the fact that almost every element is oxidised directly by it; hydrogen, fluorine, nitrogen, gold, and platinum are exceptions. Silver, which is unattacked by oxygen, is rapidly covered with the black oxide in the presence of ozone. Mercury, when even small quantities of ozone are present, at once loses its mobility and leaves a trail on glass: the nature of this action, which serves as a test for ozone, is not properly understood. Ozone is more effective when damp. This can be illustrated by placing before issuing ozone pieces of dry and of damp paper on which lead sulphide is deposited.

('Lead sulphide paper' is made by dipping a filter paper in lead nitrate solution and exposing it to hydrogen sulphide.)

The damp sulphide is very rapidly whitened owing to the formation of the sulphate. The reaction serves as another indication of ozone. Organic substances are easily attacked by ozone, and for that reason rubber tubing must never be used as a part of the delivery tube for ozone, else the rubber is spoilt and oxygen only is collected.

Ozone is formed as a side product during the slow combustion of some substances in air, and for that reason probably is found in air in slight quantity. Its activity accounts for the fact that ozone is not found in the air of towns. Ozonised air (1 per cent.) is used commercially as an antiseptic and for oxidising purposes, some useful and some deceptive.

There are many substances which indicate the presence of ozone, but the changes which they suffer are usually brought about also by other powerful oxidising substances such as chlorine and the oxides of nitrogen.

One of the best test reagents for ozone is a substance called para-diamido-diphenylmethane which, with ozone, gives a violet colour, whilst chlorine colours it blue, and the oxides of nitrogen turn it yellow.

Chemical Equilibrium.

The formation and dissociation of barium peroxide recall the analogous reactions with calcium carbonate. Both are examples of reversible reactions.

$$2BaO_2 \rightleftarrows 2BaO + O_2,$$
$$CaCO_3 \rightleftarrows CaO + CO_2.$$

In both cases a solid is 'dissociated' into another solid and a gas, and the products recombine when the conditions are reversed.

Dissociation at constant volume.

The latter change has been studied very closely, and it has been shown that if the gaseous product is not permitted to escape, then at every temperature there exists a condition of equilibrium, such that the gas exerts a definite pressure. When the temperature is raised more carbonate dissociates, and the carbon dioxide exerts a greater pressure; when the temperature is lowered, carbon dioxide and calcium oxide associate to reform carbonate, so that the carbon dioxide exerts a lower pressure. The equilibrium is the result of balanced actions.

What is true for calcium carbonate is equally true for some other compounds, many of which (for instance, water) do not begin to decompose until high temperatures are reached. On the other hand, not all reactions are reversible; for instance, on heating potassium chlorate, the chloride and oxygen are formed, but these products do not recombine on cooling.

Dissociation at constant temperature.

When, at any definite temperature, a state of equilibrium has been reached, and, without any further alteration of the temperature, the space occupied by the carbon dioxide is diminished, carbon dioxide and lime associate until the original pressure is re-established; but if the space is enlarged, more carbonate dissociates until the original pressure is re-established. The former effect may also be produced by pumping into the space extra carbon dioxide; association takes place and will continue to take place until either the whole of the calcium oxide is converted into carbonate or the supply of carbon dioxide fails. In either case the final pressure of the carbon dioxide is the same, namely, that proper to the particular temperature. On the other hand, if carbon dioxide is removed, carbonate will continue to decompose, as long as any remains, or until the carbon dioxide again exerts the original pressure. Hence the object of maintaining a good draught in lime burning, and of the alternate compression and exhaustion of the air in the baryta retorts.

It will be noticed that this law is precisely similar to that of Dalton for the vapour pressure of a liquid. In all cases of balanced reactions, raising the temperature promotes the **endo**thermic reaction, lowering the temperature promotes the **exo**thermic reaction; increasing the pressure at constant temperature causes gas to combine or to condense, decreasing the pressure causes gas to be liberated. In every case the effect of the reaction is opposite to that of the change of condition.

This tendency is expressed in **Le Chatelier's Theorem**: 'If a system in equilibrium is subjected to a constraint by which the equilibrium is shifted, a reaction takes place which opposes the constraint, that is, one by which its effect is partially annulled.'

[*Questions.* Discuss the dissociation of nitrogen peroxide in the light of this law. What effects would you expect changes of pressure to have upon nitrogen peroxide at 150° C., and upon a mixture of ammonia and hydrogen chloride gases.]

Other reversible reactions.

The first reversible reaction to be discussed in this book was the oxidation of iron by steam, and the reduction of iron oxide, so formed, by hydrogen.

$$3Fe + 4H_2O \rightleftarrows Fe_3O_4 + 4H_2$$
(*solid*) (*gas*) (*solid*) (*gas*)

In this case it is found that if steam and iron are heated together to any temperature in a sealed tube, a state of equilibrium is reached in which all four substances are present at once. The same state of equilibrium is reached if hydrogen and iron oxide are the original system. The relative (not necessarily actual) quantities of hydrogen and steam present at any particular temperature are the same whichever was the original system, provided the substances were in molecular proportions. But if an excess of either gas is added, then the action in which that gas reacts is favoured. The same reaction is likewise favoured by removing the other gas as fast as it is formed. Thus, in order to reduce iron oxide completely, a current of hydrogen is maintained through the tube to sweep out the steam produced, and, reversely, to oxidise iron completely, an excess of steam is passed over the metal to carry away the liberated hydrogen.

This is one of the best examples of **the Law of Mass action**, formulated by Berthollet in 1799. It states that the result of a chemical action depends not only upon the *nature* of the reagents but also upon their relative active masses. The relative active mass is the ratio of the amounts of the substances contained in unit volume, in other words, their relative concentration.

The same law was mathematically deduced in 1864 by Guldberg and Waage, and is often named after them. 'The rate of chemical action is proportional to the active mass of each of the reacting substances.'

[*Question.* Discuss the reaction $N_2 + 3H_2 \rightleftarrows 2NH_3$, in the light of this law.]

Other examples of mass action have been described at length under the hydrolysis of normal salts to form basic salts, and the transformation of the latter into the normal salts (Chapter XV.), $BiCl_3 + H_2O \rightleftarrows BiOCl + 2HCl$. The liberation of more volatile acids when their salts react with less volatile

acids is the result of mass action. The volatile acid under the conditions of the experiment escapes, and therefore has no *active* mass, or a very small one, in the system.

$$NaCl + H_2SO_4 \longrightarrow NaHSO_4 + HCl.$$

Similarly, when copper sulphide is precipitated from copper sulphate by means of hydrogen sulphide

$$(CuSO_4 + H_2S \longrightarrow CuS + H_2SO_4),$$

the copper sulphide is precipitated as soon as it is formed, and thus is removed from the sphere of action.

The student is advised to study as many cases of balanced action as he can. For instance, the production of anhydrous chlorides from hydrated chlorides, by heating the latter in a current of hydrogen chloride gas; under this condition the oxide or basic chloride is not formed (see page 153). Another case of interest is that represented by the equation,

$$Na_2CO_3 + BaSO_4 \rightleftarrows BaCO_3 + Na_2SO_4.$$

(See Walker's *Physical Chemistry*, Chapter XXII., and Fenton's *Outlines of Chemistry*, Chapters X.—XII.)

CHAPTER XXI.

THE OXYGEN COMPOUNDS OF CHLORINE.

POTASSIUM chlorate is prepared by saturating with chlorine a hot concentrated solution of caustic potash (Chapter V.),

$$6KOH + 3Cl_2 = 5KCl + KClO_3 + 3H_2O.$$

By the same method the chlorates of sodium, barium, and calcium may be obtained. The sodium compound is very soluble in water, and is frequently used for the preparation of other chlorates.

Chloric acid.

The fact that the chlorates of many metals are known, suggests that they are not merely oxidised chlorides, but rather the salts of an acid. Such is indeed the case, for **chloric** acid, $HClO_3$,—a true oxy-muriatic acid—is known. When one attempts to obtain this acid by the method commonly employed for acids, that is, by heating a chlorate with concentrated sulphuric acid, a yellow explosive gas is evolved which contains only chlorine and oxygen. Chloric acid is unstable, therefore its preparation must be accomplished tactfully: advantage is taken of the insolubility of the sulphate of barium. A weighed mass of pure barium chlorate is dissolved in water, and to the solution is added the equivalent quantity of dilute sulphuric acid,

$$Ba(ClO_3)_2 + H_2SO_4 = BaSO_4 + 2HClO_3.$$

A dilute solution of chloric acid is obtained; it may be concentrated at a low temperature by distillation in a vacuous flask. But even with this precaution it cannot be obtained free from water, for when the concentration has produced a 40 per cent. solution, the acid becomes unstable, and explodes with the formation of chlorine and oxygen. In consequence

of its instability and of the nature of its decomposition products, chloric acid is a very powerful oxidising agent. It is endothermic.

Care must be taken to distinguish hydrogen chloride and hydrogen chlorate. Both are strong acids, but the former is a stable hydracid and the latter an unstable oxyacid. Chloric acid ($HClO_3$) has for its salts the chlorates ($KClO_3$) but hydrochloric acid (HCl) has for its salts the chlorides (KCl).

Chlorine peroxide.

We have seen that when potassium chlorate acts on sulphuric acid, a greenish-yellow gas is evolved. The salt should be thrown, a little at a time, into concentrated acid contained in a retort, and the mixture afterwards gently warmed.

A very small quantity only of this gas should be prepared in an open hard glass tube.

When heated (the electric spark is employed) the gas decomposes explosively, yielding its own volume of oxygen and half its volume of chlorine. Its density is 34·4 (H = 1); hence its formula is ClO_2.

$$2ClO_2 = 2O_2 + Cl_2.$$

Chlorine peroxide has a chlorine-like smell. When cooled, it condenses to a vivid red liquid, which boils at 9° C. At still lower temperatures the liquid solidifies as an orange-yellow crystalline body.

Its formula shows that it is not the anhydride of chloric acid. but it dissolves in cold water to form an acid solution. When this solution is neutralised by caustic potash, and the product is evaporated at about 50° C., potassium chlorate crystals are deposited, and, on further concentration, crystals of a new salt are obtained. This salt has been shown to correspond to the formula $KClO_2$; it is therefore potassium chlorite; the corresponding acid (chlorous acid) is known free only in very dilute solutions. The chlorite and chlorous acid are, of themselves, of little importance: they are introduced here chiefly to illustrate the nomenclature of acids.

It will be observed that in combining with water to form two acids, chlorine peroxide and nitrogen peroxide behave analogously.

$$2NO_2 + HOH = HNO_2 + HNO_3$$
$$2ClO_2 + HOH = HClO_2 + HClO_3.$$

Chloric and nitric acids have analogous formulae and, when heated, both yield oxides representing the same lower stage of oxidation. But whereas oxygen also is liberated by the decomposition of nitric acid, when chloric acid—set free by concentrated sulphuric acid—decomposes, provided the experiment is carried out with great circumspection, but little oxygen escapes; and yet the oxide evolved is not chloric anhydride, in fact the last mentioned oxide (Cl_2O_5 from $2HClO_3 - H_2O$) is unknown. A study of the decomposition products of potassium chlorate will lead to the solution of the problem.

The decomposition of potassium chlorate.

It will be remembered that, when heated, the chlorate melts at 359° C., and at 372° C. begins to decompose with the liberation of oxygen. With the temporary cessation of gas evolution, the residue becomes almost solid again. If the reaction is stopped at this point, and the residue is dissolved in water, three different salts may be obtained from the solution, the chloride and chlorate, and a new salt of distinct crystalline form. This new salt is even less soluble in water than the chlorate, and may be separated from it by fractional crystallisation. The separation may be effected by an easier method: the new salt is unaffected by hot concentrated hydrochloric acid, whilst the chlorate is decomposed by it with the formation of chloride and the evolution of chlorine and chlorine peroxide.

The mixture of chlorine and chlorine peroxide evolved by the action of hydrochloric acid on potassium chlorate was once considered as a definite compound, and was named 'Euchlorine.' The relative quantities of the two gases evolved depend upon the temperature of the reaction and the concentration of the acid, hence only hypothetical cases are represented by such equations as $2KClO_3 + 4HCl = 2KCl + 2H_2O + Cl_2 + 2ClO_2$.

The chlorate having been decomposed by this process, the new substance is very easily separated from the more soluble chloride. When heated, it is found to lose 46 per cent. of its weight as oxygen, leaving a residue of pure chloride. Hence its formula is $KClO_4$; it is called **potassium perchlorate.**

The conversion of chlorate into perchlorate by heat may perhaps be represented thus: $4KClO_3 = 3KClO_4 + KCl$. At the same time oxygen is always evolved in proportions which vary with the conditions.

Potassium perchlorate is a salt of **perchloric acid** ($HClO_4$). This acid is at ordinary temperatures a solid, fairly stable towards heat, which can be vapourised without decomposition; hence it may be set free by distilling, under reduced pressure, a mixture of the potassium salt and concentrated sulphuric acid. Although in ordinary circumstances perchloric acid is quite stable, when brought into contact with readily oxidised substances, such as organic matter, it explodes violently: it is in fact a most powerful oxidiser. The anhydride of perchloric acid, Cl_2O_7, has been isolated: it is a very explosive and unstable liquid

When potassium chlorate is heated with concentrated sulphuric acid, perchloric acid is formed; that is why oxygen is not evolved in the reaction

$$3HClO_3 \longrightarrow HClO_4 + 2ClO_2 + H_2O.$$

Action of chlorine on cold dilute potash.

When chlorine gas is passed into a cold and moderately dilute solution of caustic potash, it dissolves to form a solution which, for a hundred years past, on account of its marked oxidising properties, has been largely used for bleaching. The solution had been in use for fifty years before its composition was understood. The bleaching action has been shown to be due to an unstable potassium compound. This is a salt of the formula KOCl, it therefore represents a lower stage of oxidation than a *chlorite.* As the prefix **hypo-** is used to distinguish acids less oxidised than **-ous** acids, the corresponding acid is known as **hypochlorous acid** and its salts are called hypochlorites. When a solution of either the acid or one of its salts is heated, oxidation and reduction take place, the chlorate and chloride being formed simultaneously.

$$3KClO = KClO_3 + 2KCl.$$

Hypochlorous acid decomposes in the presence of a strong acid, hence a special artifice is employed for its preparation. Chlorine is made to act upon an oxide *which does not form a hypochlorite*; such is mercuric oxide.

$$HgO + 2Cl_2 + HOH = \underset{\text{(mercuric chloride)}}{HgCl_2} + 2HOCl$$

The mercuric oxide—which must be prepared so that it is neither too coarsely nor too finely grained—is suspended in water, through which is passed chlorine. A dilute solution of the acid is obtained which may be somewhat concentrated by distillation. The conditions are met by passing chlorine into water in which chalk is suspended.

$$CaCO_3 + H_2O + 2Cl_2 = CaCl_2 + 2HClO + CO_2.$$

The composition of the acid, and therefore also those of its salts, follow from the formula of its anhydride, **chlorine monoxide**, Cl_2O. This compound is a brownish-yellow gas of disagreeable odour. Its density is 43·4 (H = 1). It condenses to a blood-red liquid. It is strongly endothermic, and is very unstable. It is very soluble; one volume of water at 0° C. dissolves 200 volumes of the gas. $Cl_2O + H_2O = 2HClO$. The solution is golden-yellow.

Chlorine monoxide is prepared by a modification of the method used for preparing the acid. The modification consists only in using perfectly dry materials; in these circumstances, however, the basic mercuric chloride is formed.

$$2HgO + 2Cl_2 = HgCl_2, HgO + Cl_2O.$$

We must notice here that no energy is supplied to the system. The formation, in these circumstances, of an endothermic substance may be explained by the fact that the reaction, as a whole, is **exo**thermic. Basic mercuric chloride is strongly exothermic, and some of the energy, which would have been evolved as heat had this substance alone been formed, is retained by the formation of the endothermic chlorine monoxide.

It will be seen that, starting with the system caustic potash and chlorine, we may pass, in steps, to the system potassium chloride and oxygen, thus:

A. $6Cl_2 + 12KOH =$
B. $6KCl + 6H_2O + 6KClO =$
C. $10KCl + 6H_2O + 2KClO_3 =$
D. $11KCl + 6H_2O + KClO_4 + O_2 =$
E. $12KCl + 6H_2O + 3O_2$

Each step is taken with a loss to the system of energy as heat, and each step leads to a more stable system. Any one or all of the steps may be omitted. For instance, if chlorine is passed into a solution of caustic potash, to which a little cobalt nitrate is added ($Co(NO_3)_2 \rightarrow Co(OH)_2$), oxygen is liberated, the oxide of cobalt acting as catalyser. The series of reactions is a good instance of a widely applicable law—the **'Law of Successive Reactions'** (Ostwald), that 'in all reactions the most stable state is not straightway reached, but *the next less* stable, or that state which is the

least stable of the possible states.' We may say that there is a *tendency* to justify the law, for when potassium chlorate is heated, only a part is transformed into the perchlorate, and most chlorates, when heated, are at once and completely converted into chlorides. $2AgClO_3 = 2AgCl + 3O_2$.

The basic chlorides must not be confused with the hypochlorites. The former are in the *same* stage of oxidation as the chlorides; they are the basic salts of hydrochloric acid (Chapter XV.), and are usually formed by the hydrolysis of normal chlorides. The hypochlorites are the salts of hypochlorous acid. Thus BiOCl represents the basic chloride of bismuth; in its molecules 2 atoms of chlorine have been replaced by 1 atom of oxygen. If a bismuth hypochlorite could exist, it would have the formula $Bi(OCl)_3$ in which the bismuth atom displaces the hydrogen of 3 molecules of hypochlorous acid.

Bleaching powder.

When chlorine is passed into a cold paste of slaked lime and water, calcium hypochlorite is formed.

$$2Ca(OH)_2 + 2Cl_2 = CaCl_2 + Ca(ClO)_2 + 2H_2O.$$

But chlorine is also absorbed by dry slaked lime with the production of a mass called 'bleaching powder' or 'chloride of lime' (not chloride of calcium). One would naturally expect this substance to be a mixture of the chloride and the hypochlorite of calcium, and some chemists maintain that view. But the substance, when pure, has remarkable and peculiar properties which are not satisfactorily explained by that assumption. Thus calcium chloride is very soluble in alcohol, yet when bleaching powder is very carefully prepared, little or no chloride can be extracted from it by agitation with alcohol; nor is bleaching powder very hygroscopic. The *whole* of the chlorine can be expelled by the weak carbonic anhydride. The percentage of such 'available chlorine' has in some samples reached 48·74. No other metal forms a compound with similar properties. For these reasons, amongst others, most chemists have accepted the formula proposed by Odling, namely $Ca(OCl)Cl$, which places bleaching powder midway between the chloride and hypochlorite.

When dissolved in water, it yields the hypochlorite

$$2Ca(OCl)Cl = CaCl_2 + Ca(OCl)_2.$$

When the powder is used as a bleaching agent, the chlorine is expelled by the addition of dilute hydrochloric acid.

Bleaching powder is often used in the laboratory for oxidising purposes instead of chlorine. Metallic peroxides

are rapidly and conveniently prepared from soluble salts by means of it. The ordinary bleaching powder invariably contains slaked lime, which first precipitates the hydroxide of the metal, and this is immediately oxidised by the hypochlorite solution. Any impurity, such as hydroxide or carbonate of calcium, is removed by washing the precipitate with dilute nitric acid. When lead nitrate is used, the reactions are

(1) $Pb(NO_3)_2 + Ca(OH)_2 = Pb(OH)_2 + Ca(NO_3)_2$.

(2) $2Pb(OH)_2 + Ca(OCl)_2 = 2PbO_2 + CaCl_2 + 2H_2O$.

Bleaching powder may also be employed to furnish oxygen. When the paste or solution, contained in a flask, is heated alone, little or no oxygen is evolved, but when a little cobalt nitrate (yielding cobalt oxide) is added and the mixture heated again, oxygen is soon evolved.

Either $2Ca(OCl)Cl = 2CaCl_2 + O_2$

or $Ca(ClO)_2 = CaCl_2 + O_2$.

When the paste is used it is covered with a layer of kerosene to restrain frothing.

Electrolysis of sodium chloride.

In consequence of the reactions which take place between chlorine and the caustic alkalis, the electrolytic production of sodium hydroxide from brine (Chapter III.) must be carried out so that the chlorine evolved does not come in contact with the solution of caustic soda. This is accomplished by the employment of a divided cell. There are several processes in use, the Castner-Kellner is one of the simplest. The cell (Fig. 105) consists of a box almost divided into three compartments by means of two vertical partitions which do not quite reach the floor. A very shallow layer of mercury seals the compartments. Water floats on the mercury in the middle chamber, and into the water the prongs of an iron kathode project. The anode consists of two carbon rods wholly immersed in a saturated solution of brine, which floats on the mercury in the two flanking compartments. When the electric current passes, chlorine is liberated in both anode chambers and is led away through tubes near the roof. The mercury forms a sort of intermediate electrode, positive to the kathode and negative

to the anode. Sodium from the brine dissolves in the mercury to form an amalgam (an alloy of mercury is called an amalgam). The whole cell is kept in gentle motion by the

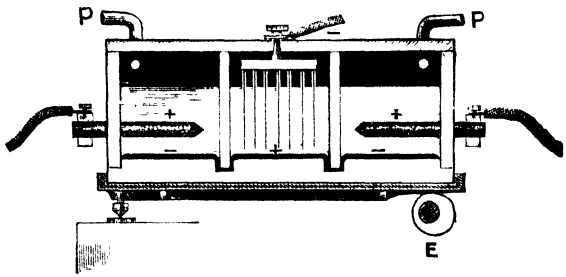


Fig. 105.

revolution of an eccentric; consequently the sodium amalgam is brought in contact with the water of the kathode chamber, the sodium, losing its charge, attacks water to form caustic soda, and hydrogen is evolved at the kathode. The chlorine liberated in the anode chambers is used for the production of either bleaching powder or calcium chlorate.

Potassium chlorate is usually made by the double decomposition of potassium chloride and calcium chlorate in solution; the comparatively insoluble potassium chlorate crystallises from the solution. This method obviates waste of the valuable potassium salt.

$$Ca(ClO_3)_2 + 2KCl = 2KClO_3 + CaCl_2.$$

Both chlorates and hypochlorites may be prepared by the electrolysis of chloride solution. Instead of separating the chlorine from the hydroxide formed, every effort is made, by agitation, to insure their mixing. With a low current density and a low temperature, a solution containing chloride and hypochlorite is formed, which is straightway used for bleaching purposes. Under different conditions the chlorate is formed.

By the electrolysis of a solution of chlorate, perchlorate may be produced.

Thermal-chemistry.

Throughout the preceding chapters we have insisted upon the importance of accounting for the total mass of the reacting bodies before and after the reaction. To the chemist

the balance is the most important apparatus. But the balance ignores the change of energy which occurs whenever substances react, and yet, from the manufacturer's point of view at least, this change is hardly of subordinate importance. We state that water contains oxygen and hydrogen in a certain definite mass proportion, but the oxygen and hydrogen are associated with much less energy when combined together than when free, hence we need not be surprised perhaps at the great difference in the properties of the elements before and after combination. Even the same element uncombined, when associated with different proportions of energy, exhibits totally different properties. We cannot know the absolute amount of energy associated with any one element, we can only measure the energy which is lost or gained when it changes to another form, or, the amount of energy lost or gained when elements enter into combination. The change of energy which takes place when the molecular weight in grams ('the gram-molecule') of a compound is formed from its elements, expressed in thermal units, is called the Heat of Formation of the compound. That of gaseous water is 68,400 calories—lost (58,000 + latent heat), that of carbon dioxide is 96,960—lost. A short consideration will convince the reader that, as a general rule, exothermic compounds are stable, and that endothermic compounds are inclined to be unstable. No hard and fast rule can be given, however, since nitric oxide, which is endothermic (− 21,600 calories), is perfectly stable under ordinary conditions, whilst solid nitrogen pentoxide, an exothermic compound (+ 13,100 calories), explodes spontaneously into oxygen and the endothermic nitrogen peroxide.

There are two important laws of thermo-chemistry. Properly speaking they are only special expressions of the Law of Conservation of Energy.

(1) Every compound has a definite heat of formation, which is the same as its heat of decomposition.

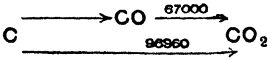
(2) The heat of formation of a substance is independent of the mode of its formation (the Law of Hess).

From these it follows that we may calculate the heat of formation of substances which cannot be formed from their elements. The direct method of forming carbon monoxide does not lend itself to thermal measurements. But its heat of combustion is easily determined,

$$2CO + O_2 = 2CO_2 + 2 \times 67{,}000 \text{ calories.}$$

The plus sign before the calories indicates that the substances on the left-hand side of the equation have lost energy in the act of combining.

Given the heat of formation of carbon dioxide from its elements, that of carbon monoxide is found by subtraction, $C + O = CO + 29{,}000$ calories.



The heats of formation of organic substances may be calculated from their **Heats of Combustion.** Thus for alcohol

$$C_2H_6O + 3O_2 = 2CO_2 + 3H_2O + 340{,}500 \text{ calories.}$$

When the same masses of these two products are formed from their elements, 399,120 calories are evolved.

$$2C + 6H + 7O = 2CO_2 + (2 \times 96{,}960 \text{ calories}) + 3H_2O + (3 \times 68{,}400) \text{ calories.}$$

This number exceeds the former by 58,620 calories, hence the heat of formation of alcohol is 58,620 calories.

The influence of conditions upon chemical reactions.

When zinc is corroded by dilute sulphuric acid there is a considerable evolution of heat. Pure zinc is not attacked by the cold dilute acid, and impure zinc is protected if its surface has been well rubbed with mercury. Copper is not attacked by dilute sulphuric acid, but a piece of zinc, which has been coated with copper by momentary immersion in copper sulphate, is instantly corroded by dilute sulphuric acid, and will even decompose water.

Evidently these reactions are influenced by the *condition* of the zinc. If a piece of pure (or amalgamated) zinc is placed in dilute sulphuric acid, and a piece of copper is immersed in the same solution, no reaction takes place so long as the metals do not come in contact, but the reaction begins at once if the copper and zinc are brought into contact, even though they touch *outside the solution only.* The zinc is corroded steadily and hydrogen is liberated, *but,* the gas makes its appearance on the surface of the copper. The copper is unattacked. It has been shown experimentally that the same amount of heat is liberated in this as in the former case. The reaction ceases when the surface of the copper plate is covered with bubbles of hydrogen, but it will begin again and continue if these are persistently removed by a camel hair brush. The reaction proceeds equally well if the copper and zinc plates are joined by a wire. If the wire is turned into several coils, a light magnet placed within the coil will be deflected: a current of electricity is passing along the wire.

For this reason it has been asserted that the corrosion by the dilute acid of impure zinc is a consequence of numerous 'short circuits' which can be set up between impurities and the metal.

The influence of conditions upon the corrosion of zinc is still more evident when we alter the **concentration** of the acid. In this case the products of the reaction are different; with moderately concentrated and warmed sulphuric acid, hydrogen sulphide is evolved, and with more concentrated acid, sulphur and sulphur dioxide are formed. These substances are the products of the progressive reduction of sulphuric acid.

When the more active oxidising agent, nitric acid, reacts with zinc, the reduction products ammonia, nitrogen, nitrous oxide, nitric oxide, and peroxide, are successively formed with the greater concentration of the acid.

The effect of **temperature** upon the course of the reaction is well marked in the above cases. A particularly good instance of it may be studied in the formation of 'water gas.' At about 500° C. carbon dioxide and hydrogen, but above 1000° C. carbon monoxide and hydrogen are produced. The thermal equations are instructive (see Le Chatelier's theorem).

$$2H_2O + C = CO_2 + 2H_2 - 19{,}000 \text{ calories}$$
$$2H_2O + 2C = 2CO + 2H_2 - 58{,}000 \quad \text{„}$$

We might consider the influence of impurities upon the corrosion of zinc by dilute sulphuric acid as an example of catalysis.

A good example of the influence of a **catalyser** upon the **course** of reactions has been given in the chemical part of this chapter. When potassium chlorate is heated alone, two reactions appear to take place simultaneously,

(1) the transformation into perchlorate and chloride;
(2) the transformation into chloride and oxygen.

The latter is favoured by a high temperature. But when the chlorate is mixed with pyrolusite, the second reaction alone takes place, and it does so below the melting point of the chlorate. This may perhaps be more correctly regarded as the influence upon the **velocity** of the reaction.

As we have seen in Chapter XX., exothermic compounds are dissociated at high temperatures with absorption of heat. It has been proved that endothermic compounds tend to be *formed* at high temperatures; we have used the electric arc to prepare nitric peroxide, and, to obtain a continuous supply of the gas, we had to pass a steady succession of sparks,

for the obvious reason that energy had continuously to be absorbed.

But the **temperature** has a very important influence upon the **speed** of reaction. As a general rule the velocity is accelerated by rise of temperature. The student may recall numerous instances of the necessity of heating a mixture to initiate a reaction. In Chapter I. particulars of the effect of temperature upon 'detonating gas' (2 : 1 by volume mixture of hydrogen and oxygen) are given. The lowest temperature at which explosion occurs is called the **ignition point**. The student must clearly understand that the temperature is a *condition* only, it has no influence upon the heat of formation. The velocities of *all* reactions tend to become slower as the temperature falls; very few reactions take place at the boiling point of hydrogen. At low temperatures hydrogen and oxygen will not combine, at very high temperatures water is dissociated. There is an intermediate temperature at which the combination proceeds with the greatest velocity. This is called the **optimum** temperature. In some laboratory experiments this is an important factor. Thus, when sulphur dioxide and oxygen are passed over platinum sponge, combination proceeds more and more rapidly as the temperature rises. At about 400° C. the optimum temperature is reached. Above 450° C. the trioxide begins to dissociate—an endothermic reaction.

The effect of **catalysers** upon the velocities of reactions has been pointed out frequently in previous chapters. 'Detonating gas' again provides a good subject, for, when it is brought into contact with finely divided platinum, combination at once takes place at the surface of the platinum. The platinum glows and the heat evolved soon raises this to the temperature of ignition, when explosion takes place. When the catalyser is exceedingly finely divided the combination may be initiated at as low a temperature as −20° C. This case is most valuable because it enables us the better to perceive that temperature is *a condition*. The catalyser only accelerates the reaction: it is still platinum at the finish. Catalysers are not always **accelerating** agents; one instance of a **retarding** agent will be given in Chapter XXVIII. Instances of the accelerating influence of **light** are given in Chapters III., VII., VIII. and XVIII.

The velocity of explosion is affected by the relative proportion of the gases present. We have had an instance of this in Chapter III. where the mixture of hydrogen and chlorine was rendered non-explosive by the presence of a moderate excess of either gas. In a lesser degree the same is true of a

mixture of hydrogen and oxygen, the velocity of explosion falls off rapidly as either constituent is in excess. The addition to detonating gas of a diluting gas, such as nitrogen, has the same effect. The student has had practical illustration of it in testing for hydrogen.

The effect of **concentration** upon the speed of a reaction is well shown in solution; thus, provided the temperature is kept constant, the corrosive action of an **acid** upon a metal becomes less and less rapid with dilution—within limits.

This can be observed by collecting the hydrogen evolved during equal times by the action of pieces of zinc of equal area upon different concentrations of hydrochloric acid; proper care must be taken to maintain the reagents at constant and equal temperature, not by any means an easy matter. This subject has already been dealt with under the Law of Mass Action.

The effect of the **solvent** upon the velocity of reaction may be considerable; in some cases it accelerates, in others it retards the velocity of reaction. An instance of the latter is shown when solutions of phosphorus and iodine in carbon disulphide are brought together. This subject will be referred to again.

The student is advised to study carefully as many as possible similar cases of the influence of conditions. The production of hypochlorite or chlorate, according to conditions, has been given in the chapter. Other cases are inadequately represented by the following sets of equations.

(A) $C_2H_5I + KOH + xH_2O = C_2H_5OH + KI + xH_2O$
$C_2H_5I + KOH + xC_2H_5OH = C_2H_4 + KI + H_2O + xC_2H_5OH.$

(B) $C_2H_5OH + xH_2SO_4 \longrightarrow C_2H_4 + H_2O + xH_2SO_4$
$2C_2H_5OH + yH_2SO_4 \longrightarrow (C_2H_5)_2O + H_2O + yH_2SO_4.$

(C) $3Fe + 2O_2 \longrightarrow Fe_3O_4$
$4Fe + 3O_2 \longrightarrow 2Fe_2O_3$ (hydrated).

(D) Also the effect of concentrated and dilute sulphuric acid on potassium ferrocyanide. (Construct equation, see Chapter XXIX.)

(E) Also the differences in the conditions for preparing gaseous hydriodic acid and phosphonium iodide.

(Consult Fenton's *Outlines of Chemistry* for other cases.)

CHAPTER XXII.

PHOSPHORUS.

In 1674 Phosphorus was discovered by Brandt, and since he made a secret of his method of preparing it, Boyle, in 1680, was obliged to rediscover it for himself.

Allotropy.

Phosphorus is known in at least two crystalline modifications; the **ordinary** (or 'yellow') and the red which is often called amorphous. The two varieties are believed to owe their differences to the greater molecular complexity of the red form; unlike ozone, which is more complex than oxygen, red phosphorus is less active than the 'ordinary' form. Ordinary phosphorus, when pure, is a **colourless** crystalline solid, almost insoluble in water but freely soluble in carbon disulphide. Its crystalline nature is shown when it is obtained by the slow evaporation of its solution. It melts at about 44° C. and at a slightly higher temperature catches fire in air. It combines directly, even at ordinary temperatures, with some elements; violently with sulphur, slowly with oxygen—hence it must be kept under water. At ordinary temperatures

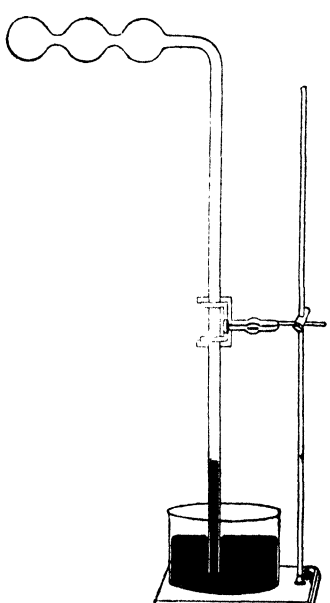
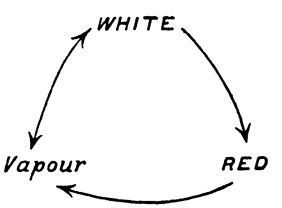


Fig. 106.

it is slightly brittle, but it may be cut with a knife. Burning phosphorus causes exceedingly painful and dangerous wounds, it should therefore never be handled except under water. Even in small doses it is a deadly poison, and since it is slightly volatile, those who work with it are subject to hideous diseases. Red phosphorus is not soluble either in water or in carbon disulphide, nor is it volatile at ordinary temperatures. It may be heated nearly to 260° C. before taking fire in air, and it is markedly less reactive with other elements than the ordinary variety. Pure red phosphorus is not poisonous, probably because it is insoluble; for this reason and because of its non-volatility it is largely used instead of the dangerous white phosphorus in the manufacture of matches, and is often preferred in the laboratory.

White phosphorus, when heated out of contact with air to about 250° C., is transformed into the more stable variety. This change can readily be shown with the tube of Fig. 106. The phosphorus is placed in the end bulb and the tube is sealed with mercury. The phosphorus is gently heated; some of it by oxidation removes the whole of the free oxygen. On heating still more strongly, the rest of the phosphorus, in the atmosphere of nitrogen, changes to the red variety. At a somewhat higher temperature the white variety is reformed. According to many the red variety is volatile and the vapour produced condenses as the white variety (see diagram). By a modification of this method Shroetter proved that the change of one variety into the other is not accompanied by change of weight.



It is advisable to cover the bench with damp sand when trying this experiment; this precaution should always be made whenever phosphorus is used.

Oxidation.

When ordinary phosphorus is exposed to moist air it oxidises slowly, and the smell of ozone becomes evident. It is said that the odour is entirely due to ozone; however that may be, the presence of ozone is easily proved. Small pieces of phosphorus are half covered with water in a large flask. The flask is fitted with two

tubes, a wide delivery tube which reaches considerably below the cork and a second tube for the admission of water. After an hour or so the ozonised air, displaced by water, is passed into a test tube which contains mercury as an indicator.



Fig. 107.

Schonbein has proved that for every 16 parts of oxygen which combine with the phosphorus, 48 parts of ozone are formed. Hence it would seem that a molecule of oxygen is split into two atoms, one of them combines with the phosphorus and its fellow combines with a second molecule of oxygen to form a molecule of ozone. This type of reaction is by no means uncommon and is termed 'autoxidation.'

During slow oxidation ordinary phosphorus is phosphorescent (whence its name[1]). It is remarkable that when phosphorus is placed in pure oxygen at ordinary pressure it ceases to be phosphorescent, but when the pressure is considerably diminished the glowing begins again. This may be illustrated with the aid of a suction pump.

When phosphorus burns (oxidises rapidly) in the air, two white solid oxides, phosphorous and phosphoric, are formed. The latter is obtained pure by burning phosphorus in a current of dry oxygen, and then reheating the product in excess of dry oxygen. When a weighed piece of phosphorus is burnt completely the proportion of the elements in the higher oxide is shown to be phosphorus to oxygen as 12·4 : 16. The atomic weight of phosphorus, as deduced from the molecular weights of its volatile compounds, is 31, hence the empirical formula of phosphoric oxide is P_2O_5, analogous to that of the anhydride of nitric acid.

The vapour density is 142 (H = 1) corresponding to the molecular weight 284, hence the formula for the vapourised oxide must be doubled (P_4O_{10}); the simpler formula is generally used in equations.

Solution of higher oxide.

Phosphoric oxide is the most efficient desiccating agent known. It absorbs water in which it dissolves to form an acid solution, phosphoric acid. When ignited, this acid is not dissociated into water and the anhydride; in this behaviour it is peculiar amongst oxyacids. Phosphoric acid, as obtained by ignition, is a colourless solid,

[1] Light bearer, from φῶς, φέρειν.

very soluble in water. It is called **glacial phosphoric acid.** When a known mass of the anhydride is dissolved in water and the glacial acid is obtained from the solution, by evaporation followed by ignition, the increase in weight suggests for the acid the empirical formula HPO_3, analogous to that of nitric acid. The formula may be confirmed in the following manner. When the solid acid is dissolved in cold water and its solution is neutralised with caustic soda (using litmus as indicator) a somewhat insoluble salt is formed. From the solution of the sodium salt silver nitrate precipitates a white gelatinous silver phosphate, which may be dried and analysed: its composition is found to correspond to the formula $AgPO_3$.

Effect of heating.

A peculiar property of this acid solution is its power to congeal a solution of albumen, such as the white of an egg. This property is of importance to physicians and is interesting to us, for, when it stands, and more rapidly when it is heated, the acid solution loses this property and acquires others equally remarkable and still more important. If equal volumes of the unboiled and boiled solutions are taken and neutralised with sodium hydroxide (using litmus as indicator), it will be found that the boiled solution needs double the quantity of base needed by the unboiled solution. The sodium salts formed are quite distinct; that from the boiled solution may be obtained, by crystallisation, as beautiful large crystals which are efflorescent in air. When redissolved this crystalline sodium salt has a *slightly* alkaline reaction to litmus. The salt has been known for a long time, and is what is generally understood by the term 'sodium phosphate.'

But Graham showed that from the heated solution two more sodium phosphates may be obtained. One is formed by adding *half as much again* of sodium hydroxide as is necessary for neutralisation. The salt which separates from the concentrated solution should be recrystallised from twice its weight of water. In solution it is *strongly* alkaline. The third salt is *acidic* to litmus, it is formed by adding to the acid *half* the mass of caustic soda necessary for neutralisation. As there are three well-defined sodium salts one seems driven to conclude that phosphoric acid (HPO_3) combines slowly with water to form a **tribasic acid,** the simplest formula for which

is H_3PO_4. This view is confirmed by the analysis of the silver salt; on adding silver nitrate to the well-boiled solution of the acid a *yellow* silver phosphate is formed, which by analysis is shown to correspond to the formula Ag_3PO_4.

The analyses, both of the white gelatinous silver salt and the yellow silver salt, are carried out by dissolving weighed quantities in nitric acid and precipitating the silver as chloride.

The formation of the acids may be represented thus:

(1) $P_2O_5 + H_2O = 2HPO_3$. (2) $HPO_3 + H_2O = H_3PO_4$.

Both acids are phosphoric acids, both have the same anhydride, from which they are formed by combination with water only: the tribasic acid needs for its formation more water, but it is at the same stage of oxidation as the monobasic acid. Although both are phosphoric acids they are quite distinct; they differ greatly in their properties and in the nature of their salts.

It is necessary to appreciate clearly that the extra hydrogen and oxygen in the tribasic acid is not water of hydration (crystallisation) but water of constitution; all three equivalents of hydrogen are replaceable by equivalents of sodium.

The acid should be compared with oxalic acid which has two molecules of water of hydration, $C_2O_4H_2$, $2H_2O$; this is true water of hydration which may be driven off, by heating to 100° C., without altering the basicity of the acid. Of the potassium oxalates, the normal salt has but one molecule of hydration, $C_2O_4K_2$, H_2O, and the acid salt is anhydrous C_2O_4HK. The normal silver oxalate is also anhydrous $C_2O_4Ag_2$.

To distinguish the two phosphoric acids the tribasic acid is named **orthophosphoric acid**[1], it is the more stable in solution. The monobasic (glacial) acid is called **metaphosphoric acid.** Although the latter is less stable in solution, it is the more stable towards heat. When the pure ortho-acid is heated strongly it loses water to reform the meta-acid. This is not decomposed but is volatilised unchanged at a bright red heat.

Orthophosphoric acid may be obtained free from water by evaporation; it remains as a thick syrup, which, on standing, becomes crystalline. The crystals melt at 38° C. The acid is obtained in the laboratory most readily by treating

[1] ὀρθός = right.

moistened red phosphorus with a little concentrated nitric acid in a round-bottomed flask set on a sand bath.

[Write the equation for the reaction, given that equal volumes of nitric oxide and peroxide are evolved.]

The phosphates.

Calcium (ortho)phosphate, $Ca_3(PO_4)_2$ occurs in nature in the mineral Apatite, and also shares with calcium carbonate most of the ash obtained by igniting bones.

From calcium phosphate, phosphorus is obtained. The older method of preparation was carried out by treating powdered apatite or bone-ash with dilute sulphuric acid. The solution of the displaced ortho-phosphoric acid was run off from the insoluble calcium sulphate, evaporated and ignited. The meta-phosphoric acid formed was mixed with carbon, and the mixture heated in retorts; hydrogen and carbon monoxide were evolved, and phosphorus distilled over and was collected under water. It was purified and cast in moulds.

$$4HPO_3 + 12C = 4P + 12CO + 2H_2.$$

Phosphorus is also prepared by exposing a mixture of calcium phosphate and carbon, mixed with sand, to the heat of the electric furnace. At the high temperature calcium silicate is formed and phosphoric acid is reduced by the carbon. The volatile phosphorus is condensed in copper vessels which contain water. Red phosphorus is obtained from the ordinary variety by heating the latter in special retorts.

Other phosphates of importance are silver phosphate, to which we have already referred; ammonium magnesium phosphate $(NH_4)\,MgPO_4$, which, being one of the most insoluble of magnesium salts, is used in analysis; and microcosmic salt, that is, sodium ammonium hydrogen orthophosphate,

$$Na(NH_4)HPO_4,\ 4H_2O.$$

All save the alkali phosphates are insoluble in water, but they are soluble in dilute acids.

In analysis dilute nitric acid is used to dissolve them, as the nitrates are generally soluble. One of the phosphates least soluble in this reagent is the light yellow ferric phosphate $FePO_4$. When an alkali is added to the acid solution of a phosphate, the original phosphate is precipitated as soon as the solvent acid is neutralised.

The three sodium ortho-phosphates are called:

Normal or trisodium phosphate (alkaline to litmus) Na_3PO_4.

Monohydrogen or disodium phosphate (nearly neutral) Na_2HPO_4.

Dihydrogen or monosodium phosphate (acidic) NaH_2PO_4.

Effects of heating phosphates.

When microcosmic salt is heated strongly ammonia and water are driven off. It should be cooled quickly. The residue is deliquescent and readily dissolves in water; from its solution, which is slightly acid, silver nitrate deposits white gelatinous silver metaphosphate. Hence the following reaction has taken place. $NH_4NaHPO_4 = NaPO_3 + H_2O + NH_3$.

Sodium metaphosphate is also formed by heating monosodium orthophosphate, NaH_2PO_4, to 204° C., but this salt is not so easy to obtain pure as microcosmic salt. Sodium metaphosphate obtained in this manner differs from that obtained by neutralisation (page 273) in several particulars, but especially in that it is much more soluble.

Metaphosphate in solution combines slowly with water to form monosodium orthophosphate, $NaPO_3 + H_2O = NaH_2PO_4$. When solid **ordinary** sodium phosphate is heated strongly, water is lost. If to a solution of the white residue silver nitrate is added, a precipitate of a white silver salt is obtained, which, whilst differing but slightly in appearance from silver metaphosphate, differs altogether in composition. If we consider the formula of ordinary sodium phosphate, we might suppose that the loss of water would leave, by the simplest reaction, a new substance of the formula $Na_4P_2O_7$

$$2Na_2HPO_4 - H_2O = Na_4P_2O_7.$$

Analysis of the white silver salt confirms this view.

The new sodium and silver salts are called **pyrophosphates**: they are the salts of a third phosphoric acid. The acid, which is relatively unimportant, may be obtained from pure orthophosphoric acid by heating the latter to 215° C. $2H_3PO_4 = H_2O + H_4P_2O_7$.

Pyrophosphoric acid (a white, very deliquescent solid) obtained in this way, is mixed with a little metaphosphoric acid. It may be obtained quite pure in solution by the following method: pure sodium pyrophosphate is dissolved in water and lead pyrophosphate precipitated,

$$Na_4P_2O_7 + 2Pb(NO_3)_2 = Pb_2P_2O_7 + 4NaNO_3.$$

The lead salt is then suspended in water into which hydrogen sulphide is passed, $Pb_2P_2O_7 + 2H_2S = 2PbS + H_4P_2O_7$. Lead sulphide is filtered off and the acid solution is concentrated in a vacuum at a low temperature.

Pyrophosphoric acid is unstable both in solution

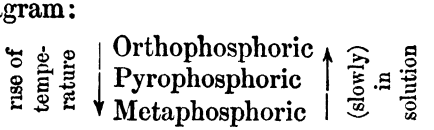
$$(H_4P_2O_7 + H_2O = 2H_3PO_4)$$

and when heated ($H_4P_2O_7 = 2HPO_3 + H_2O$). That it is tetra-

basic is proved by the composition of its salts; the hydrogen atoms are replaceable in pairs however; only two sodium salts, represented by the formulae $Na_4P_2O_7$ and $Na_2H_2P_2O_7$, are well known. The dihydrogen salt is obtained from the normal salt by the addition of acid.

Recapitulation

Three distinct acids derived without reduction or oxidation from phosphoric oxide are known, that is, there are three different phosphoric acids. They are formed by the combination of the anhydride with different proportions of water, all the hydrogen of which becomes acidic; these acids are monobasic, tetrabasic and tribasic respectively. Their relative stability is expressed by the following diagram:



The acids may be distinguished from each other by the appearance of their silver salts together with the power, possessed by the meta-acid alone, to congeal albumen. The dry salts of pyro- and metaphosphoric acids are quite stable; in solution they become mono- and dihydrogen orthophosphates respectively. From the latter solids they may be obtained again by the simple process of heating. Metaphosphoric acid is analogous to nitric acid: unlike the latter it is quite stable when heated.

Phosphorous oxide and acid.

Mention was made above that two oxides are formed when phosphorus is heated in air. We will now study phosphor**ous** oxide and its transformations. It is more volatile than the pentoxide: advantage was taken of this fact to obtain it in a pure condition. A piece of phosphorus was placed in a tube, bent so that the melted phosphorus could not escape; the tube was connected to a horizontal Liebig's condenser, surrounded by water kept at 60° C. The condenser was connected with a cooled U-receiver. Air was slowly drawn through the whole apparatus and the phosphorus was gently ignited. Most of the pentoxide fumes were deposited in the condenser, and the rest were held by

a plug of glass wool placed just in front of the end of the condenser. The lower oxide, still vaporous, passed on and was condensed in the receiver. Phosphorous oxide is, at ordinary temperatures, a white solid, M.P. = 22·5° C. The liquid substance boils at 173° C.; at a still higher temperature it decomposes with the production of an intermediate oxide and red phosphorus. When heated in the air it burns readily to form phosphoric oxide. Its vapour density corresponds to the formula P_4O_6. It is called phosphorous trioxide or phosphorous anhydride. It dissolves in *cold* water to form a solution of phosphorous acid.

Phosphorous acid is actually prepared by a much more convenient method which will be described later.

The formula of this anhydride might lead us to suppose that the formula of the acid is HPO_2; but the acid forms two series of salts, that is, it is dibasic, and moreover the disodium salt contains yet another hydrogen equivalent. From the composition of the salts the formula of the acid follows as H_3PO_3.

From this formula we see that a molecule of phosphorous acid contains two atoms of hydrogen more than a molecule of metaphosphoric acid does, but one atom of oxygen less than a molecule of orthophosphoric acid does. On exposure to air it takes up oxygen (not water) to form orthophosphoric acid. $2H_3PO_3 + O_2 = 2H_3PO_4$. It is a powerful reducing agent; it will even reduce sulphur dioxide to sulphur.

$$2H_3PO_3 + SO_2 = 2H_3PO_4 + S.$$

So great is its tendency to oxidise, that, when heated alone, it forms phosphoric acid at its own expense, so to speak, part of it at the same time being reduced with the formation of a spontaneously inflammable gas of offensive smell.

Phosphine.

This gas is evolved when phosphor*ous* anhydride is dissolved in *hot* water; phosphor*ic* acid is left in solution. When heated, the gas decomposes into red phosphorus and hydrogen. It burns readily in air, forming phosphoric oxide and water; with defect of oxygen, red phosphorus is deposited. Hence this gas must be a hydride of phosphorus. The pure substance is found to contain phosphorus and hydrogen in the proportion of 31 : 3,

and since its vapour density is 17 (H = 1) its formula is PH_3. It is called **Phosphine.** Its formula is analogous to that of ammonia, and it may be formed by methods analogous to those for the preparation of ammonia. Just as calcium nitride yields ammonia and hydroxide with water, so calcium phosphide yields phosphine under the same conditions.

$$Ca_3P_2 + 6HOH = 2PH_3 + 3Ca(OH)_2,$$
$$Ca_3N_2 + 6HOH = 2NH_3 + 3Ca(OH)_2;$$

compare also

$$CaC_2 + 2HOH = C_2H_2 + Ca(OH)_2.$$

Its formation from phosphorous acid is represented thus

$$4H_3PO_3 = 3H_3PO_4 + PH_3.$$

The impure gas is usually prepared by the method of its discovery,—by heating phosphorus with an alkali. A few small pieces of white phosphorus are placed in a small flask, and covered with a solution of caustic soda or baryta water. The apparatus is fitted up so that all air may be displaced from flask and delivery tube by a current of coal gas or hydrogen (Fig. 108). The flask is then heated gradually on a sand bath, and a gas is evolved which ignites as soon as it comes in contact with the air. The phosphoric acid, produced by the combustion, travels away in ever widening vortex rings. The gas is only slightly soluble, and may therefore be collected over water. When the gas is passed through a U-tube immersed in a freezing mixture, it loses the power of spontaneously inflaming, and it has been shown that this property is actually due to the presence of a trace of a less volatile liquid hydride whose composition is represented by the formula P_2H_4.

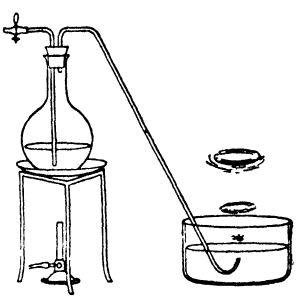


Fig. 108.

Phosphine is analogous to ammonia in more than its method of formation. Like ammonia it will combine with an acid to form a salt; hence it has basic properties. These properties are so poorly developed, however, that little more than a tendency to salt formation is exhibited by phosphine:

its salts are unstable under ordinary conditions of temperature and pressure. Even phosphonium chloride can be made only by subjecting the constituent gases to increased pressure (see page 255). Phosphonium iodide, PH_4I, alone is stable; this is the salt of hydriodic acid (HI), an *analogue* of hydrochloric acid which will be discussed in the next chapter. Although phosphonium iodide is stable when dry, it is decomposed by water into its constituents: advantage is taken of this reaction to prepare pure phosphine (see E, p. 269).

The substituted ethyl phosphonium salts are well defined, although they are not so stable as the analogous substituted ammonium salts (Chapter XVII.).

Hypophosphorous acid.

When barium hydroxide is used for the preparation of phosphine, a compound of barium of the formula $BaH_4P_2O_4$ remains in solution. It may be obtained by cautiously evaporating the residue after the latter has been freed from excess of baryta by the addition of carbon dioxide, whereby the baryta is precipitated as carbonate. When the solution of this barium compound is treated with dilute sulphuric acid, a compound of the formula H_3PO_2 is obtained in solution. It is called **Hypophosphorous acid.** On standing in the air it is oxidised to phosphorous and phosphoric acids; when heated it oxidises to phosphoric acid, part of it being reduced to phosphine and hydrogen.

Although its molecule contains three hydrogen atoms, it is monobasic. Its formation may be represented by the following equation:

$$3KOH + 3H_2O + 4P = PH_3 + 3KH_2PO_2.$$

Although the above equation represents the most interesting reaction which takes place in the flask, it by no means represents the only one. For instance, an extremely small amount of liquid hydride is formed,

$$6P + 4KOH + 4H_2O = 4KH_2PO_2 + P_2H_4.$$

Much hydrogen is evolved—about 60 per cent. by volume—partly by the direct action,

$$2P + 2KOH + 2H_2O = 2KH_2PO_2 + H_2,$$

and partly by the decomposition of the hypophosphite, the latter being unstable at the temperature of the reaction,

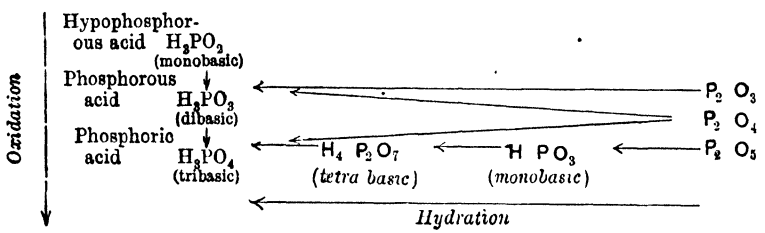
$$2H_2KPO_2 + 3H_2O = 4H_2 + K_2H_2P_2O_7.$$

Tetroxide.

When phosphorous oxide is heated in a sealed tube, it changes into a higher oxide and red phosphorus, $2P_4O_6 = 3P_2O_4 + 2P$. This tetroxide has a formula analogous to that of nitrogen peroxide. Its reaction with water recalls those of the peroxides of nitrogen and chlorine,

$$P_2O_4 + 3H_2O = \underset{(phosphorous\ acid)}{H_3PO_3} + \underset{(phosphoric\ acid)}{H_3PO_4}.$$

The inter-relation of the acids of phosphorus may be represented by the following diagram:



The chlorides.

Phosphorus combines directly with chlorine to form two chlorides. In the preparation of these compounds air and moisture must be excluded from the apparatus: dry carbon dioxide conveniently displaces the air before admitting the dry chlorine. Some pieces of white phosphorus are dried and placed on a layer of dry sand in a dry retort (Fig. 109). The retort communicates with a

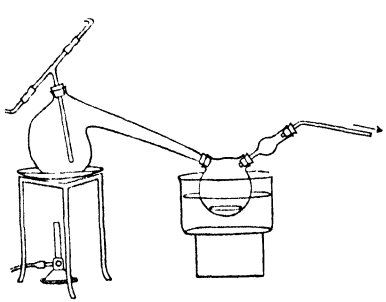


Fig. 109.

receiver immersed in iced water. The receiver leads, by means of a calcium chloride tube, to the draught. When the air has been displaced by a current of dry carbon dioxide,

a slow current of dry chlorine is passed into the retort just above the phosphorus, which is slightly warmed. The combustion proceeds energetically, and if excess of chlorine has been avoided, a colourless liquid condenses in the receiver. If, however, a rapid current (excess) of chlorine is passed through, there is formed in the neck of the retort and in the receiver a yellowish solid, phosphoric chloride.

To obtain the lower chloride free from the higher, the liquid product is redistilled after some phosphorus has been added to it. In this case there is excess of phosphorus and the pure lower chloride distils over. The lower chloride boils at 78° C.; its vapour density and composition correspond to the formula PCl_3. When chlorine is passed into the cooled liquid chloride, the higher chloride is formed. The reaction takes place with the evolution of much heat. By analysis its simplest formula should be PCl_5. From this formula one would expect its vapour density to be about 104: as a matter of fact its density is much less, and with rise of temperature decreases gradually to 52 at 300° C. This action reminds us of nitrogen peroxide, but the molecule of the chloride cannot dissociate into like parts. The colour of the vapour resembles more and more that of chlorine as the temperature rises, hence the suggestion was made that dissociation takes place into the lower chloride and chlorine. If some pentachloride is heated in an open flask over which a funnel is suspended, the smell of chlorine becomes evident and its presence may be demonstrated,

$$PCl_5 \rightleftarrows PCl_3 + Cl_2.$$

Both chlorides are good examples of what are known as 'acid chlorides.' When phosphorous chloride is passed into water, it reacts to form phosphorous and hydrochloric acids; $PCl_3 + 3HOH = H_3PO_3 + 3HCl$.

This is indeed the best method of preparing phosphorous acid; crystals of the acid may be obtained by aspirating the vapour of the chloride through a small quantity of water. The higher chloride behaves somewhat differently; when a *little* water is added to it, hydrochloric acid gas is evolved and a stable liquid remains. This liquid boils at 177° C., its composition corresponds to the formula $POCl_3$, hence it is

called **phosphorus oxychloride**, $PCl_5 + H_2O = POCl_3 + 2HCl$. It dissolves in water to form orthophosphoric acid,

$$POCl_3 + 3HOH = H_3PO_4 + 3HCl.$$

The formation of the acid from the chlorides has suggested the following formulae for the acids·

$PO(OH)_3$ orthophosphoric acid, $P(OH)_3$ phosphorous acid.

But the dibasicity of phosphorous acid and the monobasicity of hypophosphorous acid have led others to prefer $HPO(OH)_2$ and $H_2PO(OH)$ for the lower acids. According to this view the basicity of acids indicates the number of hydroxide groups contained in the molecules. Further evidence in support of both views exists, but we cannot pursue the discussion in this place.

The basicity of acids.

The doctrine of the basicity of acids was the outcome of Graham's work on phosphoric acid (1833). He first made clear the difference between ordinary phosphoric acid and the recently discovered pyrophosphoric acid, and he discovered a third acid which he called metaphosphoric acid. The term 'basicity' has already been defined in Chapter XII., and we have indicated how the basicity of an acid may be determined.

The most trustworthy method is to find **how many salts** can be prepared from the acid with a base such as caustic soda, in which one atom of metal displaces one atom of hydrogen. This evidence alone is not always sufficient however, and may even be misleading, for, as we have seen, pyrophosphoric acid is tetrabasic, although only two sodium salts are at all easily formed: hence the formula of the acid must be known. But the formula is often deduced from the basicity (nitric acid).

Valuable help is afforded by the **composition of the silver salt** (which can usually be analysed easily), for silver tends to form *normal* salts. For instance, the yellow normal silver orthophosphate is precipitated, no matter to which of the three sodium orthophosphates in solution silver nitrate is added.

The following equations represent the reactions imperfectly:

$3AgNO_3 + Na_3PO_4 = Ag_3PO_4 + 3NaNO_3$
(strongly alkaline) (neutral)

$3AgNO_3 + Na_2HPO_4 = Ag_3PO_4 + 2NaNO_3 + HNO_3$
(slightly alkaline) (acidic)

$3AgNO_3 + NaH_2PO_4 = Ag_3PO_4 + NaNO_3 + 2HNO_3$
(acidic) (acidic)

The **heat of neutralisation** also affords, in some instances, a useful confirmation of the basicity of an acid. When only half the base required for neutralisation is added to the equivalent quantity of a *monobasic* acid, only half the acid is neutralised, and only half the heat of neutralisation is evolved. For every equivalent of hydrogen of *any strong* acid neutralised by *any strong* base, the heat evolved is 13,700 calories.

$$HCl + NaOH = NaCl + H_2O + 13{,}700 \text{ calories},$$
$$HNO_3 + NaOH = NaNO_3 + H_2O + 13{,}700 \text{ calories},$$
$$HBrO_3 + NaOH = NaBrO_3 + H_2O + 13{,}700 \text{ calories}.$$

The heat evolved when weak acids are neutralised by strong bases may be more or less than 13,700 calories (hydrofluoric = 16,270, hypochlorous = 9,849 calories). But when to the dilute solution of a dibasic or polybasic acid, the base is added equivalent by equivalent, the heat evolved is rarely the same for each equivalent; whether the first or the second evolution is the greater, depends upon the acid neutralised. Thus for sulphuric acid, which for other reasons is known to be a moderately 'strong' acid, the second evolution is greater than the first.

$$H_2SO_4 + NaOH = NaHSO_4 + H_2O + 14{,}754 \text{ calories},$$
$$NaHSO_4 + NaOH = Na_2SO_4 + H_2O + 16{,}624 \text{ calories}.$$

It will be noticed that for *both* equivalents more than 13,700 calories are liberated. In the case of orthophosphoric acid, which is much weaker than sulphuric acid, the heat evolved for the first equivalent is the greatest, and that for the third is the least.

$$H_3PO_4 + NaOH = NaH_2PO_4 + H_2O + 14{,}830 \text{ cal.}$$
$$H_3PO_4 + 2NaOH = Na_2HPO_4 + 2H_2O + 27{,}080 \text{ cal. (diff. } = 12{,}250)$$
$$H_3PO_4 + 3NaOH = Na_3PO_4 + 3H_2O + 34{,}030 \text{ cal. (diff. } = 6{,}950)$$

Deductions from thermochemical data are not trustworthy for very weak acids, whose normal salts are partially or completely hydrolysed in solution. Thus hydrogen sulphide has the two salts Na_2S and $NaHS$, and is therefore dibasic. The normal sodium sulphide does not exist in solution as it is immediately hydrolysed $Na_2S + HOH = NaSH + NaOH$. Hence the thermal values are practically identical in the reactions,

$$NaOH + HSH = NaHS + H_2O + 7{,}738 \text{ calories},$$
$$2NaOH + HSH = NaHS + NaOH + H_2O + 7{,}802 \text{ calories}.$$

But the calories evolved when one, two and three equivalents of base are added to phosphorous acid (H_3PO_3) are

14,800, 28,400 and 28,400 respectively (compare with value for orthophosphoric acid). In this case the identity of the second and third evolution is actually due to the non-acid property of the third equivalent of hydrogen.

Bases are sometimes described as mon-acid, di-acid, and tri-acid, according to the number of replaceable **hydroxyl** groups.

$Na(OH)$ and $NH_4(OH)$ are mon-acid,
$Ba(OH)_2$ and $Cu(OH)_2$ are di-acid,
$Al(OH)_3$ and $Fe(OH)_3$ are tri-acid.

We have regarded basic salts as the products of hydrolysis (Chapter XV.), they may also be regarded as only partially 'neutralised' bases, and indeed some may be prepared either by adding to the base a quantity of acid insufficient for neutralisation, or by adding to the acid an excess of base. The composition of many basic salts cannot conveniently be represented by simple formulae. Basic ferric sulphate has a composition corresponding to the formula $Fe(SO_4)(OH)$, and bismuth oxychloride can be represented as $Bi(OH)_2Cl$ which has lost water becoming $BiOCl$. The 'acidity' of bases cannot be found from the number of normal and basic salts formed with a monobasic acid.

CHAPTER XXIII.

THE HALOGENS.

THREE elements, whose properties are similar to those of chlorine, are included with it in one family. These are the halogens[1]. **Chlorine** was the first to be discovered; Scheele, in 1774, liberated it by oxidising hydrochloric acid (marine acid air). He called it dephlogisticated marine acid air. Davy, in 1810, proved its elementary nature, and renamed it chlorine[2]. The second to be discovered was **iodine**[3], by Courtois in 1812. It owes its name to the violet colour of its vapour. Balard discovered the third in 1826, and, for its choking odour named it **bromine**[4]. Although Scheele, more than a century before, had recognised the existence of **fluorine** in fluor-spar, a substance used as a flux[5] in metallurgy, and had named it after this compound, the element was not isolated until 1886, when the pertinacity of Moissan was rewarded.

We have stated above that the halogens are placed in one family because of the similarity of their properties and of those of their analogous compounds; but a careful study will reveal the far more interesting truth that, with few exceptions, these properties differ in a regular manner such that, if we arrange the elements in order of atomic weight, the intensity of any one property will increase or decrease in the same order. That is to say, there is a **graded** difference, and it is in this rather than in the obvious

[1] ἅλς = sea salt. [2] χλωρός = pale green. [3] ἰοειδής = violet.
[4] βρῶμος = bad smell. [5] *Fluo* = I flow.

similarity that we recognise the halogens as members of one family. To this rule fluorine sometimes forms an exception, and differs more or less widely from the other three.

The atomic weights are:

Fluorine 19
Chlorine 35·45 (35·5)
Bromine 79·96 (80) } mean = about 80
Iodine 126·97 (127)

Chlorine, bromine and iodine are very closely related, and it is worthy of notice that the atomic weight of bromine is the mean of those of chlorine and iodine. As a comment upon their likeness, it is on record that Liebig had obtained bromine several months previous to Balard's discovery, and had even prepared several of its compounds, but he had failed to recognise its elementary nature, conceiving it to be a *chloride of iodine.*

The physical properties of the halogens may be tabulated for comparison.

		M. P.	B. P.	V. D. (air = 1)	
Fluorine	a light yellow gas	−223°C.	−187°C.	1·26	—
Chlorine	a pale green gas	−102°C.	− 33°C.	2·49	soluble in water
Bromine	a dark red liquid, heavy brown-red vapour	− 7·3°C.	+ 63°C.	5·54	slightly soluble in water, very soluble in CS_2 (yellow solution)
Iodine	a gray-black solid, violet vapour	+115°C.	+180°C.	8·8	very slightly soluble in water, very soluble in CS_2 (violet solution), soluble in alcohol and iodides (brown solutions)

All are poisonous, and their fumes are injurious to the tender membranes of nose and throat.

[*Question.* As iodine vapour is heated its V.D. gradually decreases to 4·4 (air = 1) at 1700° C. To what would you attribute this?]

Reaction with hydrogen and water.

All the halogens combine with hydrogen to form hydracids, but, as the following table shows, the intensity of the reaction decreases with the increase of atomic weight.

Fluorine. Combines with hydrogen violently, even in the dark.

Chlorine. Combines with hydrogen violently in sunlight, slowly in diffused light.

Bromine. Does not combine with hydrogen even in sunlight, but combination is *complete* when equal volumes of the two gases are passed over heated spongy platinum.

Iodine. Will not readily combine with hydrogen, and even when equal volumes of the mixed vapour and gas are passed over heated spongy platinum the combination is not complete, for the issuing gas still contains free iodine and hydrogen.

The intensity of the reaction with water to form the hydracid follows the same order.

Fluorine. Reacts so energetically to produce hydrogen fluoride that the liberated oxygen forms ozone.

Chlorine. Acts slowly in bright sunlight.

Bromine. Is more soluble than chlorine in water, but attacks it even more slowly.

Iodine. Is very slightly soluble in water, but does not react with it.

The hydrides formed are called the haloid acids. They are colourless gases, very soluble in water: from their solutions they cannot be completely expelled by boiling; in each case solutions of constant composition and boiling point are obtained. Whether dilute or concentrated solutions are boiled, a solution of definite concentration is obtained. The gases differ in stability towards heat; this is apparently related to the heat of formation.

The haloid acids.

	M. Wt.	Heat of formation	Begins to decompose at about	B. P. of pure liquid	B. P. of stable solution	Percentage composition of the solution
HF	40 (at 30°C.)	39,900 calories	?	+19·4°	120°	37 %
HCl	36·5	22,000 „	1500°	−80°	110°	20 %
HBr	81	12,300 „	above 700°	−73°	126°	47·4 %
HI	128	*400 „	180°	−34°	127°	57 %

* This is Berthelot's value for the combination of the two gases. He obtains −400 calories for gaseous hydrogen and solid iodine, a value given by Thomsen as −6060 calories.

The formation of hydrogen iodide in **solution** is strongly exothermic $H + I = HI$ (dissolved) + 18,400 calories.

[*Question.* When hydrogen iodide gas is heated brown vapour appears. To what is this probably due? From the view of Le Chatelier's theorem, what effect should pressure have upon the reactions?]

In connection with the relative stability of the haloid acids, it may be mentioned that chlorine will displace bromine from the bromides, and bromine will displace iodine from the iodides. The relative stability of the oxygen compounds is the reverse of that of the hydrides. No compound containing fluorine and oxygen has been prepared, but oxides of iodine are comparatively stable.

Preparation of the elements.

The preparation of chlorine has been fully described in Chapters III. and VII. Bromine and iodine are obtained by the same and other methods. At one time both were obtained by heating their binary compounds with concentrated sulphuric acid and manganese peroxide. The following equation is near the truth.

$$2NaBr + MnO_2 + 3H_2SO_4 = MnSO_4 + 2NaHSO_4 + 2H_2O + Br_2.$$

The salts were obtained from kelp, the dried ash of certain deep sea brown seaweeds.

It is worthy of notice that the iodides occur in sea water to such a slight extent (according to Gautier $\frac{1}{6000}$th mg. per litre at the surface, $\frac{1}{3}$rd mg. at greater depths), that many gallons must be evaporated before chemical analysis will detect them, and yet the ash of *Fucus palmatus* contains as much as 0·3 per cent. by weight of iodine.

This source has been neglected in recent years, chiefly because **Iodine** may be obtained more cheaply from the mother liquor of 'caliche' (Chapter XVIII.), which contains about 29 per cent. of sodium iodate. This iodate is reduced to iodine by sodium hydrogen sulphite ($I_2O_5 + 5SO_2 \longrightarrow I_2 + 5SO_3$).

$$2NaIO_3 + 5NaHSO_3 = 2Na_2SO_4 + 3NaHSO_4 + H_2O + I_2.$$

Bromine is prepared from the small quantity of sodium bromide contained in the Stassfurth salts, and from bromides which occur in certain mineral springs of Ohio. From both sources the element is liberated by free chlorine

$$Cl_2 + 2NaBr = Br_2 + 2NaCl.$$

Fluorine cannot be obtained by the above methods, in consequence of its great tendency to combine with hydrogen and the metals.

Moissan prepared it by the electrolysis of hydrofluoric acid. For this purpose, the acid, which, unlike the other haloid acids, is a liquid at ordinary temperatures, must be perfectly anhydrous. But the anhydrous acid does not conduct the electric current: Moissan overcame the difficulty by dissolving in the anhydrous acid dry potassium hydrogen fluoride KF, HF (whose solution is an electrolyte). As the acid boils at 19° C. a low temperature must be maintained. This is effected by rapid evaporation of a volatile liquid. The apparatus used was a platinum U-tube with platinum-iridium electrodes passed through stoppers made of fluor-spar (CaF_2), a substance at once an insulator and resistant to fluorine.

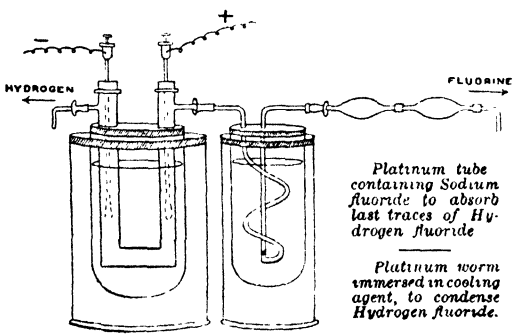


Fig. 110.

The hydrogen evolved at the kathode was allowed to escape. The fluorine evolved at the anode was passed through a spiral tube of platinum immersed in a special cooling agent, and then through platinum tubes which contained sodium fluoride; by these means it was freed from any hydrogen fluoride which had evaporated. Through platinum tubes it was led to the various reagents for research.

Even at the low temperature of the experiment the 'nascent' fluorine has a corrosive action on the anode. Fluorine is exceedingly reactive, and few elements are unattacked by it; oxides are attacked with evolution of oxygen; even silica (SiO_2) is decomposed, yielding silicon fluoride and oxygen. Chlorine is not nearly so reactive; it will indeed displace oxygen from some oxides, for instance, from zinc oxide, but to attack silica chlorine needs the

co-operation of carbon (Chapter XVI.). Bromine and iodine will attack many metals, but they show a falling off in activity from chlorine. Bromine has a distinct advantage over chlorine, in that, as a liquid it may be used in greater concentration; hence bromine is preferred to chlorine in certain oxidising actions.

NOTE. Cork or rubber stoppers are attacked by the halogens; if they are used they may be partially protected by a layer of paraffin. Cork should be kept under melted paraffin until it is saturated with the wax.

Preparation of the haloid acids.

Hydrofluoric acid is prepared from calcium fluoride by the usual method. As hydrogen fluoride attacks silica (Chapter XXX.) the preparation is carried out in platinum or leaden vessels, and the solution is stored in platinum or caoutchouc flasks. Powdered fluor-spar is treated with concentrated sulphuric acid and the mixture gently warmed (see Fig. 126). The gas and the solution are used for etching glass: the reaction will be explained under silicon (Chapter XXX.). The absolutely anhydrous acid has no effect upon glass. The fluorides are not very important; the best known natural compounds are fluor-spar, which is found in large cubes, and cryolite[1] $3NaF, AlF_3$.

The preparation and properties of **hydrogen chloride** have been sufficiently described in Part I.

Hydrobromic and **hydriodic** acids are not prepared by displacement from their salts by sulphuric acid. They decompose when heated, and they reduce concentrated sulphuric acid to sulphur dioxide or hydrogen sulphide, and are themselves oxidised to the halogen; hence the gas evolved is a mixture of the haloid acid, the halogen and sulphur dioxide in varying proportions.

$$2HBr + H_2SO_4 = 2H_2O + Br_2 + SO_2.$$
$$6HI + H_2SO_4 = 4H_2O + 3I_2 + S.$$
$$8HI + H_2SO_4 = 4H_2O + 4I_2 + H_2S.$$

Concentrated phosphoric acid may be used instead of concentrated sulphuric acid with no risk of reduction.

According to Bodenshein these haloid acids can be prepared pure only by direct combination over warm spongy platinum. The usual plan however is to prepare them (in-

[1] $\kappa\rho\upsilon o\nu$ = ice, $\lambda\acute{\iota}\theta o\varsigma$ = stone.

directly) from the phosphorus halides. The reactions are

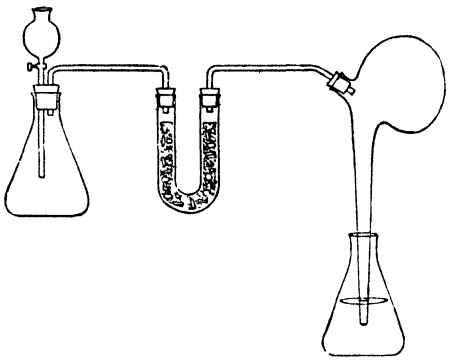


Fig. 111.

analogous to that which takes place between pentachloride and water ($PCl_5 + 4H_2O = H_3PO_4 + 5HCl$). Some red phosphorus is placed in a hard glass round bottomed flask with a little water, and bromine is introduced drop by drop from a separating funnel. **Hydrobromic acid** is at once disengaged, but the flask is not warmed until all the bromine has been added. Escaping bromine vapour is arrested by passing the gases through a U-tube which contains small pieces of damp white phosphorus separated by broken glass. The gas may be collected either by downward displacement of air, or—after drying by means of fused calcium chloride or phosphoric oxide (not oil of vitriol)—over mercury, or it may be passed into water. When a solution is to be made, a back-rush of water may be rendered harmless by the interposition of a vertical retort as a delivery tube (Fig. 111).

Hydrobromic acid may be prepared very conveniently by the action of bromine on melted paraffin at 185° C. As substitution products are formed, only half the reacting bromine is transformed into hydrobromic acid

The preparation of **hydriodic acid** is similar. A good method is to drop about one gram of well-dried phosphorus, in small pieces, upon 11 grams of powdered iodine contained in a hard glass flask cooled by water, waiting each time for the violence of the reaction to subside. 3 c.c. of water are then added, and, as soon as the first evolution of acid is over, the delivery tube is replaced; or the water may be added drop by drop through a stoppered funnel.

Another method is useful when dilute solutions only are needed. Powdered iodine is suspended in water, and a current of hydrogen sulphide is passed in. The iodine is reduced, and sulphur is deposited[1]

$$H_2S + I_2 = 2HI + S.$$

The sulphur is filtered off and the solution is concentrated if necessary. It will be noticed that as the reaction proceeds the iodine is more rapidly dissolved with the formation of a brown solution. This is due to the fact that iodine is very soluble in hydriodic acid and the iodides. This solubility is attributed to the formation of soluble tri-iodides $HI + I_2 = HI_3$. The tri-iodide, however, is easily reduced, for on passing in more hydrogen sulphide the whole of the solution becomes colourless.

The most important iodide is the potassium salt. This salt crystallises in cubes, especially as hopper crystals; it is used very largely in volumetric analysis and as a solvent for iodine (brown solution). Cupric iodide is unstable, it decomposes into solid iodine and cuprous iodide, $2CuI_2 = Cu_2I_2 + I_2$; the reduction is hastened by sulphurous acid. This reaction is made use of in analysis to remove iodides from mixtures of halides.

Iodine forms a remarkable blue coloured substance when brought in contact with cold starch. As this reaction is very sensitive, it is used as a delicate test for iodine and for starch, and as an indicator in volumetric analysis. Indirectly it answers as a test for the presence of many oxidising substances—for ozone, chlorine, or bromine, and the oxides of nitrogen.

$$2KI + O_3 + H_2O = \underset{\text{(alkaline)}}{2KOH} + I_2 + O_2$$

$$Cl_2 + 2KI = 2KCl + I_2$$

The following table gives an interesting comparison in solubilities:

	15° C.		15° C.
AgF	18·18 grams per litre	CaF_2	·0038 gram in 100
AgCl	·002 gram „	$CaCl_2$	66 grams „
AgBr	·004 „ „	$CaBr_2$	140 „ „
AgI	·0001 „ „	CaI_2	200 „ „

Oxygen compounds of bromine and iodine.

Bromine forms no oxides analogous with those of chlorine; oxyacids of bromine exist which are even less stable than the chlorine compounds.

It is to be remarked that, judged by these compounds, the properties of bromine are *not* midway between those of chlorine and iodine.

[1] The heat of formation of H_2S in solution is 9,400 calories; that of HI in solution is 18,400 calories.

On the other hand the oxides and oxyacids of iodine are *more* stable than those of chlorine; iodic acid is a crystalline solid and can easily be obtained perfectly pure, whereas chloric acid cannot be obtained in concentrated solution even.

When bromine is shaken with caustic alkalis, the bromide and **hypobromite** are formed, but the latter rapidly changes into bromide and bromate. The **bromates** are formed by shaking bromine with warmed alkali solution. The bromates, when heated, lose all their oxygen without the intermediate formation of the perbromate: they are very readily reduced by sulphurous acid. Bromic acid is known only in solution, it is a strong but unstable acid.

Iodine is dissolved by cold caustic potash, but the formation of a hypoiodite is doubtful; more probably iodate and iodide are formed at once. When the solution, so obtained, is acidified, iodine is deposited, for iodic and hydriodic acids interact thus: $5HI + HIO_3 = 3H_2O + 3I_2$. Advantage is taken of this reaction for the estimation of iodates.

Iodic and bromic acids are formed by the oxidising action of chlorine on iodine and bromine respectively; hence, when chlorine is used to displace these elements from the halides, an excess of that reagent must be avoided. **Iodic acid** is best prepared by oxidising powdered iodine with concentrated or fuming nitric acid.

The equation representing the oxidation varies with the particular reduction products of nitric acid formed. If only nitrogen peroxide were formed, it would be $I_2 + 10HNO_3 = 2HIO_3 + 4H_2O + 10NO_2$.

Oxygen compounds of		
Chlorine	Bromine	Iodine
Cl_2O ; $HClO$	—; $HBrO$	— ; (HIO?)
— $HClO_2$	— —	— —
ClO_2 —	— —	— —
— ; $HClO_3$	—; $HBrO_3$	I_2O_5; HIO_3
Cl_2O_7; $HClO_4$	— —	— ; HIO_4, $2H_2O$

Iodic acid is a white crystalline solid, soluble in water but insoluble in alcohol, hence it may easily be freed from an

excess of iodine. By heating the solid acid, **iodic anhydride** (I_2O_5) is obtained. Unlike the oxides of chlorine, iodic anhydride is exothermic. The iodates are comparatively stable bodies; as a rule they are transformed, by heating, into iodides, and are readily reduced by sulphurous acid.

Chlorine will oxidise iodates to periodates. These are rather complex compounds.

The strengths of acids.

A comparison of the strengths, that is the activity, of acids must be made under conditions, especially of temperature and concentration, which are not more favourable to one acid than to another.

Thus the strengths of hydrochloric, sulphuric, and acetic acids might be compared by observing the speeds with which hydrogen is liberated when the equivalent solution of each acid acts upon pieces of magnesium of equal surface area. The temperature must be initially the same for each acid, but as the heat evolved differs, the temperatures will not long remain equal, and, as increase of temperature accelerates the reaction, the conditions will become automatically unequal.

The apparatus of Fig. 116 may be used for obtaining rough comparisons. The speeds of the reaction are proportional to the volumes of hydrogen evolved in the same time. Immerse all three flasks in the same bath, and stir thoroughly.

For reasons which will occur to the reader, the method is not suitable in practice. If, when solutions containing equivalent quantities of two acids are mixed with one equivalent quantity of a base whose salts are soluble, it were possible to determine the proportion of the base neutralised by each acid, we should obtain data suitable for comparing the strengths of the acids in question. We should have equally trustworthy data if, when the equivalent quantity of one acid is added to the equivalent quantity of the salt of another acid, we could determine what proportion of the second acid is displaced from its salt, provided the conditions are such that the whole of the displaced acid remains in solution. And a check could be placed upon our conclusions by determining the result of adding the equivalent quantity of the second acid to the equivalent quantity of a salt of the first acid. For, competing under equal conditions, each acid would measure its strength by forming its own salt at the expense of the other.

Several investigators have determined these proportions by indirect methods. Their results agree fairly well amongst themselves, and also with those obtained by another method, based upon a non-salt forming property of acids, namely, the catalytic influence of acids upon the speed of certain reactions, such as the conversion of cane sugar into two other sugars—glucose and fructose. Similar methods are applicable for comparing the strengths of bases. In this book we cannot discuss the above methods, we can only give a list of some acids and bases arranged accordingly in the order of their strengths.

Hydrochloric acid	100	Sodium hydroxide	98
Nitric "	100	Potassium "	98
Chloric "	100	Calcium "	96
Sulphuric "	54	Strontium "	92
Oxalic "	18	Barium "	90
Phosphoric "	6·2	Tetra ethyl ammonium hydroxide	75
Formic "	1·5	Tri " " "	14
Tartaric "	1·2	Di " " "	16
Acetic "	·4	Mono " " "	12
		Ammonium hydroxide	2

The numbers give approximately the ratio in which equivalent quantities of the acids (or bases) will share an

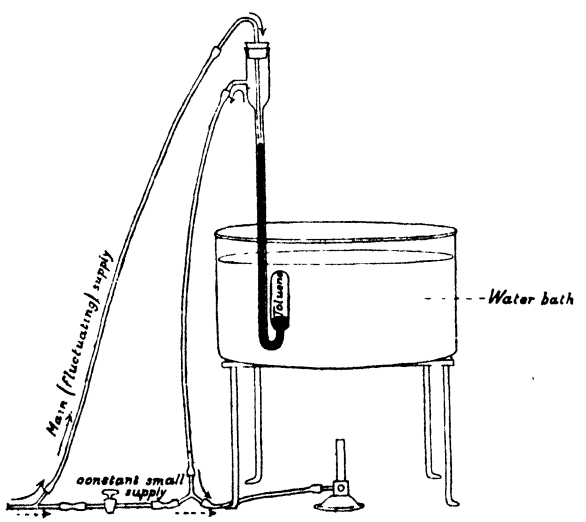


Fig. 112.

equivalent quantity of a base (or acid). Thus if equivalent quantities of sulphuric acid and sodium chloride, or of hydrochloric acid and sodium sulphate are mixed, the bases are

shared by the acids in the proportion 54 : 100, hence hydrochloric acid is approximately twice as strong as sulphuric acid.

For the maintenance of constant temperature, a **thermostat** is used. This is a bath maintained at constant temperature by means of a **thermoregulator**. That illustrated in Fig. 112 consists of a bent tube, blown into a bulb at the end. The bulb is almost filled with toluene, a substance which has a large coefficient of expansion. The rest of the bulb and the greater portion of the stem are filled with mercury. Reaching nearly to the mercury is a gas inlet tube, which will be choked by mercury when the toluene expands; the inlet tube can be 'set' to be choked at any required temperature.

The bath is heated by a burner whose gas supply is so arranged that when the main current, which passes through the inlet tube of the regulator, is choked, the flame is still fed by a constant small supply just sufficient to keep it alight. The substances to be maintained at constant temperature are placed in vessels immersed to the neck in the bath. The flame should not be left burning by an inexperienced worker.

CHAPTER XXIV.

VALENCY.

WHEN we have found the atomic weights of the elements we can, by analysis, assign true formulae to all volatile compounds, and empirical formulae[1] to non-volatile compounds also (Chapter XII.).

If we arrange the formulae of the hydrides of all those elements which form stable hydrides, we find that the number of atoms of hydrogen shown in each formula is not less than the number of atoms of the other element:

$$OH_2;\ SH_2;\ FH,\ BrH,\ ClH,\ IH;\ NH_3,\ PH_3,\ P_2H_4;$$
$$C_6H_6,\ C_2H_2,\ C_2H_4,\ CH_4.$$

An atom of hydrogen does not appear to be able to combine with more than one atom of any other element. One atom of the halogen or of sodium combines with or replaces one atom of hydrogen and no more. One atom of oxygen or of sulphur combines with two atoms of hydrogen; one atom of phosphorus or of nitrogen combines with three atoms of hydrogen; and one atom of carbon combines (in methane) with as many as four atoms of hydrogen.

The above formulae suggest that each elementary atom has the power of combining with or of displacing a definite number of hydrogen atoms, or the same number of atoms of the halogen, or one half that number of oxygen atoms. This faculty, seemingly inherent in the different atoms, is called 'valency.' The hydrogen atom is chosen as the *standard* of

[1] An empirical formula is deduced from the results of analysis and the atomic weights of the elements found in the compound. It is the simplest formula that can represent the percentage composition of the substance.

comparison, as for so many other purposes. It is described as 'monovalent,' and all those elements whose single atoms show a tendency to be 'satisfied' by combining with or displacing one atom of hydrogen are also said to be monovalent. Among monovalent elements are the alkali metals,

$$KCl,\ KBr,\ KI,\ K_2SO_4,\ K_2S,\ KNO_3,$$

silver and the halogens. Elements whose single atoms will combine with or displace two atoms of hydrogen or of another monovalent element are called divalent; these also combine together atom with atom.

The alkaline earth metals (barium, strontium, and calcium), magnesium, zinc, cadmium, mercury (HgO, $HgCl_2$), copper (CuO, $CuSO_4$), tin (SnO, $SnCl_2$), lead (PbO, $PbCl_2$), iron (FeO, $FeCl_2$), sulphur (H_2S), carbon (CO) are **divalent.**

Trivalent are aluminium ($AlCl_3$, Al_2O_3), boron (BH_3, BCl_3), iron ($FeCl_3$, Fe_2O_3), nitrogen (NH_3, NCl_3, N_2O_3), phosphorus (PH_3, PCl_3, PBr_3, PI_3, P_2O_3), and arsenic, antimony, and bismuth.

Tetravalent are carbon (CH_4, CCl_4, CO_2, CS_2), silicon (SiH_4, $SiCl_4$, $SiHCl_3$, SiO_2), lead (PbO_2, $PbCl_4$) and tin (SnO_2, $SnCl_4$).

Phosphorus is **pentavalent** (PCl_5, PF_5, P_4O_{10}).

It is obvious from these lists that several elements have more than one valency, or, as it is often stated, they do not always exert their maximum valency. Thus copper and mercury are monovalent and divalent (Cu_2O, $CuCl$ and CuO, $CuCl_2$); iron is divalent and trivalent ($FeCl_2$ and $FeCl_3$); tin and lead are divalent and tetravalent; phosphorus is trivalent and pentavalent.

If we attribute a definite valency to each atom we are able to classify elements according to their valency, and to predict formulae. Thus the chloride of a monovalent element will have the formula MCl, that of the sulphate of a divalent metal will be DSO_4, the oxide of a trivalent element will be represented by T_2O_3.

It has been our practice hitherto, to consider only such compounds as serve to establish the most important properties of the elements concerned, and to illustrate the principles of chemistry. Of these compounds many are salts whose formulae could be deduced from those of the respective acids and bases from which they are derived; hence there has been little or no occasion for further classification. When,

however, the science is more deeply studied, a need arises for the classification of many additional facts; this need is satisfied, more or less, by the doctrine of valency.

The conception has been of service chiefly in the domain of organic chemistry, and there its application has furnished an orderly classification of hundreds of compounds, and has provided a powerful stimulus in the study of the compounds of carbon.

In practice we determine the valency of an atom in a given compound by dividing the atomic weight by the number which represents the equivalent mass of the element in the substance under consideration.

Historical.

The doctrine of valency was put forward by Edward Frankland in 1852, in consequence of some successful work upon certain carbon compounds containing metals. His statement is so clear and concise that his own words are invariably quoted. In order to follow the passage, it must be remembered that Frankland accepted the following atomic weights, O = 8, C = 6, S = 16; this may have aided him in his discovery.

"When the formulae of inorganic chemical compounds are considered, even a superficial observer is struck with the general symmetry of their constitution; the compounds of nitrogen, phosphorus, antimony, and arsenic, especially exhibit the tendency of these elements to form compounds containing 3 or 5 equivalents of other elements, and it is in these proportions that their affinities are best satisfied; thus in the ternal group we have

NO_3	NH_3	NI_3	NS_3
PO_3	PH_3	PCl_3	
SbO_3	SbH_3	$SbCl_3$	
AsO_3	AsH_3	$AsCl_3$	etc.

and in the 5-atom group we have

NO_5 NH_4O NH_4I PO_5 PH_4I etc.

Without offering any hypothesis regarding the cause of this symmetrical grouping of atoms, it is sufficiently evident, from the examples just given, that such a tendency or law prevails, and that, no matter what the character of the uniting atoms may be, the combining power of the attracting element, if I may be allowed the term, is always satisfied by the same number of atoms."

Carbon is tetravalent.

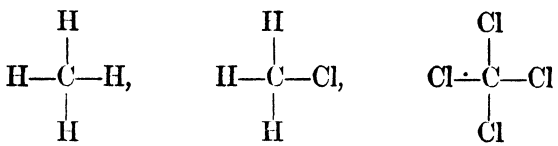
In 1858 Couper and Kekulé simultaneously asserted their belief that the carbon atom is tetravalent, and that the bewildering number of the carbon compounds is the result of the power especially developed in carbon atoms partially to 'satisfy' their own valency amongst

themselves. A short explanation of this view will be given, but a sufficient discussion of the subject is beyond the scope of this book.

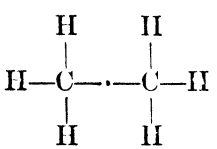
When methane (CH_4) is acted upon by chlorine, the hydrogen atoms are severally *replaced* by chlorine atoms; for instance, $CH_4 + Cl_2 = CH_3Cl + HCl$.

$$CH_4,\ CH_3Cl,\ CH_2Cl_2,\ CHCl_3,\ CCl_4.$$

The tetravalency of the carbon atom is represented by four straight lines.

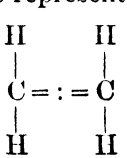


Ethane, C_2H_6, is formed by the action of sodium on chlormethane $CH_3Cl + 2Na + ClCH_3 = C_2H_6 + 2NaCl$, hence it is represented as



One valency of each carbon atom is 'satisfied' by the combination of the two CH_3- groups, and both carbon atoms are still tetravalent.

Some compounds cannot be so represented, thus ethylene C_2H_4 is for several reasons represented by



The double lines between the carbon atoms do not indicate a greater stability—the opposite rather; the second valency is said to be in abeyance, for when ethylene is mixed with chlorine, *combination* (not substitution as with ethane) takes place $C_2H_4 + Cl_2 = C_2H_4Cl_2$. Ethylene is also absorbed by concentrated sulphuric acid to form ethyl hydrogen sulphate $C_2H_5(HSO_4)$. Ethylene is said

to be 'unsaturated,' whilst ethane is 'saturated.' In acetylene the carbon atoms are joined by triple lines.

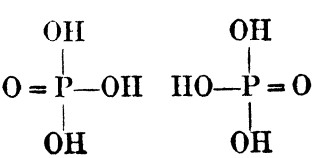


Kekulé has suggested for benzene a still more complex 'ring' formula, which trivial though it may appear has had an immense influence upon the course of modern organic chemistry.

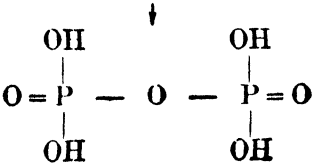
The idea of valency can be applied to **groups** of elements, or 'radicles' (historically, an incipient form of the doctrine—the theory of types—was applied to radicles first); thus the radicles $-OH$, $-HSO_4$, NH_4-, C_2H_5- (ethyl) are monovalent, $=SO_4$ is divalent, $\equiv PO_4$ is trivalent, and so on. If we represent sulphuric acid as $SO_2(OH)_2$ then the radicle 'sulphuryl' ($=SO_2$, not sulphur dioxide) is divalent. Sulphur is then hexavalent in both the anhydride and the acid. Sulphuric acid is at the same state of oxidation as its anhydride, and the view finds expression in the above 'rational' formulae.

Rational formulae are a favourite means of representing the atomic composition of acids, and serve to accentuate the prevailing opinions concerning them. (The student must resist the temptation to regard these formulae as pictures of molecules, all they portray are hypotheses.) Thus in phosphoric oxide and the phosphoric acids, phosphorus is undoubtedly pentavalent, and the changes in dehydration are by some represented thus:

2 molecules of *Orthophosphoric acid* when heated to 215° C. become



1 molecule of *Pyrophosphoric acid*; and this when strongly heated becomes



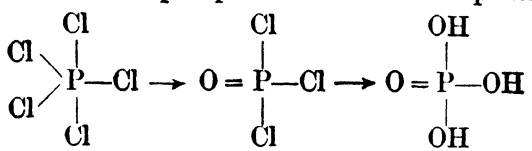
2 molecules of *Meta-phosphoric acid*, which are formed by



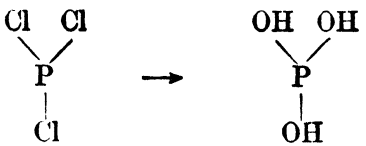
the hydration of 1 molecule of *Phosphoric anhydride*



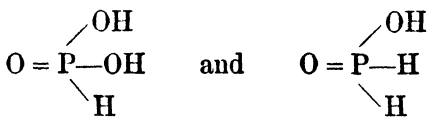
And the formation of phosphoric acid from the pentachloride



Similarly, the formation of phosphorous acid



But some chemists prefer to regard phosphorus as pentavalent in all its acids, and attribute to this, their lessened basicity



(phosphorous acid) (hypophosphorous acid)

The whole subject of valency is full of difficulties and we will not pursue it further, suffice to point out that:

(1) Amongst metals the divalent condition is the commonest.

(2) Some elements have several valencies (or do not always exert their maximum valency). Sulphur is divalent (H_2S), tetravalent (SO_2), hexavalent (SO_3).

(3) Elements having the same valency are frequently similar in chemical characteristics. Examples: the halogens, the alkali metals, the alkaline earths.

(4) When an element has more than one valency, the two (or more) series of compounds are usually totally dissimilar (the ferrous and ferric salts), whilst each series *may*

be very similar to the compounds of *other* elements of the same valency; striking examples of this will be found in Chapter XXVIII.

Here we may mention that the cuprous compounds resemble the mercurous compounds, and the cupric compounds resemble the mercuric compounds far more than the cuprous resemble the cupric, or the mercurous resemble the mercuric compounds. Another instance is supplied by lead and tin. Divalent lead and tin resemble each other to some extent and the tetravalent compounds of each are even more alike, but the two series of the tin or of lead compounds are totally dissimilar. In addition, the tetravalent compounds, especially the chlorides ($PbCl_4$ and $SnCl_4$) resemble those of silicon and carbon $SiCl_4$, CCl_4—all are liquids; and in the divalent condition the lead compounds show some resemblance to the barium compounds, $BaSO_4$, $BaCl_2$ etc.

The student should form his own opinions on this point by studying, with the aid of reference books, the cases cited.

CHAPTER XXV.

OTHER COMPOUNDS OF SULPHUR.

SOME of the properties of sulphurous and sulphuric acids were studied in Chapter VII. In this, some further reactions of these compounds and some of their derivatives will be described. Sulphydric acid was sufficiently dealt with in Chapter VIII. In the former chapter it was shown how magnesium reacts with a solution of sulphurous oxide (which contains sulphurous acid) to liberate hydrogen and to form a magnesium sulphite. But when a solution of sulphurous acid is shaken with zinc dust, the metal dissolves to form a yellowish solution but no gas of any kind is evolved; the colour soon disappears if air is present, but, when air is excluded, the solution remains permanently orange. This solution has reducing powers far surpassing those of sulphurous acid. When brought in contact with a gaseous mixture containing oxygen, this gas is absorbed, the orange colour of the solution is discharged, and zinc sulph*ite* is left in solution.

Hyposulphurous acid.

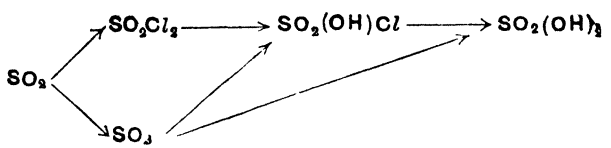
The yellow coloration has been shown to be due to the formation of a salt whose composition is represented by the formula ZnS_2O_4. We may represent its formation thus, $2H_2SO_3 - O = H_2S_2O_4 + H_2O$. The salt is therefore called zinc **hypo**-sulphite: a corresponding sodium salt has also been obtained. The hyposulphites are not important; they are mentioned here in order to avoid confusion with the very important salt which photographers call 'Hypo.'

The raising of sulphur from the tetra- to the hexavalent condition by the oxidation of sulphur dioxide to trioxide has already been described. The same *condition* can be reached by the addition of chlorine to form **sulphuryl chloride** $(SO_2)Cl_2$.

Oxidation of sulphur dioxide.

The preparation is performed by the catalytic aid of camphor. Dry sulphur dioxide is passed into a dry closed flask containing camphor. When the camphor absorbs no more of the gas the supply of sulphur dioxide is stopped, and dry chlorine is passed over the camphor. In these circumstances the chlorine and sulphur dioxide combine; the two gases may be passed alternately over the camphor until a convenient quantity of chloride has been formed. The contents of the flask are then gently heated, and the evolved sulphuryl chloride is condensed in a receiver.

This is a colourless, pungent liquid, B.P. = 69° C. It dissolves in cold water, but reacts with it when the temperature is raised, to form hydrochloric acid and 'chlor-sulphonic acid,' $SO_2Cl_2 + HOH = SO_2Cl(OH) + HCl$. **Chlor-sulphonic acid** was first obtained by the direct combination of sulphur trioxide and dry hydrochloric acid gas, $SO_3 + HCl = SO_3HCl$. It is a colourless liquid, boiling at 152° C. It reacts violently with water to form sulphuric and hydrochloric acids. It will be seen that the behaviour of sulphuryl chloride is similar to that of phosphoryl chloride ($POCl_3$). Chlor sulphonic acid may be regarded as a hydroxyl compound. These two compounds of sulphur are important only for their bearing upon the rational formula of sulphuric acid.



Sulphur trioxide combines with nitrous acid (HNO_2) also, to produce **nitrosyl-sulphuric acid,** which, like the two compounds mentioned above, may be regarded as a derivative of sulphuric acid. It is usually represented as

$$O \gg S \begin{matrix} \diagup OH \\ \diagdown O-N=O, \end{matrix}$$

on the addition of water two acids are formed

$$(SO_3HNO_2 \longrightarrow H_2SO_4 + HNO_2),$$

Damp sulphur dioxide reacts with it to form sulphuric acid and nitric oxide $2SO_3HNO_2 + SO_2 + 2H_2O = 3H_2SO_4 + 2NO$.

Production of sulphuric acid.

Sulphuric acid is probably the most generally important chemical substance made, three to four millions of tons are produced every year; some reference must therefore be made to its manufacture. The **contact**

process illustrated in Chapter VII. is coming into favour, but, at present, by far the greater proportion is made by what is known as the **lead chamber process**, which was begun in Birmingham in 1746. As to the exact chemical reactions which take place, the greatest diversity of opinion has existed, and the controversy still proceeds. The explanations offered by Davy and Berzelius are comparatively simple, those that follow grow in complexity. Some are based upon the experience that nitrosyl-sulphuric acid is likely to be formed; probably the reactions differ in the various parts of the plant. Simply, the reactions are due to the catalytic acceleration by the *oxides of nitrogen* of the oxidation of sulphur dioxide.

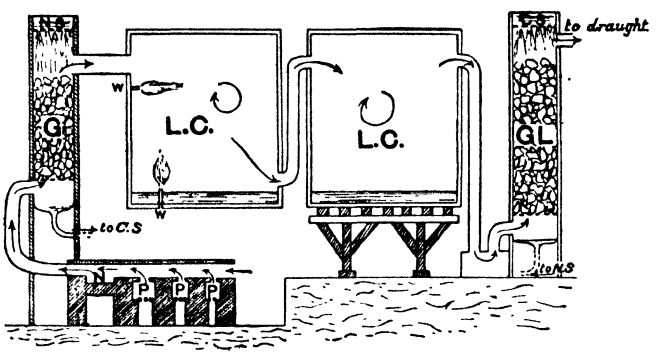


Fig. 113 (crudely diagrammatic).

The plant is complicated. Air enters at **the pyrites burners** (P). The iron pyrites are burnt, in an *excess* of air, to ferric oxide and sulphur dioxide

$$4FeS_2 + 11O_2 = 2Fe_2O_3 + 8SO_2.$$

The hot gases containing excess of air are made to circulate around the **nitre pots** (N)—which contain sodium nitrate and sulphuric acid; they accelerate by their heat the following reaction, $NaNO_3 + H_2SO_4 = NaHSO_4 + HNO_3$. The nitric acid fumes, joining the main current of gases, oxidise some of the sulphur dioxide, and are reduced to oxides of nitrogen. All the gases pass up the **denitrating tower** (G, the Glover tower); here they meet a downward stream of sulphuric acid in which oxides of nitrogen (probably nitrosyl-sulphuric

acid) are dissolved. By the action of sulphur dioxide, oxides of nitrogen are liberated

$$2SO_2(OH)(ONO) + SO_2 + 2H_2O = 3SO_2(OH)_2 + 2NO.$$

The excess air and the sulphur dioxide, together with the liberated nitric oxide, sweep aside into the **leaden chambers**, where they meet sprays of steam. In the lead chambers the main oxidation proceeds, and dilute sulphuric acid falls to the floor. The residual atmospheric nitrogen is drawn from the chambers up the **Gay Lussac tower** (GL), where it meets a shower of cold concentrated acid. This acid absorbs any of the oxides of nitrogen which may also have escaped. The 'nitrated' acid is pumped to the top of the Glover tower, where, during its descent, it gives up the dissolved nitrogen oxides. It collects at the bottom of the tower in a more concentrated condition. The chamber acid, 66°/₀, is concentrated to 94°/₀ in glass and platinum vessels successively. It cannot be obtained absolutely pure, for it begins to decompose when within 1½°/₀ of purity. From this state the pure compound is obtained by freezing—when it settles out as crystals—or, by the addition of the requisite proportion of the anhydride. Pure hydrogen sulphate begins to decompose at 30° C., losing sulphur trioxide until it is again 98½°/₀ pure; this may be heated without change to 338° C., when it distils.

Sulphuric acid absorbs sulphuric anhydride to form solutions of varying concentration. These solutions are known as **fuming sulphuric acid.** When strongly cooled the fuming acid deposits crystals (M.P. = 35° C.) of the formula $H_2S_2O_7$. This substance is regarded as a true acid, analogous to pyrophosphoric acid. Unlike pyrophosphoric acid, it has not even a temporary existence in solution,

Disulphuric acid.

$$H_2S_2O_7 + H_2O = 2H_2SO_4, \text{ compare } H_4P_2O_7 + H_2O = 2H_3PO_4.$$

Its salts are obtained by methods similar to those for obtaining pyrophosphates—the hydrogen sulphates are heated.

$$2KHSO_4 = K_2S_2O_7 + H_2O, \text{ compare } 2Na_2HPO_4 = Na_4P_2O_7 + H_2O.$$

Hence the term pyrosulphates. Like their acid, and unlike the pyrophosphates, they do not retain their individuality in solution, but pass back at once to the hydrogen sulphate.

$$K_2S_2O_7 + H_2O = 2KHSO_4.$$

A pyrosulphate, when heated to redness, loses sulphur trioxide (which dissociates into gaseous sulphur dioxide and oxygen), and is transformed into the normal (ortho) sulphate.

$$K_2S_2O_7 = K_2SO_4 + SO_3.$$

It will be seen that pyro-acids may be regarded as **condensed acids.** We shall learn that the formation of condensed acids is especially characteristic of the weaker acids; in some cases they or their salts are very complex. Condensed acids, which are formed by loss of one molecule of water from two molecules of ordinary acid, are called **di-acids,** hence this acid is disulphuric acid; like sulphuric acid it is dibasic.

Prior to 1746 a fuming sulphuric acid, having approximately the composition represented by the formula, was made at Nordhausen in Saxony (hence it was called Nordhausen acid). It was obtained by the distillation of green vitriol, $FeSO_4$, H_2O, $6H_2O$. The crystals were first roasted in air, when they lost six-sevenths of their water of crystallisation and were oxidised to basic ferric sulphate.

$$2FeSO_4,\ H_2O + O = 2Fe(SO_4)OH + H_2O.$$

This substance was then heated in retorts, and the gases evolved were condensed in suitable receivers.

$$2FeSO_4(OH) = Fe_2O_3 + \overbrace{H_2O + 2SO_3}.$$

Electrolysis of hydrogen sulphate.

When very dilute sulphuric acid is electrolysed, hydrogen and oxygen are evolved in the volume proportion of 2 : 1. If moderately concentrated acid is electrolysed in the cold with a very small anode (to produce a high current density), the oxygen evolved falls noticeably below the former proportion, and the solution acquires well marked oxidising properties. When a saturated solution of potassium hydrogen sulphate is electrolysed under the same conditions, a white crystalline salt separates out of the solution (after some time) beneath the anode. This substance is less soluble than the hydrogen sulphate. When heated it loses 35·6% of its weight, leaving a residue of normal potassium sulphate. Both sulphur trioxide and *oxygen* are expelled, but no water. The composition of the salt corresponds to the formula KSO_4. It is apparently the salt of an acid more oxidised than sulphuric acid, which, we may believe, is formed by the electrolysis of moderately concentrated sulphuric acid. The salt is called potassium **persulphate,** and the acid, **persulphuric acid.** Analogous compounds of

ammonium and barium also are known. Their acidified solutions are used for oxidising purposes. (Treat potassium iodide and ferrous sulphate with the salt.)

The formation of the salt may be represented by the equation $2KHSO_4 + O = 2KSO_4 + H_2O$[1]; and the decomposition by $4KSO_4 = 2K_2SO_4 + 2SO_3 + O_2$.

A simple, but efficient, form of apparatus for the preparation of the potassium salt is the following (Fig. 114). A large boiling tube is partly filled with a saturated solution of potassium hydrogen sulphate. A wide glass tube open at both ends is placed within it, this serves as a partial diaphragm. Within this and near the bottom is the anode, consisting of half-an-inch of platinum wire sealed into a glass tube. Encircling the diaphragm is the kathode, a ring of platinum wire just immersed in the solution (in order that the nascent hydrogen shall have no chemical effect). The boiling tube is placed vertically in water kept cold with ice. A current of 1 ampère is suitable.

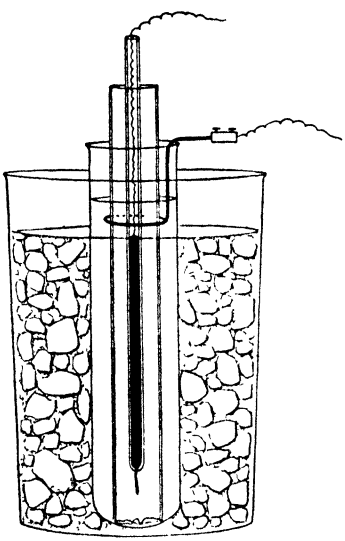


Fig. 114.

In the same manner potassium percarbonate, which also has strong oxidising power, is prepared by electrolysis of cold saturated solution of hydrogen potassium carbonate

Thiosulphate of sodium.

When sodium sulphite solution is exposed to the air it gradually absorbs oxygen to form sodium sulphate $2Na_2SO_3 + O_2 = 2Na_2SO_4$. When sodium sulphite solution is boiled with flowers of sulphur, some of

[1] The ionic theory provides another explanation of the formation. Suppose the ions formed (concentrated solution) are H and HSO_4'. The hydrions are discharged and escape. The hydrosulphanions are discharged at the small anode where they combine together. $2HSO_4' = H_2S_2O_8$.

Similarly for the potassium salt. The true formula is, for other reasons, believed to be twice the empirical formula.

the latter is dissolved, and there settle from the concentrated solution fine large colourless crystals, which differ from the sulphite in having a cool taste and a neutral reaction to litmus. The composition of the substance corresponds to the formula $Na_2S_2O_3$, $5H_2O$; it differs from sodium sulphate in that the sulphite molecule has been oxidised by an atom of sulphur instead of an atom of oxygen, hence its name sodium **thio**sulphate[1].

To prepare the salt, a solution of sodium carbonate is divided into two equal parts, one part is saturated with sulphur dioxide,

$$Na_2CO_3 + 2H_2SO_3 = 2NaHSO_3 + \overbrace{CO_2 + H_2O}.$$

The solution of acid sulphite is freed from excess sulphurous acid by heating, and to it is added the second quantity of carbonate to form the normal sulphite, $2NaHSO_3 + Na_2CO_3 = 2Na_2SO_3 + \overbrace{CO_2 + H_2O}$. The solution of normal sulphite is then boiled with flowers of sulphur, and afterwards filtered, concentrated and allowed to cool. $Na_2SO_3 + S = Na_2S_2O_3$.

Sodium thiosulphate is commonly known as '**hypo**,' a very shortened form of sodium hyposulphite, its original name. The latter name is quite inadmissible, for, although a hyposulphite should contain a smaller percentage of oxygen —or its equivalent—than a sulphite, thiosulphate is at the *same* stage of oxidation as the sulphate, that is, higher than the sulphite. Thiosulphuric acid has never been isolated, even in dilute solution; on the addition of an acid it is decomposed

$$Na_2S_2O_3 + 2HCl = 2NaCl + \overbrace{H_2O + SO_2 + S}.$$

[Observation. Mix very dilute solutions of the substances and note what happens; mix solutions of increasing concentration.]

The thiosulphates are also formed by the oxidation of persulphides in the air; some of the sodium thiosulphate on the market is obtained from calcium thiosulphate formed in this manner $2CaS_2 + 3O_2 = 2CaS_2O_3$. Potassium thiosulphate forms a considerable proportion of the solid residue of exploded gunpowder (Chapter XVIII.).

Sodium thiosulphate finds extensive application both in the arts and in the laboratory. It is used largely as a 'fixing' agent in photography because it dissolves out the unchanged silver bromide, probably forming a sodium silver thiosulphate $Na_2S_2O_3 + AgBr = NaBr + NaAgS_2O_3$ (?).

The salt is also used as an 'anti-chlor' in order to remove the excess of chlorine used in bleaching of paper.

$$Na_2S_2O_3 + 4Cl_2 + 5H_2O = Na_2SO_4 + H_2SO_4 + 8HCl.$$

[1] $\theta\epsilon\hat{\iota}o\nu$ = heavenly bolt = sulphur.

Bromine reacts in precisely the same manner as chlorine, but iodine behaves altogether differently.

When a solution of iodine (in potassium iodide) is added to a solution of 'thio,' drop by drop, the colour of the iodine disappears. If the addition of the iodine is continued until a permanent colour is obtained and the solution is evaporated, sodium iodide (cubes) is recovered from solution; in addition, another salt having the formula $Na_2S_4O_6$ is formed. This substance is called **sodium tetra-thionate.**

The thionates are the salts of a series of acids of sulphur which have the general formula $H_2S_xO_6$, where x may be 2, 3, 4, or 5, di-, tri-, tetra-, and penta-thionic acids. The special nomenclature was necessary in consequence of their peculiar composition.

The reaction is quantitative and of the greatest importance.

$$\underset{\text{(colourless)}}{2Na_2S_2O_3} + \underset{\text{(brown)}}{I_2} = \underset{\text{(colourless)}}{Na_2S_4O_6} + \underset{\text{(colourless)}}{2NaI}.$$

By means of the reaction the concentration of any solution of iodine may be volumetrically estimated, and as iodine is liberated from potassium iodide by many oxidising substances one may accurately estimate the latter by this indirect method. The volumetric operations with iodine are called **'Iodometry.'**

Thiosulphate solutions are always standardised against a standard solution of iodine. The latter is made by weighing out pure iodine, dissolving it in potassium iodide solution, and diluting to the correct volume. In order to standardise a solution of 'thio,' it is run into the standard iodine until the latter is just yellow; the end point is accurately determined by the addition of a few drops of dissolved starch—blue coloration—when the iodine is pale yellow, and completing the addition of thio until the blue colour just disappears. As a solution of thio slowly decomposes on standing, its concentration must be redetermined for each fresh series of experiments. One generally arranges to finish a titration by the addition of 'thio' to iodine. When, as sometimes happens, the solution must be slightly alkaline, the acidity of the solution may be destroyed by the addition of sodium hydrogen carbonate; excess of the latter has no chemical action on iodine, but caustic soda, or even carbonate, dissolves iodine (Chapter XXIII.).

$$6NaOH + 3I_2 = 5NaI + \underset{\text{(colourless)}}{NaIO_3} + 3H_2O.$$

Amongst the substances which may be estimated by Iodometry are chlorine and bromine, $Cl_2 + 2KI = 2KCl + I_2$, and, therefore also, substances which yield or liberate chlorine. For instance, to estimate a peroxide, a known weight of the

latter is heated with concentrated hydrochloric acid (Fig. 115), and the liberated chlorine is passed into a solution of potas-

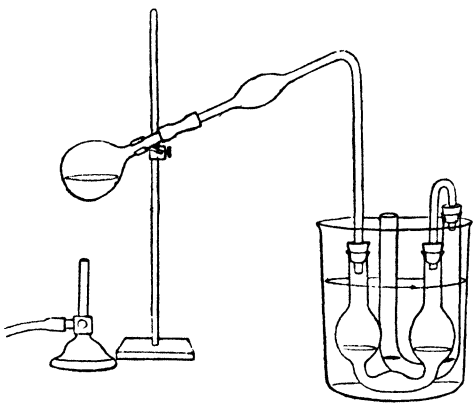


Fig. 115.

sium iodide, the displaced iodine is collected and a known proportion of it titrated with standard 'thio.'

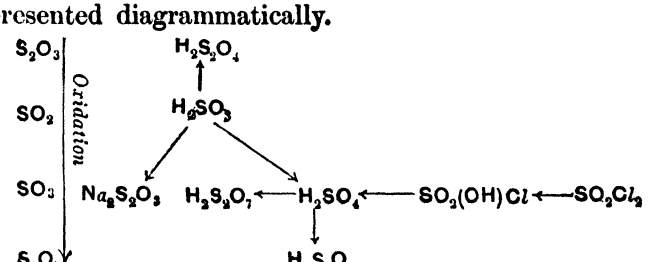
$$\underset{87}{MnO_2} \longrightarrow Cl_2 \longrightarrow \underset{254}{I_2}.$$

The 'available' chlorine in bleaching powder may be estimated by mixing a dilute solution of the powder with potassium iodide solution, and acidifying. The liberated iodine is then titrated with 'thio.' Iodine is also used to estimate arsenous and antimonous acids.

$$As_2O_3 + 2I_2 + 2H_2O = As_2O_5 + 4HI.$$

The solution of the oxide is 'neutralised' with sodium hydrogen carbonate, and the sodium arsenite is oxidised to sodium arsenate.

The relations between the oxyacids of sulphur may be represented diagrammatically.



Salts of thio acids.

In addition to the above, a few salts of acids, in which the place of oxygen is entirely taken by sulphur—the thio- or sulpho-acids (not thionic acids)—must be mentioned, because of their analytical importance.

Arsenic (at. wt. = 75) and antimony (at. wt. = 120) are two elements related to phosphorus in the same manner as bromine and iodine are related to chlorine, and they show similar gradation of properties with the increase of atomic weight. Arsenic and antimony are metallic in appearance but not in properties, for their oxides are acid forming. The strengths of the acids diminish with the increase of atomic weight of the respective elements. Arsenous oxide dissolves in caustic potash to form potassium met-arsenite, $KAsO_2$ (compare KNO_2). And from arsenic acid, potassium arsenate may be obtained, K_3AsO_4. Analogous with the two oxides of arsenic, are two sulphides, As_2S_3 and As_2S_5. These sulphides dissolve in potassium, sodium, and ammonium sulphides to form soluble **thioarsenites** and **thioarsenates.**

$$6KSH + As_2S_5 = 2K_3AsS_4 + 3H_2S,$$
$$6KSH + As_2S_3 = 2K_3AsS_3 + 3H_2S.$$

These soluble salts are decomposed by dilute acids

$$2Na_3AsS_4 + 6HCl = 6NaCl + 3H_2S + As_2S_5.$$

Thioantimonites and thioantimonates of analogous composition also exist. Arsenic is more distinctly non-metallic than antimony, and its sulphide will dissolve in sodium carbonate to produce the *analogous* **oxy**arsenite and **thio**arsenite

$$As_2S_3 + 3K_2CO_3 = \underset{\text{(arsenite)}}{K_3AsO_3} + \underset{\text{(thio-arsenite)}}{K_3AsS_3} + 3CO_2$$

Tin has two oxides; the lower, SnO, is basic (metallic element), the higher, SnO_2, is acidic (non-metallic element). Of the analogous sulphides, SnS (yellow) and SnS_2 (brown), the latter alone will dissolve in ammonium sulphide to produce ammonium thiostannate, $(NH_4)_2S + SnS_2 = (NH_4)_2SnS_3$, but the lower sulphide will dissolve in ammonium *per*sulphide because it is oxidised thereby to the tetravalent state.

$$\underset{\text{(yellow sulphide)}}{(NH_4)_2S_2} + \underset{\text{(stannous)}}{SnS} = \underset{\text{(stannate)}}{(NH_4)_2SnS_3}$$

Judging by the foregoing reactions, we may perhaps conclude that some kind of relation exists between oxygen and sulphur. This idea will probably be strengthened by a comparison of the formulae of their compounds. The following is an incomplete list:

Water	H_2O	H_2S	**Hydrogen sulphide**
oxides	PbO	PbS	sulphides
hydroxides	NaOH	NaSH	hydrosulphides
alcohol	C_2H_5OH	C_2H_5SH	mercaptan
ether	$(C_2H_5)_2O$	$(C_2H_5)_2S$	thio-ether
Hydrogen peroxide	H_2O_2	H_2S_2	**Hydrogen persulphide**
metallic peroxides	CaO_2	CaS_2	metallic persulphides
Carbon dioxide	CO_2	CS_2	**Carbon disulphide**
oxysulphide	—COS—		
carbonates	Na_2CO_3	Na_2CS_3	thiocarbonates
thionyl-chloride	$SOCl_2$	S_2Cl_2	sulphur chloride
Sulphates	Na_2SO_4	$Na_2S_2O_3$	**Thiosulphate**
arsenate, &c.	Na_3AsO_4	Na_3AsS_4	thioarsenate, &c.

The parallelism of these formulae is significant, but sulphur shows more decided relations with selenium (at. wt. 79·2) and tellurium (at. wt. 127·6). The similarity of these three elements is even more striking than that of the halogens and of the phosphorus group. It may be remarked that as fluorine and nitrogen take detached positions in the Halogen and the Phosphorus families, so oxygen might be regarded as a detached member of the Sulphur family.

Isomorphism.

Mixed salts.

In the Introductory Chapter, we mentioned that some mixtures of soluble salts may be separated by the process of fractional crystallisation. In many cases it is difficult, and in some cases it is impossible, to separate salts from their mixed solutions, even where the conditions may seem favourable. For instance, saturated solutions of green vitriol ($FeSO_4 7H_2O$) and Epsom salt ($MgSO_4 7H_2O$) contain, at 10° C., 61 and 31 parts of the respective salts per 100 parts of water, yet, no matter in what proportion the solutions are mixed, every crystal that separates from the solution contains both magnesium and ferrous sulphates in proportion which depends upon that of the solution. Such crystals are called '**mixed**' crystals.

It is obvious that crystals which can vary in composition in this manner cannot have a definite formula, but it is convenient to ignore this and to represent them by a formula; $(MgFe)SO_4 7H_2O$ is adopted, meaning that the magnesium and iron vary in the sense that they can replace each other *in equivalent proportions.*

Not only can these two salts form mixed crystals, but, if a crystal of either salt is placed in the saturated solution of the

other, the crystal will continue to grow, the second salt being deposited without change of form upon the first—the white magnesium sulphate upon the green ferrous sulphate, or the green upon the white salt. Such a crystal is said to be an **'overgrowth.'**

Ferrous and magnesium sulphates are not peculiar in this power of forming mixed crystals and overgrowths, for *any* two of the following sulphates will behave similarly

$MgSO_4 7H_2O$ $ZnSO_4 7H_2O$ $FeSO_4 7H_2O$ $MnSO_4 7H_2O$
$CoSO_4 7H_2O$ $NiSO_4 7H_2O$.

It will be noticed that all these salts have the same general formula, $DSO_4 7H_2O$. Moreover they can all crystallise in forms almost identical, belonging to the rhombic system. Such crystals are said to be **isomorphous**[1]. But whilst ferrous sulphate can, and does, crystallise in the rhombic form, it more frequently crystallises in the oblique system. It is said to be **dimorphous.** When mixed crystals of ferrous and magnesium sulphates are examined, it is found that those formed from solutions richer in Epsom salt are of the *rhombic* form, but those deposited from solutions richer in green vitriol are of the *oblique* form.

The two salts are therefore *isodi*morphous. A fair number of salts are isodimorphous as well as isomorphous. Mixed crystals are also deposited when a mixed solution of green vitriol ($FeSO_4 7H_2O$) and blue vitriol ($CuSO_4 5H_2O$) is concentrated. Now these crystals belong to different systems, the former to the oblique and the latter to the triclinic system, and moreover, since the molecules contain a different number of water molecules, they have not analogous formulae. But the crystals deposited from solutions richer in green vitriol assume the form of green vitriol and have the formula $(FeCu)SO_4 7H_2O$, whilst the crystals which are deposited from solutions richer in blue vitriol have the formula and shape of blue vitriol $(CuFe)SO_4 5H_2O$.

Isomorphous series are not by any means confined to sulphates, thus all the halides of sodium crystallise in cubes (NaCl, NaBr, NaI). The members of the following two series of carbonates are found native, both free and mixed.

I	II
$CaCO_3$ (arragonite)	$CaCO_3$ (calcite)
$SrCO_3$	$MgCO_3$ (magnesite)
$BaCO_3$	$ZnCO_3$
$PbCO_3$	$MnCO_3$
	$FeCO_3$ (chalybite)

[1] ἴσως = equal, μορφή = form.

Law of isomorphism.

In 1819 Mitscherlich drew attention to the rule that substances which are isomorphous have analogous composition. "The same number of atoms combined together in the same manner produce the same crystalline form; the crystalline form is independent of the chemical nature of the atoms, and is determined only by their number and mode of combination." He based this law—the Law of Isomorphism—upon the similarity in form and composition of the following compounds, belonging to the tetragonal system H_2KPO_4, H_2KAsO_4, $H_2(NH_4)PO_4$.

In the early days of the atomic theory this law was of considerable value in deciding between alternative formulae for compounds whose crystalline form was known. By the adoption of a definite formula for a compound, one fixes the atomic weights of the constituent elements; a striking instance of this will be given in Chapter XXVIII. At the present day the law is rarely of value for the purpose, the less so because further investigation has revealed important exceptions to it. Substances are said to be truly isomorphous if

(1) they have very similar crystalline form;

(2) they can form mixed crystals whose composition can vary within wide limits, and whose physical properties vary uniformly with the composition;

(3) they can form overgrowths.

Double salts.

Potassium and magnesium sulphates form crystals both of which belong to the rhombic system but are of different habit; when their solutions are mixed, crystals separate out containing both salts. These salts are, however, *not* isomorphous, for, although the solution may vary in composition, between certain limits, the crystals have invariably the composition represented by the formula $K_2SO_4, MgSO_4, 6H_2O$; moreover, these crystals belong to the *monoclinic* system. The substance of this formula is then a true compound. In similar circumstances potassium sulphate will form with certain other sulphates similar crystals of the general formula $K_2SO_4DSO_46H_2O$, where D = Mg, Zn, Cd, Fe, Co, Ni, Mn, Cu. Such crystals, which, formed from solutions of *varying* proportions, contain their constituents in molecular proportions, are called '**double**' salts. It must be borne in mind that the potassium sulphate is *not* isomorphous with the second member, and the two sulphates have not analogous formulae, but that the monoclinic double salts are isomorphous amongst themselves and will form both mixed crystals

and overgrowths. That is to say, if solutions of potassium and zinc sulphates are mixed in almost any proportion, a double salt of definite molecular composition will be formed, but, if solutions of the double salts $K_2SO_4FeSO_46H_2O$ and $K_2SO_4ZnSO_46H_2O$ are mixed, the crystals deposited are mixtures of both the double salts in proportion depending upon the proportion in solution.

A more important series of double salts is the **'alums,'** named after the most important member, Alum. The alums have the general formula M_2SO_4, $T_2(SO_4)_324H_2O$ where M = K, (NH_4), Ag, Na and T = Al, Fe, and some others to be mentioned in Chapter XXVIII. Ordinary 'alum' has the formula $K_2SO_4Al_2(SO_4)_324H_2O$. The alums crystallise in regular octohedra; they are isomorphous amongst themselves, forming both mixed crystals and overgrowths.

CHAPTER XXVI.

HYDROGEN PEROXIDE.

THENARD discovered peroxide of hydrogen (eau oxygénée) in 1818 as he was attempting to oxidise various acids by means of barium peroxide. A solution of hydrogen peroxide may easily be obtained by his method. Pure hydrated barium peroxide (BaO_2, $8H_2O$) is added, little by little, to sulphuric acid diluted to five times its volume. Or it may be formed by adding the barium dioxide, gradually in small quantities, to water through which a current of carbon dioxide is constantly passing. Both methods of preparation suggest the following equations, and the formula H_2O_2 for hydrogen peroxide.

$$BaO_2 + H_2SO_4 = BaSO_4 + H_2O_2,$$
$$BaO_2 + H_2CO_3 = BaCO_3 + H_2O_2.$$

When impurities will not interfere with reactions, other methods may be substituted for the above:

(1) dilute hydrochloric acid may be used

$$BaO_2 + 2HCl = H_2O_2 + BaCl_2 \text{ (dissolved)},$$

(2) or, sodium peroxide may be dissolved in cold dilute hydrochloric acid

$$Na_2O_2 + 2HCl = 2NaCl + H_2O_2.$$

By distilling, under reduced pressure, the solution prepared by the first method, there has been obtained in recent times a 90½ per cent. solution of the peroxide; and this, on a second distillation, attained 99½ per cent. purity. When the latter was strongly cooled, pure solid hydrogen peroxide separated out. Solid hydrogen peroxide melts at $-2°$ C. to a colourless and syrupy liquid which is unstable towards heat. It breaks

down into water and oxygen, $2H_2O_2 = 2H_2O + O_2$. This reaction takes place with evolution of heat, that is, it is exothermic; but inasmuch as only 23,200 calories are liberated when 16 grams of oxygen are evolved, it follows that hydrogen peroxide is exothermic.

$$2H_2O_2 = O_2 + 2H_2O + (2 \times 23{,}200) \text{ calories},$$
$$-2x \quad -(2 \times 68{,}400)$$
$$\therefore x = +45{,}200 \text{ calories}.$$

The solution is a very effective oxidising agent; sulphides are oxidised to sulphates (compare ozone, &c.)

$$\underset{(black)}{PbS} + 4H_2O_2 = \underset{(white)}{PbSO_4} + 4H_2O;$$

This reaction explains the action of the peroxide in 'restoring' oil paintings in which lead carbonate has been transformed into sulphide.

The peroxide oxidises potassium iodide to iodine (compare ozone, &c.) (see end of chapter, p. 329).

$$\underset{(neutral)}{2KI} + H_2O_2 = I_2 + \underset{(alkaline)}{2KOH}$$

Both reactions are useful for indicating the presence of hydrogen peroxide, but other oxidising substances will act similarly. There is one colour reaction peculiar to hydrogen peroxide, this is the oxidation of titanium dioxide to the brown trioxide, $TiO_2 + H_2O_2 = TiO_3 + H_2O$. The titanic oxide is dissolved in concentrated sulphuric acid, and some of the solution to be tested is added to it.

Hydrogen peroxide is formed in nature during some slow oxidations. This can readily be imitated by a simple experiment in the laboratory. Some thin sheet lead is well scraped, and placed in aerated distilled water (tap water does not answer); in a few days lead hydroxide is formed, which falls from the lead in white spangles. The solution will generally be found to answer to the test for hydrogen peroxide. Schonbein has shown that in this case the autoxidation is quantitative.

$$Pb + 2H_2O + O_2 = Pb(OH)_2 + H_2O_2.$$

A solution of hydrogen peroxide gradually decomposes with liberation of oxygen, but it is more stable when acidified. The decomposition of the peroxide is catalytically accelerated by contact with finely divided platinum or manganese peroxide (the preparation of this is given in the next chapter).

The reaction affords a simple gasometric method of determining the concentration of a solution of hydrogen peroxide.

A measured volume of the commercial preparation is placed in a small conical flask with a delivery tube leading to a gas collecting tube (Fig. 116). When all is ready, a little manganese peroxide is added, and the stopper of the flask is instantly replaced; or, to avoid opening the flask, the solid oxide may be shaken out of a small tube suspended from the cork. The volume of the oxygen expelled is measured and its weight is calculated. $2H_2O_2 = 2H_2O + O_2$. Hydrogen peroxide is also decomposed by contact with silver oxide; the reaction is peculiar however, for the silver oxide is itself decomposed also.

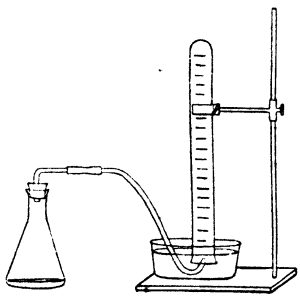


Fig. 116.

$$Ag_2O + H_2O_2 = 2Ag + H_2O + O_2.$$

Ozone and hydrogen peroxide similarly reduce each other,

$$O_3 + H_2O_2 = H_2O + 2O_2.$$

Metallic peroxides.

The metallic peroxides can be prepared by the action of hydrogen peroxide upon lower oxides, in the presence of a caustic base.

$$Mn(OH)_2 + H_2O_2 = MnO_2 + 2H_2O.$$

The peroxides may be prepared by several methods: sodium and potassium peroxides are formed by heating the respective metals in dry oxygen, or in air freed from carbon dioxide; barium peroxide is formed by heating baryta in air (Brin's process); calcium peroxide is formed by adding hydrogen peroxide to slaked lime. These peroxides do not decompose hydrogen peroxide, on the contrary it may be prepared from them by the action of dilute acids. Other peroxides, including those of lead and manganese, decompose hydrogen peroxide but do not yield it by interaction with acids: these may be formed by the action of hydrogen peroxide on their lower oxides, or by the oxidising action of chlorine (Chapter V.) or bleaching powder (Chapter XXI.).

Formula.

The empirical formula of hydrogen peroxide was determined by carefully heating a weighed quantity of the pure substance, and collecting the oxygen

evolved. The oxygen collected corresponded very nearly to that calculated from the hypothetical formula. This result however only fixes the composition of the substance as H_xO_x. That the formula is actually H_2O_2 has been proved by a method to be described in the following pages.

Molecular weights of dissolved substances.

Depression of the freezing point.

It is generally known that sea water freezes *below* 0° C., and that pure water separates out from it as ice. This is true of all *dilute* solutions, hence, for them, we may say that the dissolved substance 'depresses' the freezing point of water. Blagden, in 1778, came to the conclusion that, in general, the **lowering of the freezing point is proportional to the concentration of the solution.** The subject was again studied by de Coppet, in 1872, and more thoroughly by Raoult, in 1882. They confirmed Blagden's conclusion. Raoult, who used many solvents, showed that the freezing point of an organic solvent is depressed to the same extent when equal masses of it contain different substances (which are neither basic nor acidic) in molecular proportions. That is to say, that the **molecular masses of different substances,** when dissolved in the same mass of solvent, **produce the same lowering.** With water as solvent he obtained perplexing results; organic compounds of an indifferent nature gave depressions in agreement with his law, but acids, bases, and salts lowered the freezing point more than he expected.

Raoult determined the depressions produced by a great number of substances. From the depressions produced in solutions, made by dissolving known masses of substances whose molecular weights he knew, he calculated what depression would be produced if it were possible to dissolve the molecular weights in grams of these substances in 100 grams of the different solvents. This 'molecular depression' he designated as *K*. For water it is 18·9° C., for acetic acid 38·8° C., for benzene 50° C., and for phenol 75° C.

It must be borne in mind that Raoult, in order to obtain these constants, *assumed* that his laws would still hold true for such concentrated solutions; in practice, they do *not.* But the idea is a convenient fiction, for, by means of it, we may determine empirically the molecular weights of substances whose vapour densities cannot be found. We have only to find the freezing points of their *dilute* solutions of known concentration.

Thus ·76 gram of di-nitro-benzene, dissolved in 28·2 grams of acetic acid, was found to depress the freezing point of the solvent 0·68° C. The concentration per 100 grams of solvent is $\frac{·76 \times 100}{28·2}$. This concentration produces 0·68° C. lowering, and as the concentration that would produce 39° C. lowering (K) is the molecular weight.

$$\text{Molecular weight} : 39 = \frac{·76 \times 100}{28·2} : 0·68.$$

Whence the molecular weight = 154 (true value 168).

[In a second experiment ·774 gram of the same substance, dissolved in 28·114 grams of phenol, depressed the freezing point by 1·17° C. Find approximately the molecular weight.]

By Raoult's method, the molecular weight of hydrogen peroxide has been shown to be *about* 34 ($H_2O_2 = 34$). Similarly the formula N_2O_4 has been confirmed for nitrogen peroxide *dissolved* in acetic acid.

The most accurate apparatus for determining the depression is that of Beckmann and Raoult. A simplified form of this is illustrated in Fig. 117 (page 324).

The Beckmann thermometer reads to $\frac{1}{100}$th of a degree C. (large bulb and very fine capillary) and can be *set* for any small range of temperature by the use of the reservoir above. The thermometer is supported in the depression tube by means of a rubber stopper. The solution is agitated by the annular platinum stirrer. The depression tube is separated from the freezing mixture by the air (or alcohol) jacket. The freezing point of the solvent is first determined, a known weight of the substance is then added and dissolved, and the freezing point again determined. The weight of the tube and of the tube + solvent must also be known.

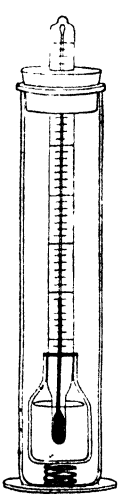


Fig. 118.

The **Eijkmann depressimeter** (Fig. 118) is easier to use, and is sufficiently accurate for most purposes. A small thermometer, reading to $\frac{1}{10}$° C., is ground into a small flask whose capacity is about 10 c.c. The weight of the depressimeter is known. Sufficient of the pure solvent is introduced to cover the bulb of the thermometer, and the apparatus is weighed again. It is placed in the cylinder, cooled slightly below the freezing point of the solvent, and then vigorously shaken. When the solvent freezes the mercury rapidly ascends in the capillary; the highest point it reaches is the freezing point of the solvent. A weighed quantity of the substance is now introduced and the freezing point determined as before.

Elevation of the boiling point.

Not only do dissolved substances depress the freezing point of a solvent, they also elevate its boiling point, provided the solvent alone is vaporised. Hence a dissolved substance diminishes the vapour pressure of the solvent (see Introductory Chapter).

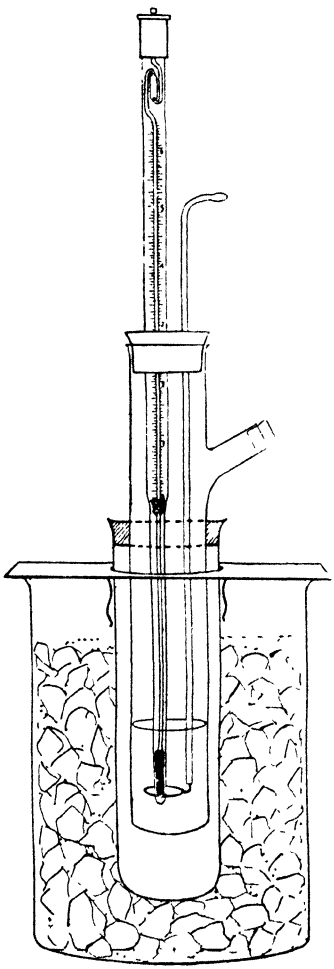


Fig. 117.

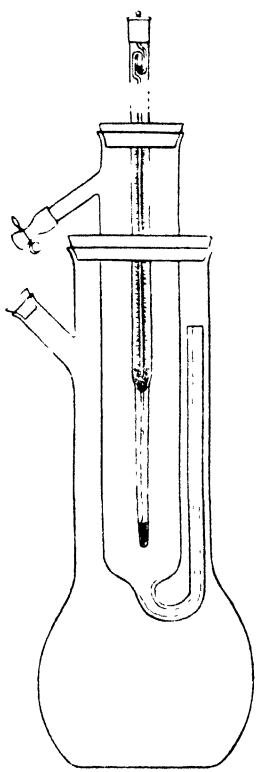


Fig. 119.

Raoult showed that his laws for the depression of the freezing point are applicable here also. That is to say, **the vapour pressure of a solvent is diminished equally by molecular**

quantities of different substances dissolved in equal masses of it. It may be shown (see Walker's *Physical Chemistry*) that the elevation of the boiling point is, for dilute solutions, very nearly proportional to the lowering of the vapour pressure. Hence approximate values may be obtained for the molecular weights of dissolved substances by measuring the elevation of the boiling point they produce. Raoult's constants, the 'molecular elevation,' are for water 5·2° C., for absolute alcohol 11·5° C., and for benzene 26·7° C. It is sometimes convenient to measure the *volume* of the solvent instead of weighing it. This alters the constant: thus K for 100 c.c. of absolute alcohol is 15·6° C.

To take an example, 2·99 grams of naphthalene dissolved in 61·4 grams of alcohol (that is 4·87 grams per 100 grams of solvent) produced an elevation of ·42° C.; hence

$$\frac{\text{molecular weight}}{11{\cdot}5} = \frac{4{\cdot}87}{{\cdot}42},$$

whence molecular weight is approximately 133·4 (true value 128).

[When ·629 gram resorcin was dissolved in 19·2 c.c. alcohol the boiling point was raised ·45° C. Find molecular weight.]

The method, as pursued by Beckmann, is very tedious in practice. The **Landsberger-McCoy modification** (Fig. 119) is sufficiently accurate, and much more rapid. The ebullition tube carries a side outlet, and, at its lower end, an upturned capillary. The tube is fixed air-tight in a flask which also has a side tube. The flask is partly filled with water, and about 20 c.c. of water is placed in the ebullition tube. The flask is placed on wire gauze and heated uniformly, the side tube remaining open until the water begins to boil. It is then closed, and the steam enters the inner tube through the capillary. By condensing, it raises the water to boiling. This temperature is noted. A weighed quantity of the substance, whose molecular weight is to be determined, is introduced into the ebullition tube, and the same operation is repeated. After the steam has been passed into the ebullition tube for about 100 seconds, as rapidly as possible, the temperature is noted, the flask outlet opened, and the outlet of the ebullition tube closed. The tube and its contents are weighed, the weight of the solvent is found by subtracting from the total weight the known weights of tube and dissolved substance.

Osmotic pressure.

Diffusion.

When a concentrated solution of copper sulphate is covered with a column of pure water, the blue coloration is found gradually to spread throughout the liquid. The liquid as a whole appears to be motionless, but it is evident that particles of copper sulphate are in motion. The salt is said to diffuse.

The concentrated solution is best introduced *under* a column of water by means of a pipette.

The first thorough investigations of liquid diffusion were undertaken by Graham in 1851. Through him and others, we know that diffusion always takes place between solutions of unequal concentration; that it is accelerated by a rise in temperature; that different substances diffuse at different rates; and that strong acids and bases diffuse most rapidly, salts less rapidly, and colloidal substances with extreme slowness.

Osmosis.

Nollet showed, 150 years ago, that when a bladder containing alcohol is immersed in water, water permeates through the bladder and may create therein a considerable pressure; but little of the alcohol escapes from the bladder. The latter is said to be *semi-permeable*, permeable to water but not to alcohol. A solution of cane sugar, or any diffusible substance, may replace the alcohol, and other colloidal substances may replace the bladder.

It might seem that the dissolved substance *attracts* the water, but we are not justified in assuming such an attraction.

The diffusion of the water across the diaphragm is called **osmosis**[1].

It may be illustrated very simply by an experiment due to Professor Crum Brown of Edinburgh. Phenol (carbolic acid) is very slightly soluble in water, and water in phenol. Phenol is slightly heavier than pure water, but is lighter than saturated calcium nitrate solution. Calcium nitrate is not dissolved by phenol. When therefore a saturated solution of calcium nitrate is shaken up with a little phenol and then poured into a narrow jar, the slight excess of phenol floats upon a solution saturated with nitrate and phenol. It should form a layer of only a few millimetres thickness. A saturated solution of phenol in water is poured very gently upon the layer of phenol.

We now have a layer of phenol acting as a partition through which water (being soluble) can easily pass, but which acts as a barrier to the passage of the nitrate. The layer of phenol, although slightly heavier than the solution of phenol above it, steadily travels up the cylinder until it floats at the top. Below it, the solution contains calcium nitrate in every part. It will be seen that the end result is the same as for the diffusion of copper sulphate.

Fasten a thin animal membrane over the rim of a thistle funnel (Fig. 120), and pour a few c.c. of sugar solution into the bowl. Place it, still inverted, in a beaker containing water. Water passes through the skin, and the solution rises in the stem of the funnel. Provided the solution is not too concentrated to begin with, the liquid will eventually cease to rise before it overflows, and for some time it will remain at a constant level. Although a state of equilibrium has been

[1] ὠσμός = drive through.

reached, it is evident that the pressure of the solution on the membrane downwards is greater than that of the water upwards. The difference between these two pressures is called the **osmotic pressure** of the solution.

Osmotic pressures can be measured in suitable apparatus (osmometers). The earliest measurements of importance were

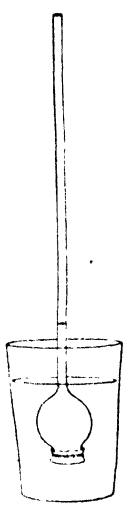


Fig. 120.

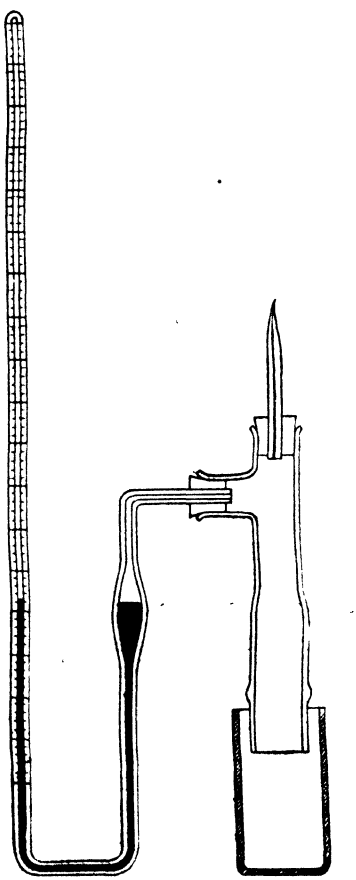


Fig. 121.

made by Pfeffer in 1877. Ordinary semi-permeable membranes are not efficient. Pfeffer found copper ferrocyanide the best. To be effective, however, this must be extremely thin, and therefore needs support to resist the considerable pressure set up. He overcame the difficulty by precipitating

the substance as a membrane within the capillaries of a porous pot—the material of the jar affords the tender membrane support like that which the mullions, transoms and traceries of a large window afford the glass. In order that the concentration of the solution should remain practically unchanged, Pfeffer used a *closed* air manometer for registering the pressure. (Fig. 121.)

A solution of cane sugar of known concentration was placed in the jar, and the latter sealed. It was then wholly immersed in a vessel of water kept at nearly constant temperature. By varying the concentration of the sugar, he obtained the following results:

Grams of sugar per 100 grams water.	Osmotic pressure in mm. mercury.
1	535
2	1016
4	2082
6	3075

It will be noticed that the **osmotic pressure varies directly as the concentration of the sugar.**

In another series of experiments, Pfeffer varied the temperature but kept the concentration constant.

Temperature.	Pressure in atmospheres (1% solution).
6·8	0·664
15·5	·684
32	·716
36	·746

The numbers show clearly that the osmotic pressure increases with rise of temperature.

Although Pfeffer did not keep the temperatures absolutely constant, Van't Hoff was able to show, from the above numbers, that **the increase of pressure is proportional to the absolute temperature.**

The student will see how these laws of osmotic pressure resemble the Gas Laws (see Introductory Chapter). For dilute solutions at constant temperature, the osmotic pressure is proportional to the *concentration* (mass per unit volume). With constant concentration the pressure varies with the absolute temperature.

Van't Hoff applied to dilute solutions the reasoning of the kinetic theory of gases. Assuming that equal volumes of dilute solutions, at the same temperature and osmotic pressure, contain the same number of *dissolved* molecules (Avogadro's law), he was able to deduce mathematically the

pressures a 1 per cent. solution of sugar should exert at the temperatures given above. His numbers are 0·667, ·688, ·727 and ·736 atmosphere respectively.

If, for the sake of argument, we accept the above assumption, it follows that we should be able to find the molecular weights of dissolved substances by determining the osmotic pressures of their solutions. This is too difficult an operation to be of practical value. It has been proved, however, that the osmotic pressure of a solution is directly related to its vapour pressure. And we have already mentioned that Raoult proved empirically that his laws hold good for the lowering of the vapour pressure. Hence we see that Van't Hoff's hypothesis provides a theoretical explanation of the Raoult Laws.

It has been shown experimentally that the osmotic pressures of solutions of most acids, bases and salts are not in agreement with the laws as deduced from the behaviour of such 'indifferent' substances as sugar; in some cases the pressures are twice, or even thrice, the calculated value. Here also, we are reminded of the exceptions to Raoult's laws. The 'exceptions' to Avogadro's hypothesis, the so-called abnormal vapour densities, seem to be analogous.

Sutton (*Volumetric Analysis*, 9th edition, page 290) advises Kingzett's method for estimating hydrogen peroxide.

Mix 10 c.c. of hydrogen peroxide (diluted to "2 volume" concentration) with 30 c.c. of dilute sulphuric acid (1 : 2); add crystals of potassium iodide in sufficient quantity; warm gently. Allow to stand for 10 minutes; add starch paste, and titrate with $\frac{N}{10}$ Thio.

$$2HI + H_2O_2 = 2H_2O + I_2.$$

CHAPTER XXVII.

THEORIES OF ELECTROLYSIS.

THE electrolysis of **water** was first accomplished in 1800.

Grotthus' Theory.

As early as 1805, Grotthus advanced the following hypothesis in explanation of the immediate and simultaneous liberation of hydrogen and oxygen at electrodes widely separated. He assumed that the particles of water consist of oppositely charged hydrogen and oxygen. When the current passes, it is supposed first to influence these particles so that they extend in chains from pole to pole, the electro-positive hydrogen of each particle being turned towards the negative pole, and the electro-negative oxygen towards the positive pole (Fig. 122 I). The oxygen at one end and the hydrogen at the other end of each chain, in contact with their respective poles, are then split off and escape (II), the other element with which each was combined does not remain free, but expels its own kind from the next water particle, and this action proceeds throughout the chain, leading to the arrangement shown in III. The water particles are then rotated into the first position (IV), and the action is repeated.

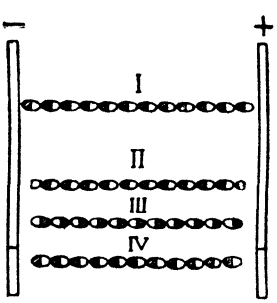


Fig. 122.

Electrolysis of salts.

At a later date, as the result of researches of Davy, Daniel and others, it was recognised that absolutely pure water is a very poor conductor of electricity, but that small traces of impurities will increase

its conductivity very considerably. The student will find, by experiment, that whilst acids, bases and salts, when dissolved in water, promote the electrolysis, many other substances, such as sugar and glycerine, do not. The former substances are called electrolytes (Chapter I.).

The products of electrolysis are found to differ with the electrolyte and the conditions. In Chapter III. we found that when *fused* **sodium chloride** is electrolysed its constituent elements are set free.

Imitate the experiment with silver or lead chloride just melted in a crucible. Use thin carbon rods for electrodes.

From *dissolved* sodium chloride, hydrogen is evolved instead of sodium at the anode: we were able to suggest the reason for this in Chapter III. Chlorine, liberated at the same time, may escape, or it may dissolve, or, as the result of its action upon water to form hydrochloric acid, an equivalent quantity of oxygen may appear instead of it. When **sodium sulphate** solution is electrolysed (Chapter IX.), hydrogen and oxygen alone are evolved, the concentration of the solution remaining practically unchanged. The electrolysis either of *dilute* **sulphuric acid**, or of dilute **caustic soda**, is attended with similar results. From a solution of **copper sulphate**, copper is deposited at the kathode, oxygen is liberated at the anode, and sulphuric acid remains in solution. We have already suggested (Chapter IX.) that perhaps the sulphate radicles, instead of escaping, attack water to form the acid and to liberate oxygen.

In 1834 Faraday formulated the laws which bear his name.

I. The amount of a substance deposited or evolved is in direct proportion to the absolute quantity of electricity which passes.

II. The amounts of different substances deposited or evolved, are in the ratio of their chemical equivalent masses.

As these and many other results became known the radicles themselves were looked upon as the bearers of the electricity, and, inasmuch as they seemed to travel through the solution, Faraday called them **ions**. Those which are discharged at the positive pole (higher potential) he called

anions (ἀνιών = that which goes **up**) and those which are discharged at the negative pole he called **kations** (κατιών = that which goes **down**). The *discharged* ions are supposed either to go free or to attack water, liberating hydrogen or oxygen as the case may be. Thus sodium will liberate hydrogen to form sodium hydroxide; the sulphate radicle will liberate oxygen to form sulphuric acid; the hydroxide radicle will lose oxygen to form water ($2HO = H_2O + O$), and so on.

Signs and nomenclature.

The ions of sulphuric acid are H, H, and SO_4; inasmuch as these are discharged in equivalent proportions, it follows that the sulphate radicle carries a charge equal but opposite to that of two hydrogen atoms. The charge carried by one ion of hydrogen is denoted by a dot, H', an equal electro-negative charge is denoted by a dash, SO_4''. The cuprous ion is written $Cu,'$ but the cupric ion is written $Cu.''$

The actual quantity of electricity needed to deposit, or liberate, a gram equivalent (the equivalent weight in grams) of any substance is 96,540 coulombs. This is now called the '**faraday**'; it must not be confused with the 'farad' an electrostatic unit.

The ions have received convenient nomenclature. The name endings of all positive radicles are changed to -ion. The word may be shortened for convenience. Thus, Hydrion (H'), Sodion (Na'), Argention (Ag'), &c. When a metal has two equivalents, a numerical prefix distinguishes the corresponding ions; thus diferrion (Fe''), triferrion (Fe'''). Negative radicles have the endings changed thus; -ide to -**idion**—as in chloridion (Cl'), hydroxidion (OH'); -ite to -**osion** as in sulphosion (SO_3''), and -ate to -**anion** as in sulphanion (SO_4''), and nitranion (NO_3').

Clausius' theory.

About fifty years after Grotthus advanced his hypothesis, Clausius declared that it is self-contradictory. If the current decomposes the dissolved compounds, it follows that electrolysis does not begin until a definite difference of potential has been established between the electrodes, and that, as soon as that condition is attained, a strong current should come suddenly into existence. But experience has shown that very small differences of potential

produce small currents which increase in strength, regularly, in accordance with Ohm's Law. And again, according to the prevalent hypothesis, before electrolysis can begin, the current must first decompose the molecule into the ions which are to convey it. This is argument in a circle. Clausius suggested that *at all times* in the act of solution a very small proportion of the dissolved molecules of an electrolyte is split into free ions. Thus whilst a solution of sodium chloride contains undissociated molecules chiefly, a few have dissociated spontaneously into chloridions and sodions. Any free ion, meeting another oppositely charged, may combine with it, so that the free ions are not necessarily identical at different times, but, provided the conditions (of concentration, &c.) remain unaltered, association of ions and dissociation of molecules take place at approximately the same rate. To meet the objection that free sodium and other radicles cannot possibly exist in contact with water, Clausius asserted that the properties of highly charged ions would almost certainly be totally different from those of the uncharged radicles, and indeed, that when discharged, they assume the properties commonly attributed to them. According to this hypothesis the ions move in all directions, under ordinary conditions, but, as soon as a difference of potential between the electrodes exists, their path tends towards one or other of the electrodes. As the ions are discharged, a supply is maintained by the continued dissociation of molecules. The difference of potential is *directive*, but not *disruptive*. The anions, in giving up their charge to the anode, tend to lower its potential, whilst the kations tend to raise that of the kathode. So long as the difference of potential between the electrodes is maintained, and this is usually effected by connecting the latter with the poles of a battery or of a dynamo, the electrolysis proceeds. In this wise the current is conveyed by the ions.

Although one chemist has just denounced it as 'destitute of common sense' this hypothesis of electrolytic dissociation has been very favourably received, and, in recent years, the Ionic Theory, which may perhaps be described as a bold extension of it applied to solutions generally, has arisen to make it of special interest.

The Ionic Theory.

Before discussing the Ionic Theory the student should consider very carefully the following points, and verify those (1, 2 and 3) which admit of simple work.

(1) A solution of silver nitrate in benzene does not conduct the electric current, nor does a solution in benzene of carefully dried hydrochloric acid gas.

Inasmuch as the aqueous solutions of these two substances are good conductors, it would appear that the solvent has a very important influence upon the behaviour of the substance dissolved.

(2) When the benzene solutions of the above two compounds are mixed, no silver chloride is precipitated, nor is there any evidence of interaction.

(3) When *dilute* aqueous solutions of different salts, at the same temperature, such as potassium nitrate and barium chloride, are mixed together, there is no thermal effect, and yet the solution is undistinguishable from one made by mixing together dilute solutions of barium nitrate and potassium chloride. But when salts are chosen which will certainly react in solution, for instance, a dilute solution of potassium sulphate with either the nitrate or the chloride of barium, a change of temperature can be registered (use a Beckmann thermometer).

(4) When a dilute solution containing the equivalent quantity of *any* strong base is added to one containing the equivalent quantity of *any* strong acid, about 13,700 calories of heat are evolved

$$HX + YOH = XY + H_2O + 13{,}700 \text{ calories.}$$

The heats of formation of the bases and acids and salts concerned differ widely, yet the thermal effect is the same no matter which base and acid may be chosen, provided both are strong. In all cases 18 grams of water are formed in solution.

(5) The reactions which most commonly take place in solution consist of exchanges of **radicles**,

$$\begin{aligned} Zn + H_2SO_4 &= H_2 + ZnSO_4 \\ Zn + CuSO_4 &= Cu + ZnSO_4 \\ BaCl_2 + ZnSO_4 &= ZnCl_2 + BaSO_4 \\ 2NaOH + H_2SO_4 &= 2H_2O + Na_2SO_4 \\ Na_2CO_3 + H_2SO_4 &= H_2CO_3 + Na_2SO_4 \end{aligned}$$

(6) When the values for the electrical conductivity of an electrolyte at different dilutions are compared, it is found that the conductivity is not halved by diluting a given solution to double its original volume. When molecular quantities

are concerned, it is found that for strong acids and bases and salts, the **molecular conductivity** (that is the product:—specific conductivity × that volume of solution in litres which contains the molecular weight in grams of the dissolved substance) **increases with the dilution** up to a certain point, above which it remains constant.

(7) Substances which when dissolved in water depress the freezing point and raise the boiling point in accordance with Raoult's laws—and these are the same substances whose solutions give osmotic pressures in accordance with Van't Hoff's laws—are non-electrolytes, whilst those substances whose solutions form exceptions to the above laws are electrolytes. The electrolytes are chiefly acids, bases and salts; the osmotic pressures of their aqueous solutions are *greater* than the values calculated from their molecular weights.

It will be seen that when electrolytes are dissolved in water the electro-negative and electro-positive portions show considerable independence of behaviour. Other evidence of this is available. The student is recommended to discover for himself the bearing of the above upon the Ionic Theory, which we shall now discuss briefly. This theory asserts that electrolytes, when dissolved in water, are **normally** in part dissociated into ions; that, in solution, all reactions take place between ions; that substances which have a high conductivity—most salts and all strong acids and bases—are greatly ionised in solution; that acidity is due entirely to hydrion, and alkalinity is due entirely to hydroxidion.

According to the theory, electrolytes differ considerably in the **degree** of dissociation, that is, in the proportion of dissociated to undissociated molecules. This is measured by the molecular conductivity of the solution, which, as we have said, increases with dilution up to a limit.

Consider a saturated solution of salt in contact with the least quantity of solid. Of the dissolved molecules, some will be dissociated into sodions and chloridions; these are constantly meeting and associating, whilst molecules, hitherto intact, are as constantly ionising: the two processes balance. If, the temperature remaining constant, the solution is allowed to evaporate, the free ions have a more limited path, and, meeting more frequently, they associate more frequently, whilst the rate of the dissociation of intact molecules is unchanged. Therefore the **degree** of dissociation is diminished (this is shown by the decrease in molecular conductivity) and the amount of associated salt in solution increases. This is a cause of crystallisation; for where the amount of salt

(associated) in solution reaches a certain value the liquid becomes saturated: but evaporation would have this effect even had there been no dissociation. If, on the other hand, the volume of the solution is increased, the free path of the ions is extended; they meet less frequently and associate less frequently, but the rate of dissociation remains unchanged. The **degree** of ionisation increases (this is shown by the increase in molecular conductivity). More solid salt goes into solution. The dilution may be continued after all the solid has dissolved, and until no associated molecules are left. This condition corresponds to the limit of molecular conductivity. It is reached most quickly by the strong acids and bases, and by salts.

Salts which are only slightly soluble can have comparatively few dissolved molecules, but these may be entirely dissociated, whilst a substance which is very soluble may have few or none of the dissolved molecules dissociated. Hence the slightly dissolved substance may be more reactive in solution than the very soluble ones. Many instances of this are known, and the molecular conductivities of the substances correspond to their chemical behaviour. Thus the sparingly soluble slaked lime is a stronger base than the very soluble ammonium hydroxide.

Take a saturated solution of ordinary impure common salt, and pass into it hydrogen chloride gas, or add the concentrated solution of acid. **Pure** salt is deposited. So far the Ionic Theory, combined with the phenomenon of saturation, has alone provided an explanation of this. By the addition of the gas, the volume of the solution is altered but little: therefore the degree of dissociation of the common salt is practically unchanged on that account. But, since it is a strong acid, the hydrogen chloride is highly dissociated, and the solution now contains chloridion from **two** sources. The chances of meetings between sodion and chloridion are greatly augmented, and association will be much more frequent. The solution should become supersaturated with common salt.

It is a common practice in analytical chemistry to make the action of a weak (slightly dissociated) acid still weaker (still less dissociated) by adding to its solution one of its own salts. For instance, acetic acid is one of the weakest stable acids; according to the theory it yields but a small concentration of hydrion. When to its solution is added some sodium acetate—which is strongly ionised—there is so great a concentration of acetanion, that this associates with **hydrion** to produce undissociated acetic acid, with consequent **decrease in the acidity** of the solution. Similarly a weak base is made weaker by the addition of one of its own salts. Ammonium hydroxide is but slightly ionised; on adding ammonium chloride to its solution, the greater concentration of ammonion causes this to associate with **hydroxidion** and the solution becomes less alkaline.

Monobasic acids and monacid bases can dissociate into two ions only, $HCl \longrightarrow H^{\cdot} + Cl'$ and $NaOH \longrightarrow Na^{\cdot} + OH'$, but it is possible for dibasic acids and diacid bases to ionise into two or more ions, according to the concentration of the solution. Thus a moderately concentrated solution of sulphuric acid seems to contain undissociated molecules mainly together with hydrion $H^{\cdot}$ and hydrosulphanion HSO_4'. At greater dilutions the latter is ionised further to hydrion $H^{\cdot}$ and sulphanion SO_4''. Conductivity values, as well as comparative activity and special reactions (see page 310), point to this conclusion.

The student should study the explanation of the hydrolysis of salts, the action of indicators &c. offered by this hypothesis (see Walker's *Physical Chemistry* and Fenton's *Outlines of Chemistry*).

[A short summary and criticism of Professor Armstrong's alternative hypothesis—Hydrate Formation—will be found in the *Annual Report of the Progress of Chemistry for 1907*, pages 21, 23—25, issued by the Chemical Society.]

CHAPTER XXVIII.

MANGANESE, CHROMIUM, AND IRON.

Manganese.

PYROLUSITE has been known from very early times. It was found in Asia Minor near the city of Magnesia, for which reason it was called magnesia. Later on, another rock was given the name magnesia, and to distinguish the two very unlike substances, pyrolusite was called magnesia nigra and the other, magnesia alba. At a still later date magnesia alba was called magnesite, and pyrolusite obtained the name of lapis manganesius. This last is a corruption of magnesia. From these names those of the metals, whose compounds the respective rocks are, have been derived. Magnesite is the carbonate of *magnesium*, pyrolusite is the peroxide of *manganese*. The two metals differ entirely in physical and widely in chemical properties.

The oxides of manganese.

Pyrolusite is the most valuable mineral which contains manganese. When strongly heated it loses 12¼ per cent. of its total weight as oxygen. The brown residue has the same properties as the red mineral **hausmannite.**

When pyrolusite is heated with concentrated sulphuric acid, 18·4 per cent. of its weight is liberated as oxygen, and the residue is dissolved in the sulphuric acid. As we pointed out on a previous occasion, this reaction marks pyrolusite as a peroxide. From the solution, pale pink crystals of sulphate of manganese separate. In order to obtain the oxide corresponding to this sulphate, the hydroxide is precipitated by caustic potash, air being excluded. The white gelatinous hydroxide must then be dehydrated in a current of hydrogen.

The corresponding oxide may also be obtained by heating the carbonate. In nature it is found as **manganosite.** If air is allowed access when the hydroxide is precipitated, the latter rapidly absorbs oxygen, eventually forming an oxide which occurs naturally as the mineral **braunite.** The sulphate, obtained by the action of sulphuric acid on pyrolusite, is isomorphous with *magnesium* sulphate, hence (by Mitscherlich's law) its formula is $MnSO_4$, and that of its oxide (manganosite) is MnO. Its chloride, obtained in the preparation of chlorine (Chapter V.), must have the formula $MnCl_2$. By precipitating the chlorine of this chloride as silver chloride, Berzelius determined the atomic weight of manganese as 55.

It follows that the formula of pyrolusite is MnO_2 and that of hausmannite is Mn_3O_4. Hausmannite is formed whichever of the oxides is heated in air. Manganosite is oxidised, $6MnO + O_2 = 2Mn_3O_4$. Manganese dioxide is, as we have seen, decomposed with a $12\frac{1}{4}$ per cent. loss.

$$3MnO_2 = Mn_3O_4 + O_2.$$

Braunite forms the same oxide with 3·4 per cent. loss: hence its formula is Mn_2O_3 ($6Mn_2O_3 = 4Mn_3O_4 + O_2$). This formula is confirmed by the following. With difficulty the oxide can be dissolved in acids; it is so weak a base, however, that its salts in dilute solution are completely hydrolysed. However, the sulphate, with much difficulty, has been induced to form an alum with potassium sulphate, hence, by Mitscherlich's law, its formula is $Mn_2(SO_4)_3$ and that of braunite is Mn_2O_3.

When hausmannite is treated with sulphuric acid it yields a mixture of manganous and manganic sulphates. It would appear, therefore, to be of the same type as ferroso-ferric oxide, Fe_3O_4.

But with dilute nitric acid it yields manganous nitrate and manganese dioxide, after the manner of minium.

The natural oxides may be tabulated thus:

Manganosite, manganous oxide, MnO—basic.

Hausmannite, trimanganic-tetroxide, Mn_3O_4.

Braunite, manganic (or sesqui-) oxide, Mn_2O_3—feebly basic.

Pyrolusite, manganese dioxide, MnO_2—a peroxide.

In these oxides manganese is di-, tri-, and tetravalent respectively.

Oxidation of pyrolusite.

When pyrolusite is heated with some potassium carbonate—or better, with small pieces of caustic potash—in an iron tray, and the mixture is constantly stirred up, the mass becomes light blue.

The reaction can be greatly hastened by the addition of some oxidising agents, powdered nitre or potassium chlorate.

This blue substance agitated with water yields a green solution, from which, with difficulty, crystals may be obtained. But if the solution is mixed with a saturated solution of potassium sulphate, mixed crystals are deposited, or, if a crystal of potassium sulphate is suspended in the saturated green solution, an overgrowth is readily formed. If the pyrolusite is heated with sodium carbonate or hydroxide instead of with the potassium compounds, and the solution of the product is mixed with sodium sulphate, crystals are more easily obtained; these are isomorphous with Glauber's salt ($Na_2SO_4 10H_2O$). The formulae of the green salts should therefore be analogous to those of sodium and potassium sulphates. They are potassium and sodium **manganates**, K_2MnO_4 and $Na_2MnO_4 10H_2O$, wherein manganese is analogous to *sulphur*. $2MnO_2 + 4KOH + O_2 = 2K_2MnO_4 + 2H_2O$.

That being so, it should be possible to obtain from them a **manganic acid.** On the addition of an acid the green colour of the solution changes to violet, and some manganese peroxide is precipitated. So sensitive is this reaction to acids that, when the green solution is left exposed to air, even the carbon dioxide will produce it. From the concentrated violet solution of the potassium compound, crystals may be obtained which are almost black. In form they resemble potassium *perchlorate* ($KClO_4$), and when the saturated solutions of the two salts are mixed, crystals are deposited which, when seen under the microscope, are obviously mixed crystals. Hence the formula of this new salt should be $KMnO_4$. It will be seen that it is more highly oxidised than the manganate (40½ per cent. oxygen as compared with 32½ per cent.). It is called potassium **permanganate.** By passing chlorine through the green solution of the manganate it can be formed without the deposition (self reduction) of manganese dioxide.

By oxidation: $2K_2MnO_4 + Cl_2 = 2KCl + 2KMnO_4$.

On acidifying:

$3K_2MnO_4 + 4HCl = 4KCl + 2KMnO_4 + MnO_2 + 2H_2O$.

Potassium permanganate obviously stands in the same relation to the manganate as persulphate stands to sulphate; hence we should expect the formulae to be analogous, and the crystalline forms to resemble each other. They are not isomorphous however, and there is other evidence for believing the formula of the persulphate to be $K_2S_2O_8$, which might account for the difference in crystalline form. For the sake of convenience, potassium permanganate is often represented by the double formula $K_2Mn_2O_8$. The evidence favours $KMnO_4$.

Permanganic acid is not well known, but its anhydride has been obtained by the very cautious addition of concentrated sulphuric acid to the potassium salt. It is a very unstable substance whose composition corresponds to the formula Mn_2O_7 (compare Cl_2O_7 and S_2O_7).

When solid potassium permanganate is heated to 250° C., it decomposes according to the equation

$$2KMnO_4 = K_2MnO_4 + MnO_2 + O_2.$$

An acidified solution of potassium permanganate is catalytically decomposed by contact with freshly precipitated manganese peroxide, more peroxide being precipitated.

$$2H_2SO_4 + 4KMnO_4 = 2K_2SO_4 + 2H_2O + 4MnO_2 + 3O_2.$$

When the reaction is finished, the solution is colourless.

Permanganate as oxidising agent.

Potassium permanganate is one of the most convenient oxidising agents known; it is used largely in Organic Chemistry, advantage being taken of the fact that, by varying the concentration and some other conditions soon to be explained, the intensity of its oxidising action may, to a considerable extent, be controlled. Oxidations carried out in *neutral* or *alkaline* solution yield **three-eighths** of the total oxygen, the whole of the manganese being deposited as *peroxide*.

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

Oxidations carried out in *acid* solution are both more intense and more complete. The manganese is left in solution as manganous sulphate, which represents a lower stage of oxidation than the peroxide; hence there is rendered available for oxidising purposes a greater proportion of free oxygen, namely **five-eighths** instead of three-eighths of the total oxygen.

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

It is sometimes convenient to construct the equation by means of a 'dissected' formula, as follows:

$$\left\{\begin{array}{l} K_2O + H_2SO_4 \\ 2MnO + 2H_2SO_4 \\ 5O \end{array}\right. = \begin{array}{l} K_2SO_4 \\ +2MnSO_4 + 2H_2O \\ +5O \end{array}$$

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

A very curious reaction takes place with hydrogen peroxide in acid solution; both substances are reduced and free oxygen escapes.

$$\left\{\begin{array}{l} K_2O + H_2SO_4 \\ 2MnO + 2H_2SO_4 \\ 5O \qquad +5H_2O_2 \end{array}\right. = \begin{array}{l} K_2SO_4 \\ +2MnSO_4 + 2H_2O \\ 5H_2O + 5O_2 \end{array}$$

$$2KMnO_4 + 3H_2SO_4 + 5H_2O_2 = K_2SO_4 + 2MnSO_4 + 8H_2O + 5O_2$$

This reaction affords a rapid method for estimating the concentration of hydrogen peroxide solution. A tenth equivalent solution of permanganate is run into a given volume of a dilute solution of the peroxide to which some dilute sulphuric acid has been added. Oxygen at once escapes, and the colour of the permanganate is instantly discharged. The permanganate is its own indicator, and the reaction is complete when the next drop permanently colours the solution pink (see page 329).

It is best to use permanganate in a burette with a glass stopcock. An equivalent solution of permanganate is of such a concentration that one litre of it will yield 8 grams of oxygen (H : O = 1 : 8); an equivalent solution therefore contains 31·6 grams of the salt, and a tenth equivalent solution contains 3·16 grams per litre, or 0·00316 grams per cubic centimetre.

To prepare a standard solution a definite weight of the salt may be weighed out exactly and transferred to the graduated flask; but inasmuch as the solid salt is reduced by organic particles in the air, it is more usual to standardise it by means of a standard solution of oxalic acid (see Chapter XVIII.). Another method of standardising this salt will be given in this chapter.

Sulphites and sulphurous acid are oxidised in solution, $Na_2SO_3 \longrightarrow Na_2SO_4$. Some manganese di-thionate is formed, hence the reaction is not used for estimations. But the most important titration with permanganate is the estimation of iron salts. The iron is oxidised from the ferr*ous* to the ferr*ic* condition $2FeO \xrightarrow{+O} Fe_2O_3$, that is, two mole-

cules of the ferrous salt must account for one atom of oxygen; hence two molecules of permanganate will oxidise ten molecules of the ferrous salt, $10FeO + 5O = 5Fe_2O_3$. Or we may regard the oxidation in another light: we may say that two molecules of ferrous sulphate need another acid radicle to become ferric sulphate, $2FeSO_4 + (SO_4) = Fe_2(SO_4)_3$. The acid radicle is forthcoming from the added sulphuric acid, provided its two atoms of hydrogen are oxidised to water; and that is the function of the permanganate.

$$\left\{\begin{array}{l} K_2O + H_2SO_4 \\ 2MnO + 2H_2SO_4 \\ 5O + 5H_2 \\ \quad\quad 5SO_4 \end{array}\right\} = \begin{array}{l} K_2SO_4 \\ 2MnSO_4 + 2H_2O \\ +5H_2O \end{array}$$

$$10FeSO_4 \quad 5Fe_2(SO_4)_3$$

$$2KMnO_4 + 8H_2SO_4 + 10FeSO_4 = 5Fe_2(SO_4)_3 + K_2SO_4 + 2MnSO_4 + 8H_2O$$

If we wish to determine the purity of a piece of iron, a weighed piece (scoured from rust) is dissolved in dilute sulphuric acid, with the precaution against oxidation given in Chapter VII.; the solution is made up to a definite volume in a marked flask, and known fractions are withdrawn and titrated.

If the exact purity of a sample of iron is known, a weighed quantity may be dissolved and made up to a known volume, and this solution used to standardise permanganate. Unfortunately, owing to the presence of carbon compounds which become oxidised, the error may be from 1 to 2 per cent.

A solution of ferric sulphate may also be estimated by permanganate. It is first reduced to the ferrous condition, and the iron determined as before. The ferric salt is best reduced by adding to the acidified solution some zinc; a known fraction is withdrawn as before

$$Fe_2(SO_4)_3 + 2H = 2FeSO_4 + H_2SO_4.$$

The zinc sulphate present has no effect.

Similarly a mixture of ferrous and ferric sulphates may be completely estimated. The ferrous sulphate is first determined; the ferric salt is then reduced; a second titration gives the *total* iron as ferrous iron.

Hydrochloric acid is rarely used for acidifying iron solutions in permanganate estimations. Permanganate oxidises hydrochloric acid in moderately concentrated solution, but when both solutions are dilute a mixture of the two may be warmed without action. But if a trace of iron salt is present, even with very dilute solutions, the iron compound catalytically accelerates the interaction of acid and permanganate. On the other hand, manganous sulphate has a retarding catalytic effect on the same reaction. Hence, if ferrous chloride is to be estimated by permanganate, a considerable quantity of manganous sulphate must be added.

Precipitated manganese dioxide may be obtained by adding to a cold *dilute* solution of permanganate some alcohol, little by little, with stirring. The alcohol is oxidised to carbon dioxide and water, or to substances which have peculiar odour. The permanganate is reduced to peroxide.

Chromium.

Chromium, in its chemical behaviour, is in some respects the complement of manganese. Its compounds are even more highly coloured; green and yellow predominate. To a yellow compound it owes its name[1]. Its chief ore is chrome-ironstone, which contains oxides of iron and chromium.

Dry method of oxidation.

This mineral is crushed, mixed with sodium carbonate, and the mixture heated in a current of air; an oxidising agent may or may not be added. A yellow colour appears, and the substance formed may be dissolved out by water; from its saturated solution yellow transparent crystals are deposited, isomorphous with Glauber's salt and sodium manganate. The corresponding potassium compound is deposited as a yellow salt, isomorphous with potassium sulphate and manganate. These yellow compounds then are **chromates,** K_2CrO_4 and $Na_2CrO_4 10H_2O$.

Effect of acidifying chromate.

When a solution of potassium chromate is acidified, its colour changes to orange. The colour change recalls that of the manganate under similar conditions; the reaction differs, however, in that no oxide is deposited. From the solution large reddish-orange crystals may easily be obtained. These crystals are *not* isomorphous with perchlorate or permanganate. Their solution is neutral, or but slightly acidic. The addition of some potassium hydroxide to the solution causes the colour to change back to yellow, and now chromate will crystallise out. Clearly these two salts are at the same stage of oxidation, and the orange solid is not a **perchromate.** From the solution acidified with hydrochloric acid, potassium chloride may also be obtained. The orange solid may possibly be formed according to the equation

$$K_2CrO_4 + HCl = KHCrO_4 + KCl.$$

[1] $\chi\rho\tilde{\omega}\mu\alpha$ = colour.

The compound, however, is only slightly acidic, and its orange crystals are quite unlike those of hydrogen potassium sulphate. Moreover they behave differently towards heat. For potassium hydrogen sulphate, when heated, loses water (see Chapter XXV.), $2KHSO_4 = K_2S_2O_7 + H_2O$. And the 'pyro' sulphate breaks up, on further heating, into sulphate and sulphuric anhydride. The sulphuric anhydride, at the high temperature, dissociates into oxygen and the lower sulphur dioxide, $K_2S_2O_7 = K_2SO_4 + SO_3$, and $2SO_3 = 2SO_2 + O_2$. But when the orange compound of chromium is heated very strongly it yields, besides the yellow chromate, a green powder and some oxygen—but *no water*; hence it cannot be the hydrogen chromate, it may, however, be a pyrochromate. This view is confirmed by the following experiments. The chromate is removed from the green compound by solution in water, the green powder can then be dissolved, *without evolution of gas*, in sulphuric acid. The solution is green when warm, but red when cold. After some time there separate from the red solution, which must not be too concentrated, purple crystals of a salt isomorphous with aluminium sulphate, and which, with potassium sulphate, forms a fine alum. Hence the sulphate should correspond to the formula $Cr_2(SO_4)_3$, and the green powder should be an oxide of the formula Cr_2O_3.

From a solution of this green chromic sulphate, ammonium hydroxide precipitates chromic hydroxide as a green jelly. This hydroxide is a far stronger base than manganic hydroxide. Its salts are not very greatly hydrolysed. Their solutions have peculiarities which sometimes prevent crystallisation.

So far then the orange solid, when heated, acts in a manner analogous to potassium pyrosulphate; oxygen is liberated and an oxide is set free—which, however, is at a lower stage of oxidation than sulphur dioxide.

When an excess of concentrated sulphuric acid is added to a saturated solution of the orange solid, crystals of hydrogen potassium sulphate separate out. The red liquid is decanted off and strongly cooled. Red crystals are deposited, which may be deprived of the adhering vitriol by filtration through a filter funnel plugged with glass wool. Upon the glass wool they are washed with concentrated nitric acid. The nitric

acid is removed from the crystals by absorption on a porous plate. Finally they are dried in a crucible over a very small flame. These red crystals, when heated, lose 24 per cent. of their weight as oxygen, and leave as residue the green chromic oxide (Cr_2O_3). In water they dissolve readily to form a strongly acid solution, which, on neutralisation, gives potassium chromate or the orange salt. It is obvious therefore that the scarlet compound is the anhydride of chromic acid, CrO_3, and we can account for all the reactions only by giving to the orange solid the formula $K_2Cr_2O_7$,

$$2K_2CrO_4 + H_2SO_4\,(\text{dil.}) = K_2SO_4 + K_2Cr_2O_7 + H_2O,$$
$$K_2Cr_2O_7 + 2H_2SO_4\,(\text{conc.}) = 2KHSO_4 + 2CrO_3 + H_2O,$$
$$4CrO_3 = 2Cr_2O_3 + 3O_2,$$
$$4K_2Cr_2O_7 = 4K_2CrO_4 + 2Cr_2O_3 + 3O_2.$$

The orange salt is a pyrosalt. It is sometimes called potassium bichromate. The prefix bi- is the survival of an old idea, still commonly used, for hydrogen (acid) salts—thus $KHSO_4$ is often called potassium bisulphate—hence it is misleading for the orange salt. If the student refers to the remarks about pyrosulphuric acid he will see that this new salt may be regarded as the salt of a condensed acid, and its formula shows that it may conveniently be called **dichromate.** It is analogous to pyrosulphate and pyrophosphate. But how different from them! The pyrosulphate probably exists only in saturated solution, becoming at once a salt of the ordinary acid ($K_2S_2O_7 + H_2O = 2KHSO_4$); pyrophosphate slowly combines with water to form the hydrogen ortho-salt ($Na_4P_2O_7 + H_2O = 2Na_2HPO_4$); but potassium dichromate is quite stable in solution—the true 'bi'chromate is not known. By the addition of a base it is transformed into the normal chromate $K_2Cr_2O_7 + 2KOH = 2K_2CrO_4 + H_2O$.

Chromium trioxide is the analogue of sulphur trioxide. It is a very powerful oxidising agent—hence the necessity of filtering it on glass and of washing it free from sulphuric acid by means of another strong oxidising agent.

Chromic anhydride.

It is used largely in Organic Chemistry, and sometimes as a depolariser in modified Poggendorf galvanic cells.

$$3H_2SO_4 + 2CrO_3 + 3H_2 = 6H_2O + Cr_2(SO_4)_3.$$

The solution of chromium trioxide may contain either the condensed acid ($H_2Cr_2O_7$) or the ordinary chromic acid (H_2CrO_4), or both together; neither has been isolated.

A compound of importance in analytical chemistry is **chromyl chloride** (CrO_2Cl_2); this is a reddish volatile compound, analogous to, and formed by, the same method as that for sulphuryl chloride (SO_2Cl_2). $CrO_3 + 2HCl = CrO_2Cl_2 + H_2O$. A mixture of sodium chloride and powdered dichromate is treated with concentrated sulphuric acid. Hydrochloric acid and chromic anhydride are liberated simultaneously in the presence of a dehydrating agent. If the chromyl chloride is passed into a solution of ammonia, ammonium chromate is formed

$$2H_2O + CrO_2Cl_2 \longrightarrow \begin{matrix} H_2CrO_4 \longrightarrow (NH_4)_2CrO_4 \\ 2HCl \longrightarrow 2(NH_4)Cl \end{matrix}$$

from whose solution, lead nitrate will precipitate yellow lead chromate, $PbCrO_4$. The formation of lead chromate in the receiver indicates, by the following chain of reasoning, the presence in the retort of a chloride.

$$\text{Chloride} \longrightarrow \underset{\text{(volatile)}}{\text{chromyl chloride}} \longrightarrow \underset{\text{(dissolved)}}{\text{chromic acid}} \longrightarrow \underset{\text{(precipitated)}}{PbCrO_4}.$$

Neither bromides nor iodides give a chromyl compound.

The following chromates are of importance:

Lead chromate, found native as crocoisite, a yellow insoluble salt precipitated from either soluble chromate or dichromate.

Barium chromate, an insoluble yellow salt.

Silver chromate, an insoluble red salt, used as an indicator in silver titrations (Chapter XVIII.).

Ammonium dichromate, when heated, breaks up into nitrogen, water and chromic oxide (compare NH_4NO_2).

$$(NH_4)_2Cr_2O_7 = N_2 + 4H_2O + Cr_2O_3.$$

The oxide liberated has the appearance of green tea and is very light. This reaction was used to determine accurately the atomic weight of chromium, Cr 52·1. It affords a very simple laboratory experiment; use the tube of Fig. 40, and take about ·2 gram. In one experiment this quantity gave ·173 gram. of green oxide: at. wt. = 52·5.

Sodium chromate may be prepared by the **wet** method.

Wet method of oxidation. A solution of sodium peroxide oxidises chromic salts to sodium chromate.

$$2CrCl_3 + 5Na_2O_2 = 2Na_2CrO_4 + 6NaCl + O_2.$$

Manganese compounds, under the same conditions, are oxidised no further than the peroxide. The reason of this will become evident when one remembers that any hydrogen peroxide set free from sodium peroxide and any manganate produced would decompose each other (p. 321).

Potassium dichromate can suffer further oxidation by means of hydrogen peroxide. When to an acidified solution of potassium dichromate a little hydrogen peroxide is added, an intense blue colour appears. When the solution is shaken with ether, the ether dissolves out most of the blue coloured substance. This delicate reaction is used as a test both for chromates and hydrogen peroxide. The ether must not be added beforehand in analysis, as it may generally be trusted to give the colour of itself. The composition of the blue substance is not certainly known; it is quite unstable: it is believed to be a **perchromate**, analogous to permanganate.

Dichromate as oxidising agent.

Potassium dichromate is readily reduced to the chromic condition, hence it finds application as an oxidising agent. In Organic Chemistry it is used instead of permanganate when a more gentle oxidiser is needed. Permanganate, in acid solution, falls from the heptoxide condition to the manganous oxide condition,

$$Mn_2O_7 = 2MnO + 5O,$$

but dichromate falls only from the trioxide to the sesquioxide condition. It will be seen that every molecule of dichromate yields three atoms of oxygen. With sulphurous acid

$$K_2Cr_2O_7 + 3H_2SO_3 + H_2SO_4 = K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O.$$

Potassium sulphate and chromium sulphate are formed in molecular proportions. When the solution is evaporated down to a purple colour, potassium chrome-alum settles out. This explains the formation of chrome-alum in the Bichromate battery.

Probably dichromate is a less energetic oxidising agent than permanganate on account of its superior stability, both in solution and as solid. It has no oxidising action on hydrochloric acid in the cold, hence it may be used conveniently for estimating iron solutions in presence of hydrochloric acid. Unfortunately the colour changes are such that an outside indicator is necessary. For this purpose potassium ferricyanide is used; for reasons to be explained in the next chapter, ferrous salts colour this substance blue, but ferric salts colour it yellow. Hence, when the titration solution

just fails to produce a blue colour with the indicator, all the ferrous compound has been oxidised.

As the colour is permanent the indicator cannot be placed in the titration flask, but from time to time a drop of the iron solution is added to a drop of the indicator. Generally a first rough and a second more exact trial are necessary before attempting an exact titration.

As one molecule of dichromate yields three atoms of oxygen, it follows that six molecules of ferrous chloride will be oxidised by one molecule of dichromate, $6FeO \longrightarrow 3Fe_2O_3$.

$$\left\{\begin{array}{l} K_2O + 2HCl \\ Cr_2O_3 + 6HCl \\ 3O + 6H \\ \quad\quad 6Cl \end{array}\right\} = \begin{array}{l} H_2O + 2KCl \\ 3H_2O \quad\quad + 2CrCl_3 \\ 3H_2O \end{array}$$

$$+6FeCl_2 \quad 6FeCl_3$$

$$K_2Cr_2O_7 + 14HCl + 6FeCl_2 = 6FeCl_3 + 7H_2O + 2KCl + 2CrCl_3$$

(dilute solution pale orange) (pale green) (pale yellow) (light green)

Dichromate is generally obtained pure from the dealers, and even for standardised solutions the once recrystallised salt may be weighed out, or, like permanganate, it may be standardised against iron. Another method is to cause a known mass of it to oxidise potassium iodide in acid solution, and to estimate the iodine displaced.

$$K_2Cr_2O_7 + 14HCl + 6KI = 3I_2 + 8KCl + 2CrCl_3 + 7H_2O.$$

An equivalent solution of dichromate contains $\frac{1}{3 \times 2}$th of the molecular weight in grams per litre.

Chromous compounds.

Chromous compounds are known corresponding to the manganous compounds. They are instantly oxidised on exposure to the air, hence they are not met with in the laboratory. The chloride has a beautiful sky blue colour. When a solution of green chromic chloride (made by heating trioxide with hydrochloric acid) is reduced in a flask by means of hydrogen—zinc and hydrochloric acid —the sky blue **chromous chloride** is formed, as soon as all air has been displaced. When air enters, this salt is at once oxidised to the green chromic chloride.

If by means of the apparatus of Fig. 123 the blue solution is forced, by the pressure of excess hydrogen, into another flask (shown on right) from which air has been expelled by carbon dioxide, and which contains sodium

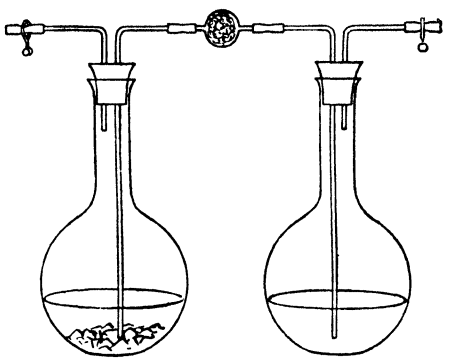


Fig. 123.

acetate, the red **chromous acetate** is precipitated. The acetate is much less rapidly oxidised than other chromous salts, and may be isolated and bottled with comparative ease.

From a solution of chromous chloride, air-free potash precipitates brown **chromous hydroxide.** From its hydroxide chromous oxide cannot be obtained, for a reaction occurs even with the water of constitution,

$$2Cr(OH)_2 = Cr_2O_3 + H_2O + H_2.$$

Review.

A comparison of the analogous compounds of chromium and manganese will illustrate what was meant by the statement at the beginning of this section, that manganese and chromium are, to some extent, complementary.

The salts of divalent manganese are but slightly oxidised in the air; but chromous compounds are instantly oxidised. Manganic oxide (trivalent) is an excessively weak base, and its salts are completely hydrolysed; on the other hand, although the carbonate and sulphide do not exist in solution, chromic salts are comparatively stable. There is no oxide of chromium corresponding to peroxide of manganese. Both elements behave as non-metals in their higher stages of

oxidation. With manganese the permanganate, but with chromium the chromate (dichromate), is the more characteristic condition.

MnO, unstable in air.	CrO, unknown.
$Mn(OH)_2$ basic, salts stable in solution and stable in air.	$Cr(OH)_2$, basic, salts stable in solution, but unstable in air.
Mn_3O_4.	—
Mn_2O_3, very feebly basic, salts hydrolysed.	Cr_2O_3, basic, salts moderately stable in solution.
MnO_2, a peroxide, possibly slightly acidic.	—
—	CrO_3, acidic oxide, well known.
Manganates.	Chromates and dichromates
Mn_2O_7, acidic, unstable.	—
Permanganates.	(perchromic acid doubtful).

Iron.

The chemical properties of iron are, in some respects, intermediate between those of manganese and chromium. Thus there are two series of iron salts. The ferrous salts are isomorphous with the manganous salts, but are more readily oxidised in the air. The ferric salts are hydrolysed by water, but they approach the chromic compounds in stability, and the sulphate readily forms alums.

There are two double salts of iron and ammonium, both of which are important and must be clearly distinguished.

Iron ammonium salts.

Ferrous ammonium sulphate, $(NH_4)_2SO_4$, $FeSO_4$, $6H_2O$. This double salt is not the alum. It is isomorphous with the series M_2SO_4, DSO_46H_2O. It is more stable in air than ferrous sulphate $FeSO_47H_2O$, and therefore is often used instead of green vitriol. It may be used very conveniently for standardising solutions of permanganate. It contains one-seventh of its weight of iron.

Iron ammonium alum, $(NH_4)_2SO_4$, $Fe_2(SO_4)_324H_2O$, can be obtained in large, light purple octohedra.

The fixing of the atomic weight of iron is connected with the formula of this substance. Berzelius showed that the two oxides of iron contain, for a fixed mass of iron, oxygen in the ratio of 2 : 3. He therefore gave to them the formulae FeO_2 and FeO_3; and to the oxides of all metals whose sulphates are isomorphous with green vitriol, or which form alums, he accordingly gave analogous formulae; thus MnO_2, ZnO_2, MgO_2, or CrO_3, MnO_3, &c.

When it was discovered that potassium chromate and manganate are isomorphous with potassium sulphate, whose formula is definitely known to be K_2SO_4, it was recognised that chromates and manganates must have the formulae K_2CrO_4 and K_2MnO_4. Consequently the *red* chromic anhydride must have the formula CrO_3. But this formula had been assigned to the lower *green* oxide, because it was the alum-forming oxide. And in the two oxides of chromium, for the same quantity of chromium, the oxygen ratio is 1 : 2. Therefore the green oxide must have the formula $Cr_2O_3[CrO_{1\frac{1}{2}}]$, and its sulphate must have the formula $Cr_2(SO_4)_3$. Hence, as all isomorphous sulphates have analogous formulae, that of ferric sulphate is $Fe_2(SO_4)_3$ and that of ferric oxide Fe_2O_3. From this formula, that of ferrous oxide follows as FeO (instead of FeO_2) and that of ferrous sulphate as $FeSO_4$. As a result of these changes the atomic weight of iron was halved, and the atomic weights of all metals whose sulphates are isomorphous with ferrous sulphate were halved also, for the formula of their sulphates must be DSO_4 instead of $D(SO_4)_2$.

Higher oxides.

A peroxide of iron is not known, but the corresponding sulphide occurs as **pyrites** FeS_2. When pyrites are heated with exclusion of air, ferroso-ferric sulphide is formed, $3FeS_2 = Fe_3S_4 + 2S$.

An oxide corresponding to hausmannite is found as **magnetic iron ore** (Fe_3O_4). This substance, without its magnetic properties, is formed when iron is oxidised at a high temperature in air or steam.

Iron has but slightly developed non-metallic properties; potassium ferrate K_2FeO_4 is probably formed when iron is oxidised by nitre.

Iron filings and nitre are mixed in proportion of 1 : 3, and heated in a glass bulb. From the cold residue, water dissolves out the compound to form a purple solution. It may also be prepared by passing chlorine into a beaker in which ferric hydroxide has been precipitated by an excess of potash.

Unlike the manganate and chromate the ferrate is unstable and loses oxygen readily.

Resemblances.

Iron, then, is related to manganese and chromium through its oxides and salts whose properties are intermediate in character. The relation is not comparable however to that between the halogens or the members of the phosphorus family. The atomic weights of the three elements are chromium 52·1, manganese 55·0, iron 55·9.

In the same manner all three elements are related in salts of the divalent stage to zinc and magnesium, and in those of the trivalent stage to aluminium. And this supports the contention that the compounds repre-

senting different stages of oxidation of the same metal resemble each other less than they resemble analogous compounds of another metal. Thus divalent manganese resembles divalent magnesium; trivalent manganese resembles trivalent aluminium; in the manganates, manganese resembles sulphur in sulphates; and heptavalent manganese (in permanganates) resembles chlorine in perchlorates.

The iron family.

Iron is very closely related to two other metals, namely cobalt and nickel. In this case the relationship is of the same nature as that which holds between the halogens. Both for cobalt and nickel the divalent condition is the most stable. The atomic weights of the elements of the iron family are very nearly equal, Fe = 55·9, Co = 59·0, Ni = 58·7.

Note on Oxidation.

The student may have recognised that a compound is oxidised by the addition to it of oxygen or of any other electro-negative atom or radicle, or by the removal of an electro-positive atom or radicle. Similarly an element is oxidised by the addition of oxygen or other electro-negative element or group of elements. Thus potassium chloride is oxidised to chlorate. Here it is to be noticed that the potassium is not oxidised, for it still takes the place of one hydrogen atom and no more. But one may regard the chlorine as oxidised to the pentavalent state. Similarly, when potassium manganate is oxidised to permanganate $K_2MnO_4 \longrightarrow KMnO_4$, the radicle ($MnO_4$) is oxidised by loss of electro-positive potassium to the compound, or, we may say, the hexavalent becomes heptavalent manganese.

Notice that to increase in a compound the percentage quantity of the electro-negative group, does not necessarily oxidise it. In the following two changes the first is, but the second is not, a case of oxidation.

(1) $Hg_2SO_4 \longrightarrow 2HgSO_4$.

(2) $K_2SO_4 \longrightarrow 2KHSO_4$.

CHAPTER XXIX.

OTHER COMPOUNDS OF CARBON.

Carbon monoxide.

THE composition of carbon monoxide was deduced in Chapter X. Mention was there made of its poisonous action upon human beings. This is due to the formation of a too stable compound with the red colouring matter of the blood, whereby the latter is prevented from exercising its function in the process of breathing (Chapter XXXI.). To form additive compounds is characteristic of carbon monoxide. It is absorbed by a solution—either acidic or ammoniacal—of cuprous chloride, to form **carbonyl cuprous chloride**—Cu_2Cl_2CO; from this compound it may be recovered by pumping: the reaction serves to remove the oxide from gaseous mixtures. When carbon monoxide is mixed with its own volume of chlorine, and the mixture is exposed to sunlight, combination takes place with the formation of **carbonyl chloride** or phosgene gas ($\phi\hat{\omega}\varsigma$ = light) $COCl_2$.

Carbonyl chloride is of considerable theoretical importance. When passed into water it behaves like sulphuryl chloride; hydrochloric acid and carbonic anhydride are produced, $COCl_2 + H_2O = CO_2 + 2HCl$. When carbonyl chloride is treated with alcohol (C_2H_5OH), a substance of the formula $CO(OC_2H_5)_2$ is formed; this is analogous to sodium carbonate and may be called ethyl-carbonate. Its formation in this manner leads chemists to adopt the formula $CO(OH)_2$ for carbonic acid.

$$COCl_2 \longrightarrow CO(OC_2H_5)_2 \longrightarrow CO(ONa)_2 \longrightarrow CO(OH)_2.$$

Carbonyl chloride also reacts with ammonia to produce hydrochloric acid and urea; the reaction fixes the rational formula of urea.

$$COCl_2 + 2NH_3 = CO(NH_2)_2 + 2HCl.$$

Formic acid.

When carbon monoxide is heated for several days at 100° C. with a stick of caustic potash, potassium formate, $KHCO_2$, is produced. Hence carbon monoxide may perhaps be regarded as the anhydride of

formic acid. When formic acid is treated with concentrated sulphuric acid carbon monoxide is liberated again.

$$H_2CO_2 - H_2O = CO.$$

This is the best method of obtaining carbon monoxide, sodium formate being used instead of the acid.

Formic acid obtained its name from the fact that it was first obtained by distilling red ants (formica = ant). It is a colourless liquid, and has a corrosive action on the skin. It is the painful substance ejected from the stinging hairs of the nettle (*Urtica dioica*). As it is a monobasic acid its formula is written HCO(OH). It readily takes up oxygen to form carbonic acid, $CO(OH)_2$, and is therefore a good reducing agent.

Composition of organic compounds.

The method of finding the composition of substances which contain carbon, hydrogen and oxygen is important. The apparatus used is similar to that described under nitrogen peroxide (Chapter XVIII.). Instead of copper (to reduce), copper oxide (to oxidise) fills the combustion tube. If the organic substance is solid, a weighed quantity is mixed with copper oxide, and heated in a

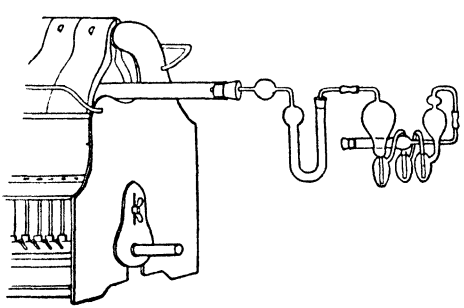


Fig. 124.

current of dry oxygen; the products of combustion, steam and carbon dioxide, are swept out of the tube by the current of oxygen and collected in calcium chloride tube and potash bulbs respectively. From the weights of carbon dioxide and water collected the weights of carbon and hydrogen in the compound are deduced, and the weight of oxygen is found by difference. The proportions by *weight* of the three elements being known, the proportion by *atoms* can be found by dividing each proportionate weight by the respective atomic weight. Volatile substances, such as formic acid, are contained in a tube (compare nitrogen peroxide). The vaporised substance is completely oxidised as it passes with the current

of oxygen over the heated copper oxide. A certain substance was found to contain

Carbon .....31·85 °/₀	by mass	$\frac{31·85}{12}$ = 2·65	the same ratio in integers 3	proportion by atoms.
Hydrogen..... 4·05 °/₀		$\frac{4·05}{1}$ = 4·05		
Oxygen.....64·1 °/₀		$\frac{64·1}{16}$ = 4·01		

As there cannot be a fraction of an atom the empirical formula for the substance is $C_2H_3O_3$.

When carbon dioxide is heated with sodium *metal*, sodium oxalate is formed $2Na + 2CO_2 = Na_2C_2O_4$.

Oxalic acid.

Oxalic acid may be obtained by cautiously warming cane sugar with dilute nitric acid (Chapter XVIII.), but it, or rather its sodium salt, is prepared commercially by heating wood-dust (cellulose) with caustic soda, with free access of air; indeed oxalic acid is formed in a multitude of similar reactions. By the combustion method its simplest formula is shown to be CO_2H, but, as it is a dibasic acid, this formula must at least be doubled, $C_2O_4H_2$ or $C_2O_2(OH)_2$. When oxalic acid is heated with concentrated sulphuric acid it suffers decomposition, thus $C_2O_4H_2 = H_2O + CO_2 + CO$. The elements of hydrogen and oxygen are abstracted in the atomic proportion of 2 : 1, and the oxides of carbon are evolved. Carbon monoxide is usually prepared from oxalic acid by this method; the dioxide is removed by passing the gases through milk of lime or caustic potash solution.

Oxalic acid is oxidised by acidified permanganate to carbon dioxide and water. As oxalic acid crystals $C_2O_4H_2, 2H_2O$ are easily obtained pure the acid is used to standardise permanganate. One molecule of oxalic acid needs, for complete oxidation, one atom of oxygen, therefore

$$2KMnO_4 + 3H_2SO_4 + 5C_2O_4H_2[2H_2O] = 10CO_2[+10H_2O] + 8H_2O + K_2SO_4 + 2MnSO_4.$$

The oxidation is rapid at 65° C., therefore the titration is carried out at about that temperature.

Further use is made of this reaction. Calcium oxalate is very insoluble in water, hence the concentration of calcium salts may be found, volumetrically, by precipitating them as oxalates by an *excess* of standard ammonium oxalate, afterwards estimating that excess by standard permanganate.

Oxalic acid may conveniently be used for estimating the percentage purity of pyrolusite. Manganese dioxide oxidises the acid completely in presence of sulphuric acid. A weighed quantity of the specimen (about 2 grams) is heated with 50 c.c. *N.* oxalic acid, to which about 5 c.c. concentrated sulphuric acid are added. The solution is boiled until all black particles have disappeared, and the excess of oxalic acid is found by $\frac{N}{10}$ permanganate.

$$\left\{\begin{matrix}MnO + H_2SO_4 \\ O + \end{matrix}\right. \quad \begin{matrix} \\ C_2O_4H_2 \end{matrix} = \begin{matrix} MnSO_4 + H_2O \\ + H_2O + 2CO_2. \end{matrix}$$

$$MnO_2 + H_2SO_4 + C_2O_4H_2 = MnSO_4 + 2H_2O + 2CO_2$$

Oxalic acid is a colourless, well crystallised solid; a moderately strong acid, it may be neutralised with litmus as indicator.

Its salts are of considerable importance. **Potassium hydrogen oxalate** is only slightly soluble in water. In the wood sorrel (*Oxalis acetosella*) it occurs in molecular combination with the acid as salts of sorrel or potassium 'quadrant oxalate.' **Calcium oxalate** crystals are abundant in the bark and leaves of plants, and seem to be an excretion product. A thin section of a leaf stalk of a begonia will generally reveal several crystals; as they are not dissolved by acetic acid, they may easily be distinguished from calcium carbonate crystals. When heated, calcium oxalate yields the carbonate and carbon monoxide $CaC_2O_4 = CaCO_3 + CO$. At a higher temperature the oxide is obtained by dissociation of carbonate. When **lead oxalate** is heated, some lead is produced $PbC_2O_4 = Pb + 2CO_2$.

Acetic acid.

In Chapter XIX. we have referred to the oxidation of alcohol during fermentation. The acetic acid is used for culinary purposes as vinegar (3 per cent.).

$$C_2H_5OH + O_2 = C_2H_4O_2 + H_2O.$$

On a commercial scale, some acetic acid (pyroligneous acid) is prepared by the distillation of wood. Pure acetic acid has a pungent odour, and causes severe wounds to the skin. It melts at 16·7° C., and boils at 118° C. Its vapour burns with a blue flame to carbon dioxide and water; it is generally *stable* towards oxidising agents. Deduced from its percentage composition, its simplest formula is CH_2O, and it is monobasic; but on account of its chemical reactions, it has been found necessary to double this formula, and to represent the acid by $CH_3.CO(OH)$.

The above formula is confirmed by analysis of the silver salt. 0·2445 gram of silver acetate when heated yielded 0·157 gram of silver. Hence 108 grams of silver are combined with 59·65 grams of the acid radicle. Therefore the

molecular weight of the *acid* is approximately 59·65 + 1 = 60·65 grams, or a multiple of this. The calculated molecular weight, corresponding to CH_3COOH, is 60.

It is a very weak acid and, for that reason, is used in analysis to produce feeble acidity.

Many acetates are important. **Sodium acetate**, CH_3COONa, $3H_2O$, and ammonium acetate are very soluble in water. They are used in analysis to weaken the acidifying action of acetic acid. **Copper acetate**, $(CH_3COO)_2Cu$, H_2O, forms dark green crystals; the basic salt 'verdigris,' is used as a pigment. **Lead acetate**, or 'sugar of lead,' is one of the few soluble lead salts. It is very poisonous, and, as it has a sweet taste and is not unlike cane sugar in appearance, it is insidious. The basic salt is readily formed when lead is exposed to the fumes of acetic acid in the presence of air. This salt is the intermediate product in the preparation of 'white lead,' basic lead carbonate $2PbCO_3$, $Pb(OH)_2$, and is formed by the mass action of carbon dioxide upon the basic acetate, the acetic acid being liberated. **Ferric acetate**, $(CH_3COO)_3Fe$, is used in analysis. It is deep red in colour. When its solution is boiled, hydrolysis takes place to form brown *basic*-ferric acetate. The reaction is reversible, for, on cooling, the normal salt is reformed

$$(CH_3COO)_3Fe + HOH \underset{\text{cooling}}{\overset{\text{heating}}{\rightleftharpoons}} CH_3COOH + (CH_3COO)_2(OH)Fe.$$

Aluminium acetate is used as a mordant in dyeing.

Tartaric acid.

Tartaric acid is a colourless, well crystallised solid. It melts at 170° C., but above this temperature it chars, evolving fumes of characteristic smell. It is dibasic, and has the formula $C_4O_6H_6$.

Its hydrogen potassium salt, 'cream of tartar,' is somewhat insoluble; it is found in grape juice. Potassium sodium tartrate $(C_4O_6H_4NaK)\,4H_2O$ is used in analysis; it is called Rochelle salt.

From our point of view, tartaric acid is important because it forms soluble salts of some heavy metals and of antimony. The antimony salt is called 'tartar emetic' or antimonyl tartrate $(2C_4O_6H_4SbO.K)\,H_2O$, a poisonous substance which must not be confused with cream of tartar. This salt is soluble, and therefore enables us to obtain *electro-positive* antimony in solution. It may be prepared by boiling antimonous oxide with cream of tartar.

$$Sb_2O_3 + 2C_4O_6H_4HK = (2C_4O_6H_4SbO.K)\,H_2O.$$

It is used in Iodometry for the estimation of antimony; excess of acid is 'neutralised' by the addition of sodium hydrogen carbonate. Tartaric acid forms a soluble blue

salt of copper, which is not decomposed even by excess of caustic potash. Hence its formation enables one to obtain an *alkaline* solution of cupric compounds without the aid of ammonia. Glucose reduces this solution to cuprous oxide, a reaction largely used both for estimating glucose and for preparing cuprous oxide.

The cyanides.

When nitrogen is passed over a strongly heated mixture of carbon and baryta, carbon monoxide is evolved and a substance of the formula BaC_2N_2 remains. If fused caustic potash, containing finely divided carbon, is treated with nitrogen, a substance of the formula KCN is formed. $2KOH + N_2 + 3C = 2KCN + H_2O + CO$.

This potassium compound dissolves readily in water; the solution has the peculiar smell of bitter almonds, and gives an alkaline reaction. When the compound is distilled with *dilute* sulphuric acid an intensely poisonous gas, having the bitter almond smell, is evolved, and can be condensed in a freezing mixture. Its formula is HCN. It is an acid, one of the weakest known; its solution just affects litmus. From one of its compounds—prussian blue—it derives its two names, prussic acid and **hydrocyanic acid**[1]. Several of its salts are important; they may be prepared in the laboratory from the potassium salt. Its alkali salts are nearly always formed when the respective metals are heated with organic substances which contain nitrogen. Hydrocyanic acid is formed during the distillation of coal from the carbon and nitrogen contained in coal, and this is an important source of the valuable potassium cyanide.

The suffix -ide denotes a binary compound, whilst these cyanides are ternary; yet, the suffix is well and subtly applied.

When potassium cyanide solution is added to silver nitrate, insoluble silver cyanide is formed. This salt has the appearance of silver chloride and likewise dissolves in ammonia. When heated, silver cyanide evolves an exceedingly poisonous gas whose density is 26—hence its molecular weight is 52. This burns with a purple flame to form nitrogen and carbon dioxide. Its mixture explodes with twice its volume of

[1] κυάνος = dark blue.

oxygen to yield its own volume of nitrogen and twice its volume of carbon dioxide. Hence its formula is C_2N_2.

$$C_2N_2 + 2O_2 = N_2 + 2CO_2$$

The gas is **cyanogen**, the free radicle of the cyanides. This free radicle $(CN)_2$ shows some similarities to the free radicle of the chlorides $(Cl)_2$. Both radicles combine with hydrogen to produce the acids, HCN and HCl, which however, as regards strength, differ extremely. The silver salts of both are formed as insoluble curdy precipitates, soluble in ammonia. Both radicles combine directly with potassium to form the respective salts. They undergo similar reactions with dilute caustic potash.

$$2KOH + Cl_2 = KCl + KClO + H_2O.$$

$$2KOH + (CN)_2 = KCN + KCNO + H_2O.$$

KCNO is called **cyanate** not hypo-cyanite; there is no compound corresponding to the formula $K(CN)O_3$. Potassium cyanate is always prepared by the oxidation of cyanide, the latter being a reducing agent

$$KCN + PbO = KCNO + Pb.$$

Other cyanates are prepared from the potassium salt. When one attempts to obtain the ammonium salt by concentrating a solution of ammonium sulphate and potassium cyanate mixed in molecular proportions, potassium sulphate separates first but leaves in solution **urea**. It will be seen that ammonium cyanate and urea have the same *empirical* formula CN_2H_4O. They probably have the same molecular weight, but each belongs to a separate series of compounds which are totally dissimilar. That the urea is formed by transformation of the cyanate is proved by the transformation of the solid ammonium cyanate. This may be prepared from ammonia gas and cyanic acid vapour. At a moderate temperature the change takes place spontaneously. The different properties of the two substances are attributed to different molecular arrangement. This theory is expressed in the rational formulae

$$NH_4OCN \longrightarrow CO(NH_2)_2.$$

They are said to be **isomeric** (ἴσως = equal, μέρος = a part). The change was discovered by Wohler in 1828.

In solution the reaction is reversible, equilibrium being attained when 95 per cent. of urea is present. This urea may be separated from the solid residue by hot alcohol.

The radicles Cl_2 and $(CN)_2$ differ very considerably in their action on water, for cyanogen, which is very soluble (1 part in 4), yields some ammonium oxalate by a peculiar kind of 'hydrolysis'

$$C_2N_2 + 4HOH = 2NH_3 + C_2O_4H_2 \longrightarrow (NH_4)_2C_2O_4.$$

This reaction has given to oxalic acid the formula $(COOH)_2$.

But it is in the power possessed by their salts to form remarkable complex salts that the resemblance between these two radicles is especially expressed. Potassium cyanide combines with ferrous cyanide to produce a body whose formula was at one time written $4KCN, Fe(CN)_2$, and with ferric cyanide it forms $3KCN, Fe(CN)_3$; both compounds crystallise well, the former is yellow and the latter red.

Unlike potassium cyanide, neither of these is poisonous when pure: a remarkable change for *double* salts. The addition of ammonia to their solutions fails to precipitate the iron hydroxides, and in fact both compounds are devoid of the properties usually connected with ferrous and ferric salts, and, no less remarkable, they have lost the properties of cyanides. When concentrated hydrochloric acid is added to a saturated solution of the yellow ferrous salt, a bluish-white precipitate is deposited whose composition is represented by $4HCN . Fe(CN)_2$; this substance dissolves in water to yield a strongly acidic solution, whereas hydrocyanic acid is very weak. One concludes therefore that the yellow salt is *not* a double cyanide, but that it is the (single) potassium salt of a complex acid. The salt is called potassium **ferrocyanide**, and the acid is called Hydroferrocyanic acid. It follows that the red salt should be called potassium **ferricyanide**. The formulae are now written $K_4Fe(CN)_6$ and $K_3Fe(CN)_6$.

It will be noticed that these salts show the same kind of relationship as exists between manganate and permanganate.

K_2MnO_4	$KMnO_4$
$K_4Fe(CN)_6$	$K_3Fe(CN)_6$

the acid radicle in both sets being unchanged; in both cases change in composition is marked by change of colour. The higher salt is prepared from the lower by the action of chlorine

$$2K_4Fe(CN)_6 + Cl_2 = 2K_3Fe(CN)_6 + 2KCl$$

(compare) $$2K_2MnO_4 + Cl_2 = 2KMnO_4 + 2KCl.$$

Potassium ferrocyanide is readily prepared by treating iron or a ferrous salt with potassium cyanide

$$6KCN + Fe(OH)_2 = K_4Fe(CN)_6 + 2KOH$$
$$6KCN + Fe + 2H_2O = K_4Fe(CN)_6 + 2KOH + H_2.$$

There are many interesting ferrocyanides, but the most interesting are the iron salts. When ferrous sulphate is added to potassium ferrocyanide *Ferrous* ferrocyanide is formed,

which is rapidly oxidised in the air to blue *Ferric* ferrocyanide. $K_4Fe(CN)_6 + 2FeSO_4 = Fe_2.Fe(CN)_6 + 2K_2SO_4$.

The ferric ferrocyanide is formed directly from ferric chloride. It is prussian blue.

$$3K_4Fe(CN)_6 + 4FeCl_3 = Fe_4'''[Fe(CN)_6]_3'''' + 12KCl.$$

Similarly, ferrous sulphate precipitates from potassium ferricyanide, Turnbull's blue, which possibly is ferrous ferricyanide $Fe_3''[Fe(CN)_6]_2'''$. Ferric chloride gives a yellow colour with ferricyanide which may be ferric ferricyanide, $Fe'''[Fe(CN)_6]'''$, but more probably is merely ferric cyanide $2Fe(CN)_3$. These two colorations explain the use of potassium ferricyanide as an indicator in dichromate titrations.

When copper sulphate is added to a solution of potassium ferrocyanide, **cupric ferro**cyanide is formed, $Cu_2.Fe(CN)_6$; this salt was used by Pfeffer in his osmometer.

Analogous to the ferricyanides are the cobalticyanides $K_3Co(CN)_6$ and nickelicyanides $K_3Ni(CN)_6$. The cobalt compound is less stable than the iron, and the nickel is still less stable.

These salts, although they are single salts of definite acids, are called **'complex'** salts. At one time they were definitely classed apart from all double salts, but it has been shown recently that some double salts (for instance ammonium magnesium chloride NH_4Cl, $MgCl_2 + 6H_2O$) have some right to be regarded as complex salts, especially in concentrated solution. The connection between the two classes of salts is completed by those undoubted complex cyanides—such as the cadmium compound—which are unstable in solution, decomposing into the simple cyanides.

$$K_2Cd(CN)_4 \rightleftharpoons 2KCN + Cd(CN)_2.$$

Silver cyanide dissolves in excess of potassium cyanide to form potassium argenticyanide, $KAg(CN)_2$. This salt is used instead of the nitrate for electroplating.

In this salt the silver would appear to be in the electro-negative radicle. To account for the *rule* that the silver is deposited on the kathode, some chemists assume that it is always partly dissociated into potassium and silver cyanides

$$K \mid Ag(CN)_2 \longrightarrow K' + Ag' + CN' + CN',$$

with the consequent formation of electro-positive silver. Other chemists explain the deposition otherwise; they believe the positive potassium is

discharged at the kathode and instantly attacks the salt with deposition of silver

$$K + KAg(CN)_2 = 2KCN + Ag \text{ (deposited).}$$

The electro-negative argenticyanidion, discharged at the same time, combines with the silver of the anode

$$Ag(CN)_2 + Ag = 2AgCN.$$

Hence potassium cyanide accumulates around the kathode and silver cyanide about the anode, and indeed the bath must be agitated constantly

$$AgCN + KCN = KAg(CN)_2.$$

Copper salts likewise dissolve in potassium cyanide to form the stable, colourless cuprocyanide, $K_3Cu(CN)_4$.

Potassium cyanide, with the aid of atmospheric oxygen, will dissolve gold to form auricyanide. Potassium cyanide is used in immense quantities on the gold fields for this purpose.

$$4Au + 8KCN + O_2 + 2H_2O = 4KAu(CN)_2 + 4KOH.$$

Complex salts, comparable with the above, are found amongst the chlorides. The more familiar instances are those formed by combination between the chlorides of monovalent metals and tetravalent metalloids. Thus lead and tin tetrachlorides form with potassium chloride compounds of the formulae K_2SnCl_6 and K_2PbCl_6.

Far more important than these are the analogous compounds of platinum. When platinum tetrachloride, a substance stable in air, is dissolved in concentrated hydrochloric acid, a very deliquescent solid may be obtained from solution. When this is redissolved and a salt of potassium or ammonium is added to it, a yellow crystalline powder is precipitated, which is very insoluble in alcohol. It has the formula K_2PtCl_6. The corresponding sodium compound is quite soluble in water, forming a neutral solution, which gives neither the reactions of platinum salts nor those of chlorides. Hence the compounds are regarded as alkali salts of an acid—**(hydro)chloroplatinic acid,** H_2PtCl_6.

The solubility of the sodium and the insolubility of the potassium salt is taken advantage of, both in qualitative and gravimetric analysis.

When heated, ammonium chloroplatinate yields ammonia, hydrochloric acid and chlorine, which are evolved, and spongy platinum which remains. The reaction is used for the estimation of the substituted ammonias, which form analogous salts. When fibres of asbestos are soaked in chloroplatinic acid and then ignited, finely divided platinum is left on the fibres.

$$H_2PtCl_6 = Pt + 2HCl + 2Cl_2.$$

CHAPTER XXX.

SILICON AND BORON.

In the foregoing chapters of Part II., we have learned that many properties of one element may be shared to a greater or less extent by two or more other elements. Such a group of elements is classed as a distinct family. The halogens served us for the **type** of the commonest kind of family. In families whose members are similarly related there may be three or more elements, but three of them are more particularly related, and it is found that the atomic weight of that one which has intermediate properties is the mean of those of the other two. In such a group, it is not so much the *similarity* as the *gradation* of properties which significantly marks them as of one family.

Other important families of this type are the alkaline earths (calcium, strontium and barium), the arsenic family (phosphorus, arsenic, antimony and bismuth), the zinc family (magnesium, zinc, cadmium and mercury) and, less important, the sulphur family (sulphur, selenium and tellurium).

The valency of each element of a family is the same. Iron, cobalt and nickel, which likewise show a gradation of properties, form an undisputed family. Each metal has the same valencies, but the atomic weights are approximately equal. Similar in these respects also are the palladium and platinum families.

Between chromium, manganese and iron there appears to be a close relation, the likeness being shown in compounds presenting the same valency. The gradation of properties is not so strongly marked as in the halogen or the cobalt-iron families. In one or more compounds they resemble widely differing elements such as chlorine, sulphur, aluminium and magnesium, and in such a manner that the common

properties would almost seem a result of that which determines their valency. So often do we find that similarity of properties goes with equality of valency, that we might hardly look to elements of unlike valency for similarity in properties. Yet *tri*valent boron and *tetra*valent silicon resemble each other in so many ways that it will be convenient to describe these elements together. Silicon, it is true, is closely related to tetravalent carbon, but boron shows only vague signs of relationship with aluminium or other trivalent elements.

Properties of the elements.

Both silicon and boron are obtained by reduction of their oxides by means of magnesium powder.

To obtain silicon, silica and magnesium are mixed together in the given proportion ($SiO_2 + 2Mg = 2MgO + Si$). To limit the violence of the reaction, one quarter of their weight of magnesium oxide, free from carbonate, is added. *All the substances must be perfectly dry.* The mixture may be heated in an iron tray lined with dry magnesium oxide, and covered with another tray, or, for smaller quantities, merely a hard glass tube may be used. After the reaction, hydrochloric acid is cautiously added to dissolve the magnesium oxide, and impure amorphous silicon remains. Amorphous boron is prepared by a precisely similar reaction.

$$B_2O_3 + 3Mg = 3MgO + 2B.$$

Amorphous silicon dissolves in molten zinc; it separates out again on cooling as crystalline (graphitic) silicon. When heated in air, both elements burn to form their respective oxides. Both are acted upon by caustic bases, with liberation of hydrogen, to form the alkali salts of boric and silicic acids respectively, The atomic weights of these elements are deduced approximately from the vapour densities of their volatile compounds. The accurate determination was, in both cases, a matter of considerable difficulty; that of silicon has been found by the oxidation of silicon to silica (SiO_2).

Silicon is not found free in nature, but in silica and the silicates it is, after oxygen, the most abundant element upon the earth's crust. Boron is not nearly so common; it occurs in boric acid and certain borates.

Boric acid.

For many years the chief source of boric acid was the 'lagoni' of Monte Rotunda in Tuscany. These lagoni receive their supply from the 'suffioni' or hot vapour jets near by. The water of the lagoni (con-

taining about 2 per cent. of boric acid) is concentrated by the heat of the suffioni. Boric acid is also obtained from the sodium, magnesium and calcium salts which occur native. The most important compound of boron is borax: the water of Lake Borax in California contains one pound of borax per thirteen gallons.

Boric acid may be obtained from borax by the addition of concentrated hydrochloric acid to the hot saturated solution. Boric acid settles out in small crystals, and sodium chloride is left in solution. Boric acid (also called boracic acid) is only moderately soluble in water; its solution has little effect upon litmus, but attacks magnesium ribbon readily. Although it is a very weak acid, it affects turmeric paper like a base. It is used largely as an antiseptic. The acid displaced from borax has the composition represented by H_3BO_3; it is called **ortho-boric** acid.

Although some salts of this acid are known, the meta-borates are better known (KBO_2).

When the ortho-acid is heated to 100° C. the meta-acid is formed. At a higher temperature the acid anhydride is obtained, $2HBO_2 = B_2O_3 + H_2O$.

Boric oxide is a white powder, but little affected by heating, whilst the acid is comparatively volatile. This is the opposite of the usual condition, for most anhydrides are more volatile than their acids (compare sulphuric acid). Boric oxide is very hygroscopic, absorbing water to reform boric acid. Like many weak acids boric acid tends to form 'condensed' salts, that is, salts containing a higher percentage of the anhydride than the normal ortho-salts; indeed with boric acid these condensed (or pyro) borates are more stable than the ortho- or meta-borates.

Borax.

The only borate of consequence is **Borax**, whose formula is $Na_2B_4O_7, 10H_2O$. It is the salt of a condensed (tetra) boric acid. When heated, borax swells up and loses water of hydration.

By this reaction the atomic weight of boron has been determined accurately. The loss is 47·13 per cent. of the total weight, therefore

$$\underbrace{Na_2B_4O_7, 10H_2O}_{(46+4x+112+180)} = Na_2B_4O_7 + \underbrace{10H_2O}_{(180)}$$

$$100 \qquad 47{\cdot}13$$

Sodium tetraborate may also be obtained as an octohedral penta-hydrate by crystallising at 75° C.

Borax is sometimes used instead of sodium carbonate for standardising acids. For, as boric acid is very weak, its salt, borax, is hydrolysed in solution and methyl orange is turned yellow by the freed caustic base. But in addition, boric acid has no effect on methyl orange, hence a sharp end point occurs as soon as the quantity of strong acid added to the solution of borax is sufficient to react with the whole of the base (see page 176). Melted anhydrous borax dissolves some metallic oxides to form characteristically coloured 'glasses.' This reaction is used for the detection of certain metals in their compounds.

A loop of 3 or 4 mm. diameter is made at the end of a platinum wire. Borax is melted in the loop, a trace of the salt to be analysed is added, and the bead is again fused. Find the parts of the flame in which

Chromium	compounds	give an	emerald green	bead.
Copper	„	„	blue green	„
Iron	„	„	yellow green	„
Cobalt	„	„	blue	„
Nickel	„	„	pinky brown	„
Manganese	„	„	amethyst purple	„

Besides silica and the silicates, and borax and boric acid these elements have but few important compounds, but for the sake of establishing more clearly their similarity, their halides will be considered at some length.

The halides of boron and silicon.

The respective **chlorides** are formed when chlorine is passed over the heated elements, or over a heated mixture of carbon and the oxide.

$$2B + 3Cl_2 = 2BCl_3,$$
$$Si + 2Cl_2 = SiCl_4.$$

Silicon tetrachloride is, at ordinary temperatures, a liquid boiling at 59° C. Boron trichloride boils at 17° C. Both chlorides are decomposed by water to yield hydrochloric acid, and either boric or silicic acid as the case may be.

$$SiCl_4 + 4HOH = 4HCl + Si(OH)_4,$$
$$BCl_3 + 3HOH = 3HCl + B(OH)_3.$$

By precipitating all the chlorine as silver chloride the chlorides were analysed accurately (compare with chlorides of phosphorus).

The **fluorides** of both elements are formed by the action of hydrofluoric acid on the oxides

$$B_2O_3 + 6HF = 2BF_3 + 3H_2O,$$
$$SiO_2 + 4HF = SiF_4 + 2H_2O.$$

These compounds are prepared by gently warming a mixture of the respective oxides and calcium fluoride with concentrated sulphuric acid. Towards water they behave rather differently from the chlorides, probably because of secondary actions. Both fluorides are gases at ordinary temperatures. When boron fluoride is passed into water, reaction does not immediately take place, but in solution it eventually gives rise to boric acid and fluorboric acid, a substance having the formula HBF_4.

Apparently, liberated hydrofluoric acid combines with a second molecule of boron fluoride to form fluorboric acid. This complex acid is comparable with chloroplumbic and chloroplatinic acids (Chapter XXIX.).

The silicon fluoride reacts immediately with water to form silicic and fluorsilicic acids. The former is insoluble, and therefore the apparatus of Fig. 125 must be used when the fluoride is passed into water. The delivery tube dips under mercury (the mercury valve) so that the gas does not meet the water as it leaves the tube, otherwise the way would soon be choked by the gelatinous silicic acid.

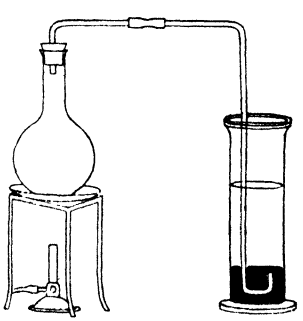


Fig. 125.

$$3SiF_4 + 3H_2O = H_2SiO_3 + 2H_2SiF_6.$$

(Hydro)fluorsilicic acid is soluble in water; it is strongly acid to litmus, and attacks magnesium ribbon with ease, liberating hydrogen. Its potassium and barium salts are somewhat insoluble, wherefore it is sometimes used in analysis to confirm the presence of salts of these metals.

Owing to the ease with which silicon tetrafluoride is formed by the action of hydrofluoric acid upon silica and the silicates, this acid is used for etching glass, for glass is essentially a mixture of silicates.

A piece of sheet glass may be etched in the following manner. Run a thin layer of melted paraffin over one side of the glass; when the wax is hard, write the words to be etched with a pointed instrument, so that the glass is exposed. Place the glass over a leaden dish which contains a mixture of powdered fluor spar and vitriol, and warm over a very small flame (Fig. 126). Afterwards melt away the wax. The greatest care must be taken to avoid contact with the acid; otherwise dangerous wounds are sustained.

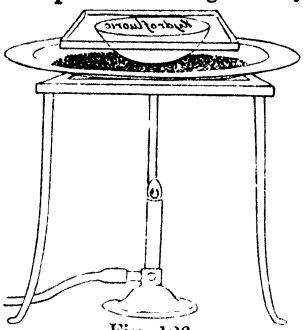


Fig. 126.

Many silicates and some forms of silica can be brought into solution by the decomposing action of hydrofluoric acid only, hence the latter is used in analysis.

Some silicates and some kinds of silica are transformed into sodium silicate by continued heating with sodium carbonate.

Silicic acid.

Hence glass apparatus is not used in quantitative work when bases are to be heated.

For this purpose the finely powdered silicate is heated with a considerable quantity of sodium carbonate in a platinum crucible by means of a blowpipe flame until the whole is fused. The sodium silicate produced is dissolved out by hot water, and the solution is treated with hydrochloric acid.

The dilute sodium silicate solution may be dialysed; the dialysis is greatly hastened by adding hydrochloric acid to displace all the silicic acid. The silicic acid is left in a colloidal condition (a 'hydrosol') and is said to have the composition corresponding to H_4SiO_4.

If the solution is heated the free silicic acid is gelatinised and a solid mass of silicic acid and water is formed (a 'hydrogel'). This is thought to have the formula H_2SiO_3. A solution of this substance has a slightly acid effect on litmus but appears to have no corroding action on magnesium powder—perhaps because it is almost insoluble. On attempting to dry this acid it loses all its water, leaving finely divided silica (SiO_2).

By the foregoing series of reactions the silica in some silicates may be estimated gravimetrically.

Silica occurs in nature as sand and as quartz or rock crystal. Quartz is found in igneous rocks such as granite, and lining metalliferous veins. It is a hard colourless substance, occurring in hexagonal prisms, horizontally striated, with hexagonal pyramid ends. When it is coloured feebly purple by impurities, it is known as amethyst. Silica is found also as loose sand; in compact sandstones; and in the close textured quartzites. In the hydrated form it occurs as agate, chalcedony, carnelian, chrysoprase, onyx, jasper, flint, and chert; and in the amorphous hydrated form as opal. Hydrated silica is readily brought into solution as alkali silicates by caustic bases, but these solvents have no effect upon quartz. Many silicates are decomposed by the natural **weathering** of the rocks, and the dissolved silicic acid is subsequently deposited as hydrated silica. This deposition of silica appears sometimes to be immediately due to the action of organisms. Much of the flint seen in chalk, for instance, is found to have been deposited around fossils. From the silicic acid swept down to the sea, certain animals and plants secrete the silica of their testae, &c. The diatom testa is pure silica, and in the past large deposits, consisting almost entirely of their microscopic testae, have been formed: such is the origin of kieselguhr, the earth used for dynamite. To-day similar deposits are being formed in many a lake and on the sea floor. Radiolaria also have silicious testae. Certain plants absorb considerable quantities of silica, notably the grasses and the horse-tails.

Hot water can dissolve fair quantities of silica: around the vents of geysers this may be deposited as **sinter** (hydrated silica).

Silicates.

The silicates form the greater part of the earth's crust, and although for this fact they are of immense importance, yet they occur in such marvellous variety and for the most part are so complex that their constitution is comparatively little known. The complexity is partly due to the fact that silicates are usually 'condensed' salts.

Amongst the best known mineral silicates are olivine, a mixed ferrous and magnesium silicate; muscovite (white mica) a potassium and aluminium silicate; augite, a mixed magnesium, calcium, ferrous and manganous silicate; orthoclase felspar, a potassium aluminium silicate.

Other well-known minerals are hornblende, plagioclase, biotite, albite, anorthite, talc, and asbestos.

Rocks are usually mixtures of certain minerals. Thus granite consists of quartz, one or more felspars, and one or two micas.

Although the silicates are very stable towards heat, they vary considerably in their resistance to the mass action of water and carbon dioxide, and in the course of time are 'weathered.' The felspars are generally the first to be attacked, and with their decomposition the rock disintegrates. Thus the felspars of granite are transformed into soluble potassium, calcium, and sodium carbonates, and dissolved silicic acid, which are swept into the sea or are absorbed by soil, and aluminium silicate, which is swept down to lower levels to form **clay**. In exceptional circumstances the hydrated aluminium silicate may remain undisturbed above the unweathered rock. It is then known as kaolin (china clay) and is valuable for the manufacture of porcelain.

Bricks.

The clays are the disintegration products of the older rocks, they differ very widely in composition according to their origin: the hydrated silicate of aluminium, calcium and magnesium carbonates, with iron oxide and silica, &c. predominate. When heated, the hydrated silicates lose their water of hydration and with it their plasticity. Once baked they do not become rehydrated in contact with water, but remain porous, hard, and resistant. This is the chemistry of brick making.

Mortar.

For building purposes bricks are held together by mortar. Mortar is a mixture of calcium hydroxide and sand. The mortar binds the bricks all the more firmly because it makes its way into the superficial pores of the bricks. The slaked lime at first loses water and **sets** to a porous mass, then gradually it is transformed to the carbonate. The sand assists in keeping the mortar porous, and thus it ensures completer transformation of the lime. But in course of time it also reacts to form the exceedingly hard calcium silicate: to this tardy reaction the Romans owe their reputation as makers of peerless mortar.

Cement.

Mortar cannot set under water. In such situations 'hydraulic' cement is used. This consists of slaked lime and burnt clay, made by 'burning' argil-

laceous[1] limestone. The cement hardens beneath water because of the formation of calcium silicate and calcium aluminate.

Glass. Glass is made by melting together sodium or potassium carbonate, silica (sand or flint) and calcium carbonate. It is essentially a mixture of calcium and alkali silicates. Although the free alkali silicates are soluble, combined in glass they become insoluble. The best glass for chemical experiments, because of its resistance to boiling water and because of its high fusion point, is Jena glass; this is a calcium potassium silicate. For optical purposes lead silicate takes the place of calcium silicate. For a special kind of glass boric anhydride is used instead of silica.

Glass is used as a 'glaze' for earthenware. Earthenware is naturally porous, inasmuch as it is merely baked clay, but, by covering it with a glaze, it becomes impervious to water. The cheapest method of glazing is to throw into the furnaces, which contain the baked earthenware, common salt which volatilises and reacts upon the hot surface of the earthenware to form a cohering layer of sodium aluminium silicate, that is, to form an artificial felspar. Porcelain differs from ordinary earthenware in that, after the first baking, it is dipped in a milk of felspar which soaks into the pores. It is then fired again when vessel and felspar fuse to a homogeneous translucent mass. Porcelain is much more resistant than glass to heat, and to water and other chemicals.

NOTE The chemistry of brick-making is described in Harris's *Science of Brickmaking* (Montgomery) and the weathering of earths from the point of view of husbandry in Bailey's *Principles of Agriculture* (Macmillan), Fletcher's *Soils* (Constable), and A. D. Hall, *The Soil*.

[1] *argilla* = clay.

CHAPTER XXXI.

RESPIRATION AND NUTRITION.

WHEN we observe a large animal in active movement and consider that the 'work' done by any animal is proportional to the weight of its body and to the distance which it moves, we begin to realise that the living organism must be a very efficient machine for providing 'energy' of some sort and converting it into the work of movement. Nor is the external movement the whole of the work done, internal movements of the heart and breathing muscles go on without cessation, and also movements of growth; and many chemical changes within the body demand continuous supplies of energy.

The energy for all this movement and vital activity is obtained as chemical energy from the food consumed by the animal. The food materials absorbed by the animal are ultimately oxidised with the oxygen taken in by respiration, and heat and chemical energy are set free. The former maintains the temperature of the animal and the latter supplies the energy of life. Food materials may be oxidised or burnt as fuel in an ordinary engine, and the heat evolved used to produce movement (of the parts of the engine) apart from vital action.

A truss of hay may be used as fuel in a traction engine or may be given as food to a horse. In both cases the result is work done—say in dragging a heavy load up hill—and it is interesting to note that there is less waste when it is used in the living machine; that is, a horse is a more efficient machine than a steam engine for converting the chemical potential energy of food into mechanical work.

In both combustion and vital respiration identical changes take place. For instance, hay consists chiefly of starch and cellulose, of the composition $(C_6H_{10}O_5)_n$, and the oxidation in both cases results in the production of carbon dioxide and water.

$$C_6H_{10}O_5 + 6O_2 = 6CO_2 + 5H_2O.$$

These waste products are given out in one case as the respiration of the animal, in the other case as the gases from the furnace of the steam engine.

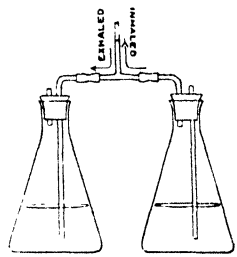


Fig. 127.

Experiment I. To show that exhaled air contains a greater proportion of carbon dioxide than inhaled air, it is usual to breathe through the apparatus of Fig. 127: its action is sufficiently clear without description. Both flasks contain lime water.

Respiration of plants.

When we return from the actively moving animal to the other type of living being, the stationary plant, things seem to be different. But though the plant consumes no energy in moving over the surface of the ground yet its growth movements are very vigorous, and it needs energy also for its internal processes. So we find that respiration is as indispensable for plants as for animals, though it is very rarely so vigorous.

Experiment II. To show the production of carbon dioxide, place some germinating seeds in a jar with well-fitting stopper (Fig. 128). After this has stood for a whole day in a warm place remove the stopper gently and lower a burning taper into the jar. The taper will be extinguished at once.


Fig. 128.

Experiment III. To show that this production of carbon dioxide is accompanied by the disappearance of the oxygen of the air, germinating seeds should be placed in a flask (Fig. 129) with a side tube dipping in water. The

test-tube contains potash solution which absorbs the carbon dioxide as fast as it is formed by the seeds. The decrease of pressure, due to the consumption of the oxygen, is shown by the rise of the liquid in the side tube.

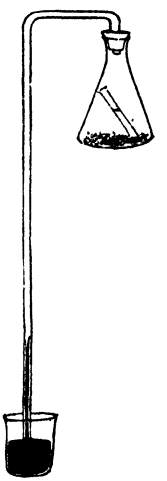


Fig. 129.

Experiment IV. In the equation for the combustion of carbohydrate given above, it will be seen that the volume of carbon dioxide produced is equal to the volume of oxygen consumed. So it is with respiration; this can be shown by setting up an experiment like the last but omitting the caustic potash. In this case there will be no serious alteration of the level of water in the side tube, unless, indeed, the temperature of the room is changing.

A 'control flask' set up beside the other, but quite empty, will show solely the effects of change of temperature.

Food synthesis.

We have now to consider the important question of how the plant obtains continual new supplies of energy for its vital processes and for its growth. Clearly the animal obtains its new supplies of energy by absorbing food which is rich in potential chemical energy, such as carbohydrates and proteids in which there is an excess of carbon in relation to oxygen. A measure of the potential energy of substances is the heat given out when they undergo combustion, and in the case of the food materials of the animal (*e.g.* sugar and cellulose) this is very high. Green plants, however, do not take in food of this nature: they flourish on air and water in a sandy soil where an animal would straightway starve to death. Their flourishing growth under these conditions is due to their power of building up or synthesising their own food by a process usually called **assimilation.** This process is exactly the reverse of the process of respiration or combustion, and may be represented by the equation

$$6CO_2 + 5H_2O = C_6H_{10}O_5 + 6O_2.$$

Carbon dioxide from the atmosphere is made to react with the water in the bright green cells of plants, and thus starch or other carbohydrate is formed and gaseous oxygen is liberated. As the equation representing respiration shows a liberation of energy, so the reversed equation representing assimilation will involve a consumption of energy. The energy for assimilation is obtained from the radiant energy of the light of the sun and sky falling upon the green parts of plants. Assimilation, or the building up of carbohydrate, can only go on in the light: in the dark, the plant lives upon the stores of carbohydrate formed when the plant was previously lighted. In bright light the process of assimilation may go on very briskly, so that in a single hour's light enough carbohydrate may be formed to last the plant for twelve or more hours of respiration in the dark.

Only the green cells of plants have the power of carrying on assimilation, because it is the green leaf-pigment, **chlorophyll**, which alone can absorb, from sunlight, the proper energy needed for this 'photosynthesis' of carbohydrate.

We must now prove the existence of this process of assimilation in the light by suitable experiments.

Experiment V. The production of starch is most easily shown in the following way. Early in the morning, darken part of a green leaf either with a strip of tinfoil pressed closely to it, or by painting black letters on it with indian ink. A leaf still on the plant, or a cut off leaf in water, may be used, but the leaf should have been kept dark since the day before so that there shall be no starch in it at the beginning of the experiment. The leaf is then to be exposed to bright light of the sky (direct sunlight is not essential) till late in the afternoon, when it is to be brought into the laboratory and tested for starch. This test is carried out as follows. The leaf is boiled in water for two minutes and then placed in a beaker of methylated spirit kept warm in a saucepan of hot water. The green colour dissolves in the spirit and the leaf becomes quite white. Then the leaf is transferred to a solution of iodine and potassium iodide in water, sufficiently concentrated to show a medium brown colour. The starch in the leaf will, in a few minutes, absorb iodine from this solution and will exhibit a bright blue colour.

Some plants form sugars, not starch, during assimilation and cannot be used for this demonstration. The sunflower, scarlet runner, tobacco, clover, and nasturtium are especially suitable plants.

The distribution of this blue colour over the leaf should show that abundant starch has been formed everywhere except in the darkened patches of the leaf, which now show up quite pale or a little browned by the iodine. This experiment demonstrates how necessary the energy of light is for the process of assimilation.

According to our equation oxygen should be formed as well as starch. This is most easily shown by experimenting with water plants.

Experiment VI. Prepare a wide-necked flask with a funnel as in Fig. 130. Collect some fresh submerged water-weeds and pack them into the flask, which should then be completely filled with tap-water and set up as pictured, with an inverted test tube full of water supported in the middle of the funnel of water. If the flask is now exposed to bright light, bubbles of gas will be seen to escape from the water plants and rise upwards to collect in the inverted test tube. The gas that collects can be shown to be oxygen by the re-kindling of a glowing taper. If this apparatus is kept darkened no bubbles are given off. The amount of oxygen liberated depends, of course, on the amount of carbon dioxide in the water available for assimilation, and when the carbon dioxide is all used up the process must stop.

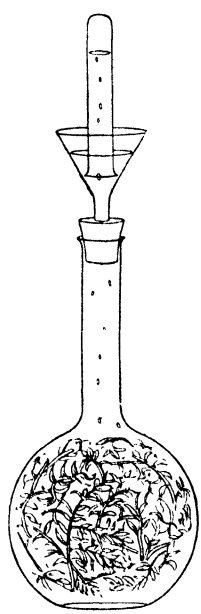


Fig. 130.

Experiment VII. will show more clearly the dependence of this oxygen bubbling upon the presence of carbon dioxide.

Take a single sprig of a water-plant and place it in a beaker of water that has been recently well boiled, to drive off the dissolved carbon dioxide, and then quickly cooled.

To keep the plant well under water, tie it to a glass rod (Fig. 131). When this is exposed to the light, there will be no bubbles of oxygen formed (or just a few, if some carbon dioxide has diffused in from the air). If CO_2 is now added to the water either from a carbon dioxide generator or by blowing into the water through a glass tube, vigorous bubbling will be started. The bubbles can be seen to form at the cut ends of the stems or at other spots where there are openings into the interior of the plant. The effect of darkening can be conveniently tried on this single shoot.

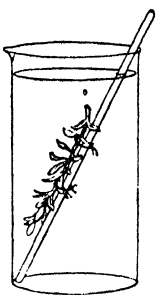


Fig. 131.

Living plants and animals are largely made up of water, and any alteration in the amount of water present will affect the *fresh* weight of the organism. A truer guide to what is happening to an organism is obtained by taking the *dry* weight, after all the water has been driven off at 100° C. Consideration of the equation for respiration teaches us that this process involves a decrease in the dry weight of the respiring organism. It follows that if a lot of seeds be germinated in the dark where they cannot assimilate, they must go on steadily losing dry weight day by day. This is the more surprising because the seed is all the time growing into a much larger structure, the seedling.

The seedling in the dark is, however, very rich in water, but actually contains less dry matter than the seed from which it sprouted. This can easily be proved by experiment.

Experiment VIII. Take two lots of grains of wheat of equal weight. Dry one lot in a steam oven, and determine the dry weight. Soak the other lot, and keep them moist in a tall tin or jar in a dark warm place. When they have grown to tall seedlings remove them carefully, and dry them at 100° C. It will be found that they dry down to a smaller weight than did the lot of ungerminated seeds.

As respiration involves a *loss* of dry weight, so assimilation produces a *gain* of dry weight, and a green leaf, which has been forming starch in the light, is the heavier when dried at the end of the day by just the weight of starch formed

in it. To prove this fact by experiment is not very easy. To obtain accurate results a number of precautions must be taken, an account of which may be found in practical books on the physiology of plants (cf. Darwin and Acton, *Practical Physiology of Plants*).

In summary, we may say that the living parts of all plants inhale oxygen and exhale carbon dioxide in respiration, while, for the purpose of food synthesis, the green parts of green plants absorb carbon dioxide and liberate oxygen.

Transpiration current.

When a plant is incinerated there always remains some incombustible matter—the ash. This usually consists very largely of potassium carbonate[1] with sodium, magnesium, calcium and iron compounds such as the sulphate, the phosphate, the chloride or the silicate. The nature and relative proportions of the constituents vary with the nature of the soil. How are they absorbed and for what purposes, if any? It is a matter of common knowledge that plants wilt and die in dry soil. The amount of water absorbed from the soil by them is immensely greater than that retained in their bodies: by far the greater proportion of it is evaporated from the leaves. Suitable experiments show that this process, which is called **transpiration,** takes place mainly through stomata, minute pores in the green leaves. The organs which absorb the water are the root hairs, filamentous outgrowths from the younger parts of the roots. Root hairs may be seen upon mustard seedlings grown in damp sawdust.

Experiment IX. Cut off a small shoot of a leafy plant, and clasp the stem firmly in the split cork of a jam jar. Nearly fill the jar with water, and replace the cork so that the stem dips in the water. Seal the cork with wax, and then invert a similar jar over the shoot. Notice what takes place, and account for it.

Some idea of the activity of transpiration may be obtained by tying up the flower-pot of a potted plant in oiled silk, and drawing the edges closely about the stem of the plant. The pot is then poised on a balance.

Experiment X. Place shoots of willow, as nearly alike as possible, in jars containing spring water and rain water respectively. Plug the mouths of the jars lightly with cotton

[1] Hence the word *alkali*, Arabic for ash.

wool, and place them in bright sunshine. In winter, a warm room with a well lighted window will suffice. Renew the water frequently, and pare the cut ends of the shoots from time to time.

It will be observed that the shoot in the rain water does not grow, whereas that in spring water makes undoubted progress. Now while rain water is nearly pure, spring water contains dissolved solids such as we know to be present in the soil and in the ash of plants. When different parts of plants are ignited, it is found that the greatest proportion of ash comes from burnt leaves. This we might expect, for, since the water is transpired from the leaves as vapour, the dissolved solids must remain behind. When the leaf falls, much of this mineral matter is thrown off with it, but, as the plant will not flourish unless the salts are supplied, these evidently play some important part in plant nutrition.

The truth of this view may be proved by growing different plants in solutions from which the various constituents of the ash are in turn withheld. It is found that salts containing potassium, calcium and magnesium, sulphur and phosphorus are indispensable. In addition to these a nitrate must be present. The experiment is not easy to perform successfully, but, with repetition, the results repay the patience and care which must be expended.

Experiment XI. (Culture Experiment). Make a solution as follows:

Distilled water	1–1·5 litres.
Potassium nitrate	1·0 gram.
Magnesium sulphate	·5 „
Calcium sulphate	·5 „
Calcium or potassium phosphate	·5 „
An iron salt	a trace

The shoots or seedlings of wall flowers, or the cut stems of plantain, are placed in perfectly clean vessels, each of which contains half a litre of the solution, and the mouths of the vessels are lightly plugged with cotton wool.

At least one other experiment should be made, in which the potassium nitrate is left out, and the difference in the result observed.

If duckweed is grown in the above solution and in others from which some of the constituents are omitted, the number of fronds formed will afford a rough means for comparison of the suitability of the solutions.

The experiments, when very carefully carried out, show that none of the above constituents can be omitted without serious disadvantage. Hence, if for no other reason than to supply these salts, the transpiration current is essential: the solution is so very dilute (less than $\frac{1}{100}$ equivalent) that large quantities of water must be absorbed to obtain them in appreciable quantities.

More concentrated solutions are actually harmful to plants.

From these salts and the starch and sugar found in the leaves, the living substance (protoplasm) builds up new protoplasm and the cellulose cell walls, which may be transformed afterwards into wood and cork. For this work the plant depends upon the energy set free by respiration.

Nitrogen.

It is a remarkable thing that whilst plants cannot exist without nitrogen in some form, with few exceptions they cannot make use of the free element, although they live in an atmosphere containing 80 per cent. of it.

Among the few exceptions to this rule are certain members of the pea tribe, notably the clovers. These plants actually store up nitrogen compounds when grown in soil which has been so far exhausted of nitrates that other plants cannot live thereon. Clovers are found to have upon their roots nodules which contain numbers of comparatively large bacteria. The suggestion having been made that these bacteria have some part in the accumulation of the nitrogen compounds, clover was grown in sterilised soil—that is, soil deprived of bacteria. Under such conditions the clover did not thrive, nor were the nodules formed, but, when some unsterilised soil was added, nodules appeared and the plants flourished. From what has been said in Chapter XIX. it would seem probable that these bacteria can oxidise the free nitrogen in the porous soil to nitrite and nitrate, in which form the plant is able to assimilate nitrogen.

These bacteria are not found plentifully in every soil. In Germany the surface soil of land well stocked with them is borne to soils in which clovers do not flourish. Experiments are now being carried out on experimental farms to study the effect of adding cultures of these bacteria ('nitragin') to poor soils.

The ash.

Although only those salts included in the above culture solution are absolutely necessary for plant growth, others are contained in the ash, and broadly speaking all soluble salts are likely to be absorbed, the constituents of the ash depending upon the nature of the soil. But the ashes of different species of plants grown side by side will be found to differ in their relative composition. The additional salts, although not necessary for *growth*, may be necessary for perfect development. Thus grasses and horsetails assimilate much silica, which serves to support their slender haulms. Seventy per cent. of the dry weight of wheat straw may consist of silica.

If a piece of the stem of a horsetail is boiled in hydrochloric acid (1 in 4), or heated directly in the flame, a beautiful silicious skeleton is left.

Plants exhibit great variety in the nature of the additional salts they can use, and to this apparent selection is due, to some extent, the wide differences between the flora of one district and another. These preferences must be remembered by the gardener, thus his asparagus bed should be supplied with rock salt.

Not only do plants absorb from the soil such salts as are necessary for or are helpful to their growth, but they may take up others which are even poisonous to them. The ashes of trees which grow in soil derived from copper bearing rocks may contain as much as 1 per cent. of copper: yet copper compounds are very poisonous to plants.

Manuring.

When crops are removed from a soil, they leave it poorer in the particular compounds which they absorb; if the cropping is often repeated the ground becomes impoverished, so that it can no longer support the same crop as before. Other plants, however, which draw less upon the particular compounds which have been extracted, may still grow there. This is the principle of **rotation of crops.** Sooner or later, however, the soil becomes barren. If for several years it is left '**fallow,**' that is to say untilled, or ploughed but not sown, it gradually recovers some of its old productiveness. This recovery is due to '**weathering.**' Carbon dioxide and moisture are continually attacking the particles of the soil and rendering them soluble and ready for absorption (Chapter XXX.). As long as nothing is sown the

weathered soil accumulates, but the process, although continuous, is too slow to keep pace with the needs of a succession of crops.

The roots of plants are able to assist this weathering action, probably by the excretion of carbon dioxide by the roots. Plants grown in damp sawdust (or in water) upon a marble slab will make a perceptible etching where the roots meet the slab.

In Canada the soil of regions recently brought into cultivation is so rich that its fertility seems in no way diminished by the abundant and rapid harvests, but in the valley of the Nile, whose soil has been cultivated for thousands of years, the success of each season depends upon the alluvium deposited by the annual floods.

To increase the area annually fertilised the Nile dam was constructed.

Where natural fertilising, through weathering or deposition, proves inadequate, cultivators have recourse to manures. Besides ordinary stable manure, guano and blood, an increasing use is made of chemical manures. These include basic slag (containing calcium phosphate), the Stassfurth deposits (containing potassium sulphate, &c.), caliche (impure sodium nitrate), acid calcium phosphate—commonly known as superphosphate of lime—and many others.

Experiment XII. Allow some broad beans to germinate and grow in damp sawdust, separate them into two lots, grow one lot in sawdust kept moist with pure water, grow the second lot in sawdust kept moist with culture solution. Compare the growth of these seedlings with that of others grown in good soil. If dwarf beans or peas are used the yields may be compared.

Experiment XIII. Place a potato tuber on the rim of a glass full of rain water, and keep it in the window.

Seeds and tubers often contain so much stored food that they can germinate, flower, and even yield seed without drawing upon the soil for nourishment of any kind, but the seed is not so well developed, nor so well provided with reserve material, as it would be under normal conditions.

Respiration and nutrition of animals.

To render the chapter more complete, a short account is appended of the corresponding actions in animals. These do not lend themselves to practical treatment in an elementary manner.

The lower animals respire by the diffusion of oxygen across skin, which in their case is thin. The higher animals

have the breathing area limited to special organs; in the case of some marine animals such as the fishes—but not the whales, seals, and kindred animals—these organs are called gills. The breathing organs in terrestrial higher animals and the whales, &c. are called lungs.

A lung consists of a collection of tubes ramifying from the windpipe and ending blindly in thin-walled sacs, in whose walls run the still more thin-walled blood vessels. As the blood courses through these vessels their walls are traversed in one direction by carbon dioxide and water leaving the blood, and in the other direction by oxygen entering the blood. The vehicle of both gases in the blood is the haemoglobin (red colouring matter) of the red corpuscles. Each gas forms with it an easily decomposed compound, oxy-haemoglobin is scarlet, carboxy-haemoglobin is purple. Gills are filamentous thin-walled organs richly supplied with thin-walled blood vessels. As the water passes over them, dissolved oxygen is absorbed, and dissolved carbon dioxide is expelled.

The oxygenated blood is carried into every part of the body, giving up to the different tissues the oxygen by means of which they are burnt, and relieving them of the products of combustion, mainly carbon dioxide and water.

In order to make good the loss due to the combustion of their tissues animals need food; and as they cannot manufacture it for themselves, either they must feed upon green plants or the stored food of green plants as found in the seeds, fruits, roots, or they must devour animals which feed upon plants. Hence we may conclude that the energy of animals is ultimately derived from the sun. The food is taken into the intestine where, by ferment action and by emulsification, it is prepared for absorption into the blood. This takes place in blood vessels in the walls of the intestine. The food is then carried in the blood currents to the tissues into which it exudes, and is built up into living substance—into protoplasm. Thus while the waste of tissue is continuous in both animals and plants, in both also, the provision made for its renewal is more or less periodic.

The compounds of which animal tissue consists, contain, in addition to carbon, hydrogen, and oxygen, smaller proportions of nitrogen, phosphorus and sulphur. The combustion products therefore must also contain these elements. In plants these valuable substances are lost at intervals only, but in animals complex nitrogenous and other substances are poured into the blood and excreted continuously. The nitrogenous waste products are converted into urea in the liver. Urea and phosphates (microcosmic salt for instance) are removed from the blood by the kidneys.

CHAPTER XXXII.

THE PERIODIC CLASSIFICATION OF THE ELEMENTS.

Historical.

BEFORE the appearance of an important paper by Cannizzaro in 1858, there was considerable divergence of opinion amongst chemists as to the right values to be assigned for the atomic weights of the most common elements. That pamphlet, which advocated a logical method of revising atomic weights, was followed within a few years by a classification of the chemical elements based upon the new values. The system in question—the Periodic Classification of the Elements—is still found to be broadly in keeping with chemical discovery even the most recent, and has as yet no successor.

In 1864 the Englishman Newlands showed that if the elements are arranged in the order of increasing atomic weight, the properties of any element are repeated to some extent in those of the eighth element following or preceding it. He propounded the **'Law of Octaves'** which laid down that "the eighth element, starting from a given one, is a kind of repetition of the first, like the eighth note in an octave of music," and he illustrated the law by the following table:

H(1)	Li(2)	Be(3)	B(4)	C(5)	N(6)	O(7)
F(8)	Na	Mg	Al	Si	P	S
Cl(15)	K	Ca	Cr	Ti	Mn	Fe
Co, Ni(22)	Cu	Zn	Y	In	As	Te

The proposals of Newlands found little acceptance among his own countrymen. In 1869 the German Lothar Meyer and the Russian Mendeléef, working independently, made a

great advance upon the work of the English chemist. The greater success of these two men was due to their clearer grasp of the principles underlying the method. They recognised that probably the existing elements had not yet all been discovered; they felt it necessary to break through the limitations imposed by the 'octave'; and, when a given element was found not to possess the properties implied by its position in the strict order of the ascending atomic weights, Meyer and Mendeléef left as many blank places in their tables as seemed to be necessary, the element displaced falling, later on, into a position in accord with its properties. To meet certain difficulties they proposed an eighth group of elements, thus departing finally from the Law of Octaves. In this way they were able to exhibit, in improved tables, the relation existing between the properties and the atomic weights of the elements; their final statement of the 'Periodic Law' ran as follows:—

The properties of the elements, and therefore the properties of the compound bodies formed from them, are in periodic dependence on their atomic weights.

Mendeléef's table, modified to include the most recently discovered elements, is given on the folding sheet facing page 390. It consists of twelve horizontal **series** of elements which fall into eight vertical **groups**. Each group consists of elements which display many similar properties. The arrangement is not without inconsistencies, leading to qualifications which impair its simplicity. We shall here point out its most noteworthy features, leaving to the student the interesting task of testing and amplifying each statement from the evidence at his disposal.

Valency.

As the arrangement groups together elements of similar properties, we should naturally expect that the property of valency would find some expression therein; since, however, this property is so complex we should hardly look for a perfect illustration of it in a table based, in the first instance, upon a single property of the elements. But we may say that the elements of any one *group* exhibit the *same* valency, whilst in any one *series* a regular *increase* in the valency of the elements accompanies the increase of atomic weight; and it will further be seen

that the valency, *as shown by oxides*, increases from one to eight as we pass from Group I. to Group VIII. but, *as shown by the hydrides* (*or halides*), it rises to a maximum of five, and then falls to one: both rise and fall are regular. Group 0 contains the inert gases, the elements which form no compounds and have therefore no valency. Group I. consists of the monovalent metals, the alkalis, and the noble metals. Of the latter copper and gold are respectively di- and trivalent in some of their compounds. The elements of Group II. are all divalent metals, but mercury can also be monovalent. The elements of Group III. are trivalent, those of Group IV. are tetravalent, though tin and lead can be divalent also. Group V. contains elements which are both penta- and trivalent. Group VI. consists of elements which are hexavalent and divalent, with the exception of oxygen which appears to be divalent only. Group VII. contains elements which are monovalent where they form hydrides, but in their higher compounds with oxygen they are heptavalent (Cl_2O_7, $KMnO_4$, HIO_4). Group VIII. is peculiar in that families of the iron type take the place of the individual elements of other groups; several of the elements possess tetroxides and other compounds corresponding to a valency of eight.

Subgroups.

A secondary arrangement within the groups was made in recognition of the especially intimate resemblance observed to exist between the alternate members of many groups; the subgroups thus obtained consist of elements whose atomic weights exhibit, in a number of cases, the particular relationship shown on page 287, and which was first pointed out by Döbereiner.

A study of Group II. will make this clear; calcium, strontium and barium in the 4th, 6th and 8th series respectively, constitute a very closely related subgroup, whilst mercury, cadmium, zinc and magnesium, of the 3rd, 5th, 7th and 11th series, form another subgroup rather less well defined. It will be seen that this secondary arrangement divides the groups into subgroups of **odd** and of **even** series, and is broadly applicable throughout the whole table.

The subgroups are distinguished by placing the elements of even series to the left, and those of the odd series to the right of the spaces. This arrangement is suggestive rather

than universally exact, as may be seen from the following. Hydrogen, having no evident relative, is placed alone in Series 1. The properties of the elements of Series 2 are such as to render their relationship with the other elements of their respective groups somewhat vague; and a tendency is found in the earlier members of this series to anticipate, so to speak, the characteristic properties of the following group. This tendency is especially marked in the case of the element boron. A comparative table of the properties of the elements sodium, lithium and calcium, and their compounds, will show this tendency exhibited by lithium. The resemblance between beryllium and aluminium is quite as close as between beryllium and magnesium, while boron, as we have seen in Chapter XXX., may conveniently be described in company with silicon.

'Typical' elements.

Partly as a consequence of the tendencies quoted above, the members of Series 3 have come to be regarded as 'typical' elements. The term is not strictly defensible, but the facts underlying the use of it have led many writers to describe the elements of this series minutely, and to compare the other elements of their several groups with them. In previous chapters we have constantly made use of the term 'alkali' compound, because analogous compounds of sodium or potassium may often be used indifferently. This alone shows how similar are the properties of the two elements; the resemblances may easily be over-estimated, and the student is urged to compare their compounds. He will find some noteworthy differences which extend to matters of more importance than relative solubility and molecules of hydration.

Further study will show that potassium is more closely allied to rubidium and caesium than to sodium, while this latter element finds its nearest relative in lithium. The noble metals, gold, silver and copper, are of doubtful position. They have points of association with the metals of Group VIII.; they show very few with the 'type' element of Group I. Magnesium, the type element of Group II., should be compared with calcium on the one hand and with zinc on the other. The positions at present assigned to tellurium and argon, on the basis of their properties, are

not in agreement with those demanded by their atomic weights, but all attempts made to 'revise' the accepted values have hitherto proved unavailing.

Mendeléef showed that the properties of an element (being a function of its atomic weight) may be deduced from those of the elements above and below it in the group, and right and left of it in the series. So great was his belief in this principle that in 1871 he went so far as to describe in detail the properties of three elements whose discovery he foretold, and which were represented by gaps in his table. His conviction was abundantly justified when, in 1875, 1879 and 1886, these three elements—**gallium, scandium** and **germanium**—were discovered, and their properties investigated.

The student is advised to deduce the properties of zinc from those of its 'atom analogues,' magnesium and cadmium, copper and gallium; and similarly those of sulphur and tellurium, arsenic and bromine.

It is particularly interesting to trace the relationships of the elements described in Chapter XXVIII. Chromium occurs in Group VI. and is related to sulphur through the chromates and sulphates, in which compounds the two elements are hexavalent. Manganese is brought into relation with sulphur through the resemblance between the manganates and chromates. Manganese occurs in Group VII., and as a heptavalent element it is related with chlorine through the resemblance of the permanganates and perchlorates. Both chromium and manganese as divalent and trivalent elements resemble iron which is found in Group VIII., and a reciprocal tendency is shown by iron in the formation of an unstable potassium ferrate.

In its characteristic complex salts, the ferrocyanides, iron comes into relation with the platinum family.

The Periodic Table suggests no explanation for the strong resemblance of divalent iron to magnesium, or of trivalent iron to aluminium.

Short and long periods.

The periodicity of the properties of the elements with the increase of their atomic weights is illustrated graphically by the curve of Atomic Volumes drawn by Lothar Meyer. The 'Atomic Volume' is the ratio of the atomic weight to the density of the solid element. When this is plotted against the atomic weight a curve of periodic form is produced. The alkali metals occupy the crests. The 2nd series occupies the first part of the curve from crest to crest, the 3rd series occupies the second part; the following parts of the curve contain two

series each. Hence Series 2 and 3 are called **short periods,** and the following double series are called **long periods.**

The student is advised to construct for himself a similar curve for melting points.

Finally, we will shortly indicate some other tendencies illustrated by Mendeléef's table: (1) As we pass along the series from left to right, we observe a gradual disappearance of the well-marked metallic character shown by the earlier members of the series, and as the change takes place earlier in the upper than in the lower series, the non-metals occupy the right hand upper corner of the table, that is, if we neglect the elements of Group VIII.

Thus in Series 3, sodium is a strongly base-forming metal, magnesium has a sulphide which is readily hydrolysed, while aluminium hydroxide is a weak base, which will also react with sodium hydroxide. Silicon hydroxide is a very weak acid, and has no basic properties. Silicon also forms an unstable indifferent hydride. The hydride of phosphorus is feebly basic; the oxide forms well defined though weak acids. The hydride of sulphur is weakly acidic, its oxide (SO_3) is strongly acidic and quite stable. Chlorine forms a very stable and strong hydracid, and also unstable but very strong oxyacids.

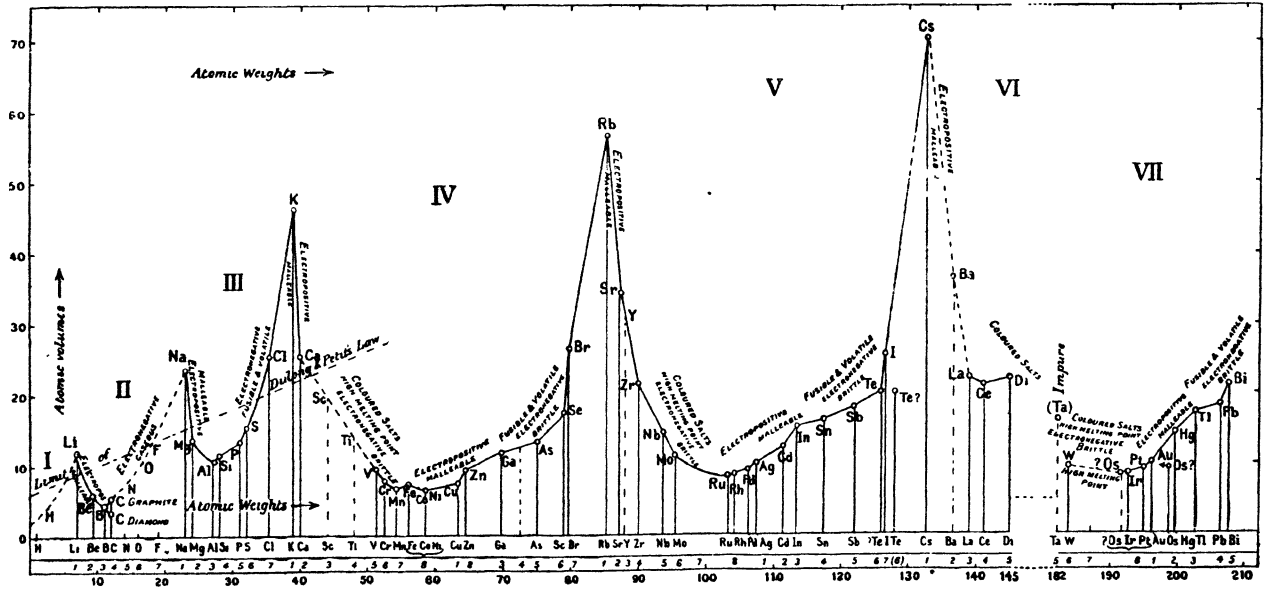
(2) A gradation in the opposite direction is met with in the groups, the base-forming tendency becomes stronger as the atomic weight of the elements increases.

Thus among the odd members of Group V., nitrogen forms the strong nitric acid and the stable basic ammonia. Phosphoric acid is weak although stable, while phosphine is unstable and only very slightly basic. Arsine forms no inorganic salts, and the acids of arsenic are very weak. The antimony acids are still weaker and not well defined. Stibine has no basic properties and is very unstable. Bismuth is a true metal; its hydroxide is purely basic. A hydride of bismuth has not been prepared.

THE PERIODIC CLASSIFICATION OF THE ELEMENTS.

GROUPS	0	I		II		III		IV		V		VI		VII		VIII
SUB-GROUPS		A	B	A	B	A	B	A	B	A	B	A	B	A	B	
Series 1			H = 1·008													
„ 2	He 4		Li 7		Be 9·1		B 11		C 12		N 14·01		O 16		F 19	
„ 3	Ne 20	Na 23			Mg 24·36		Al 27·1		Si 28·4		P 31		S 32		Cl 35·45	
„ 4	Ar 39·9	K 39·15		Ca 40·1		*Sc 44·1*		*Ti 48·1*		*V 51·2*		Cr 52·1		Mn 55		Fe 55·9 Co 59·0 Ni 58·7
„ 5			Cu 63·6		Zn 65·4		*Ga 70*		*Ge 72·5*		As 75		*Se 79·2*		Br 79·96	
„ 6	Kr 81·8	*Rb 85·5*		Sr 87·6		*Y 89*		*Zr 90·6*		*Cb 94*		*Mo 96*		—		*Ru 101·7 Rh 103 Pd 106·5*
„ 7			Ag 107·93		Cd 112·4		*In 115*		Sn 119		Sb 120·2		*Te 127·6*		I 126·97	
„ 8	Xe 128	*Cs 132·9*		Ba 137·4		*La 139*		*Ce 140*				—		—		
„ 9			—		—		—				—		—		—	
„ 10		—		—		—				*Ta 181*		*W 184*		—		*Os 191 Ir 193* Pt 194·8
„ 11			Au 197·2		Hg 200		Tl 204·1		Pb 206·9		Bi 208		—		—	
„ 12		—		*Ra 225*		—		*Th 232·5*		—		*U 238·5*				

Lothar Meyer's Curve showing the Relation between Atomic Volumes and Atomic Weights.


Atomic volumes
Atomic Weights
I
II
III
IV
V
VI
VII
Lothar Meyer's Curve of Atomic Volumes
Atomic Weights
Dulong & Petit's Law
Impure
Li
Na
K
Rb
Cs
Ba
La
Ce
Di
Br
Cl
S
Se
Te
I
Te?
Y
Zr
Nb
Mo
Ru
Rh
Pd
Ag
Cd
In
Sn
Sb
Ta
W
Os
Ir
Pt
Au
Hg
Tl
Pb
Bi
Th
U
Mn
Fe
Co
Ni
Cu
Zn
Ga
As
Sr
Ti
V
Cr
Mg
Al
Si
P
Ca
Sc
C Graphite
C Diamond
Electropositive Malleable
Electronegative Brittle
Fusible & Volatile Electronegative Brittle
Coloured Salts High Melting Point Electronegative Brittle
Electropositive Malleable
Coloured Salts
Fusible & Volatile Electropositive Brittle
Coloured Salts High Melting Point Electronegative Brittle
Electropositive Malleable
Fusible & Volatile Electropositive Brittle
Coloured Salts High Melting Point Electronegative Brittle
Electropositive Malleable
Fusible & Volatile Electropositive Brittle
Coloured Salts
Electropositive Malleable
Fusible & Volatile Electronegative

CHAPTER XXXIII.

ON QUALITATIVE ANALYSIS.

THE methods of qualitative analysis as practised to-day were developed during the first half of the last century; Berzelius, Heinrich Rose, and Fresenius were amongst the most prominent investigators.

There are two methods of analysis, the dry and the wet. The latter is the more exact and has been more completely systematised, but the dry method is of great assistance, and in skilful hands is almost sufficient by itself. The wet methods are based upon the precipitation of insoluble salts of the metals, those most commonly serviceable are the sulphides, hydroxides, chlorides, and carbonates. The student is strongly recommended to prepare for himself, by the aid of a reference book (e.g. *Fenton's Tables*), a table setting forth particulars of the above salts (the stability in water, colour) of the following metals—silver, lead, mercury, arsenic, antimony, tin, bismuth, copper, cadmium, iron, aluminium, chromium, manganese, zinc, cobalt, nickel, calcium, strontium, barium, magnesium, sodium, and potassium. For the purposes of analysis ammonium must be regarded as a metal also. When a metal has two series of stable salts, each series should be treated separately.

Chromous and cuprous compounds will not occur. (Why?)

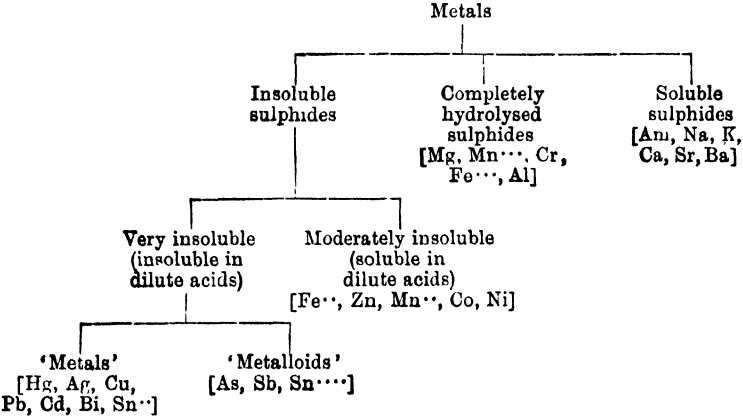
Classification according to sulphides.

The metals may be classified into three groups according as their sulphides are insoluble in, soluble in, or completely hydrolysed by water. To the second class belong ammonium, sodium, potassium, calcium, strontium, and barium; in the last class are magnesium,

aluminium, chromium, iron (ferric), and—rarely—trivalent manganese. The remainder may be divided into two subclasses according to the *relative* solubility of their sulphides. (1) Those whose sulphides are moderately insoluble, so that the presence of a dilute strong acid prevents precipitation (Chapter VIII.): such are manganese(ous), iron (ferrous), cobalt, nickel, and zinc. (2) Those whose sulphides are very insoluble and are precipitated even in the presence of free acid: lead and cadmium belong to this class, but their sulphides are not completely precipitated unless the acid is quite dilute.

It must be borne in mind that the analytic separation of the metals depends upon arbitrarily imposed conditions, and, therefore, that the student must constantly exercise his intelligence. The relative solubility of the sulphides is such that *no sharp dividing line* can be drawn.

So far then we can rearrange the metals into four classes, according as they have (1) soluble sulphides, (2) hydrolysible sulphides, (3) moderately insoluble sulphides, (4) very insoluble sulphides. Class 4 may be subdivided into 'metals' and 'metalloids.' The latter subclass includes arsenic, antimony, and stannic tin, whose sulphides are dissolved by alkali sulphides to form soluble thiosalts (Chapter XXV.).



Group I.

The choice of acid for the separation of the moderately and very insoluble sulphides lies between the three strong mineral acids, nitric, sulphuric, and hydrochloric. The first is an oxidising agent, oxidising sul-

phides to sulphates for instance, and is therefore inadmissible. The addition of sulphuric acid would cause the precipitation of barium sulphate, some strontium sulphate, and possibly some lead and calcium sulphates, if salts of the metals are present: hence the use of sulphuric acid would introduce confusion. The addition of hydrochloric acid would cause complete precipitation of mercurous and silver chlorides and the partial precipitation of lead chloride; but as these metals are members of the ten which have very insoluble sulphides, their precipitation as chlorides actually simplifies the general separation. These three metals are called Group I. or The Insoluble Chloride Group.

Bismuth and antimony oxychlorides may also be precipitated as crystalline salts on the addition of the acid, but the addition of more acid will re-dissolve them, $BiOCl + 2HCl = BiCl_3 + H_2O$.

Group II. After the removal of any insoluble chlorides, hydrogen sulphide is passed into the acid solution, under suitable conditions of dilution and temperature. Any precipitated sulphides are treated with ammonium sulphide to separate the 'metalloid' sulphides from the rest.

Group III. The solution now contains no metals of Group I. or Group II., that is to say, no metals which have very insoluble sulphides; hence it may be neutralised. If hydrogen sulphide is still present the moderately insoluble sulphides (FeS, MnS, ZnS, NiS, CoS) will be deposited, as soon as the strong acid is neutralised. In addition the hydroxides of metals whose sulphides are completely hydrolysible (Cr, Al, Fe, Mn, Mg) will also be deposited. But the precipitation will not be complete, for, as the hydrogen sulphide is used up, strong acids will be set free, and will accumulate, until the precipitation of sulphides and hydroxides is balanced by the reverse actions (Chapter VIII.).

$$FeSO_4 + H_2S \rightleftarrows FeS + H_2SO_4.$$

Hence, to insure complete precipitation, an *excess* of alkali must be added. But this will introduce new conditions such that all the above metals will be precipitated as hydroxides; aluminium, chromium and zinc hydroxides will re-dissolve in the excess of caustic base (Chapter XIV.). Instead of caustic alkali, one generally uses ammonium hydroxide. In this

hydroxide nickel, cobalt, and zinc hydroxides re-dissolve, on account, it may be, of the formation of new soluble complex salts which contain ammonia in the electro-positive portion (kation). The previous addition of ammonium chloride so weakens the alkalinity of ammonium hydroxide (Chapter XXVII.) that manganous hydroxide is not precipitated, and, either for the same reason or because of the formation of a complex salt ($NH_4Cl, MgCl_2, 6H_2O$) with the magnesium in the anion, magnesium hydroxide is not precipitated. Hence the addition of ammonium chloride and ammonia to the filtrate from Group II. leads to the precipitation of ferrous, ferric, aluminium, chromium, and manganic hydroxides when their salts are present.

Group IV.

These hydroxides are filtered off, and to the solution, which still contains ammonium chloride and ammonia, hydrogen sulphide (more often ammonium sulphide) is added: the sulphides of cobalt, nickel, manganese, and zinc are precipitated; and, but for the fact that ammonium chloride was added, magnesium hydroxide (hydrolysed sulphide) would also be precipitated.

Group V.

These sulphides are filtered off, and to the solution, which still contains ammonium chloride and ammonia, ammonium carbonate is added: the carbonates of the alkaline earths (Ba, Sr, Ca) are precipitated; basic magnesium carbonate also would be precipitated but for the presence of the ammonium chloride.

Magnesium.

After these carbonates are filtered off, sodium phosphate (Na_2HPO_4) in the presence of ammonia is added to the solution, and so insoluble is magnesium ammonium phosphate that even the complex salt is decomposed to form magnesium ammonium phosphate,

$$NH_4MgPO_4.$$

EXAMPLE OF ANALYSIS.

DATE.....

DESCRIPTION. *A white amorphous powder, slightly tinged with yellow, slightly soluble in water. Solution is alkaline to litmus.*

EXPERIMENT	OBSERVATION	INFERENCE
Heated solid in hard glass tube	colourless gas evolved, which ignites glowing splinter. Solid fuses.	possibly a nitrate, chlorate, perchlorate or peroxide.
Heated solid on Charcoal	becomes incandescent. A gray solid residue which turns blue damp red litmus.	possibly oxide of alkaline earth metal is produced
Heated in borax bead	no coloration	
Heated in flame	apple green coloration	probably compound of *barium*
Match test and silver coin test	no reaction	The oxide of the metal is not easily reduced, nor is it a compound of sulphur
Treated solid with dil. HCl.	moderately soluble, an effervescence	
Gas evolved passed into lime water	a slight turbidity produced	some carbonate present
Treated with conc. HCl	chlorine evolved	an oxidising substance.
" conc. H_2SO_4	oxygen evolved—colourless gas	not a chlorate or perchlorate, certainly not a nitrate, possibly a peroxide
To solution in dil. HCl added H_2S solution	sulphur deposited	not a metal of Groups I. and II. An oxidising agent
Heated with nitric acid, proved absence of oxalate, added solution of NH_4Cl and ammonia.	no reaction	
To solution added ammonium sulphide	sulphur precipitated	
Added sol. of $(NH_4)_2CO_3$	an immediate white precipitate which gave a green flame coloration	compound of an alkaline earth metal, probably *barium*
Washed pp. dissolved it in acetic acid		
To part added $CaSO_4$, Aq.	an *immediate* white precipitate	probably *barium*
To part added K_2CrO_4, Aq	an immediate blue colorisation, which faded whilst a gas evolved. Whereupon a yellow precipitate formed	confirmed *barium*
	the gas evolved was oxygen	probably a *peroxide*

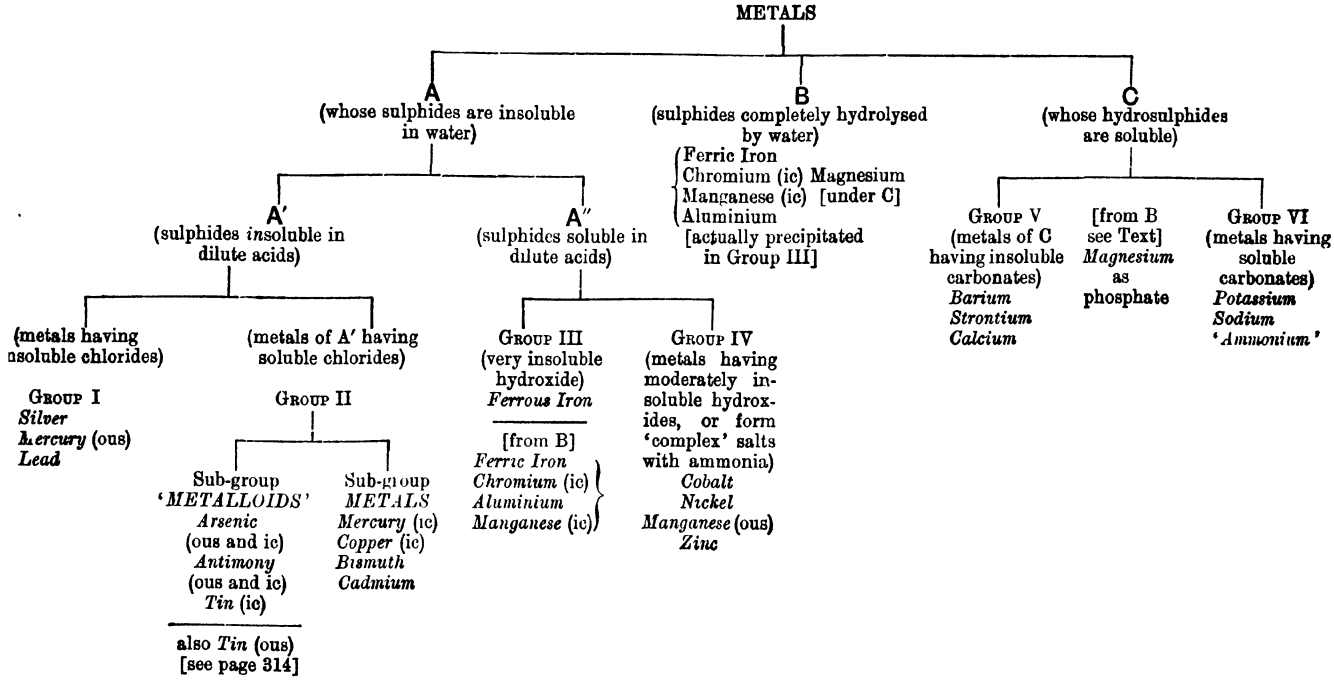
The systematic tests for acids failed to indicate one.

SUMMARY. The metal has a soluble sulphide, insoluble white carbonate and sulphate, and yellow chromate: colours the flame green. Hence it is *barium*.

The substance answers no acid test, but yields oxygen on heating, alone and with conc. sulphuric acid. Its acid solution oxidises hydrogen sulphide to sulphur and hydrochloric acid to chlorine. In addition its acid solution gives the chromium test for hydrogen peroxide. Hence it is a *peroxide*. The substance is **Barium Peroxide.**

$BaO_2 + 2HCl = BaCl_2 + 2H_2O_2$. $BaCl_2 + (NH_4)_2CO_3 = BaCO_3 + 2NH_4Cl$.

$Ba(CH_3COO)_2 + K_2CrO_4 = BaCrO_4 + 2CH_3COOK$.


METALS
A
(whose sulphides are insoluble in water)
B
(sulphides completely hydrolysed by water)
Ferric Iron
Chromium (ic) Magnesium
Manganese (ic) [under C]
Aluminium
[actually precipitated in Group III]
C
(whose hydrosulphides are soluble)
A′
(sulphides insoluble in dilute acids)
A″
(sulphides soluble in dilute acids)
(metals having insoluble chlorides)
(metals of A′ having soluble chlorides)
Group I
Silver
Mercury (ous)
Lead
Group II
Sub-group 'METALLOIDS'
Arsenic (ous and ic)
Antimony (ous and ic)
Tin (ic)
Sub-group METALS
Mercury (ic)
Copper (ic)
Bismuth
Cadmium
also Tin (ous)
[see page 314]
Group III
(very insoluble hydroxide)
Ferrous Iron
[from B]
Ferric Iron
Chromium (ic)
Aluminium
Manganese (ic)
Group IV
(metals having moderately insoluble hydroxides, or form 'complex' salts with ammonia)
Cobalt
Nickel
Manganese (ous)
Zinc
Group V
(metals of C having insoluble carbonates)
Barium
Strontium
Calcium
[from B see Text]
Magnesium as phosphate
Group VI
(metals having soluble carbonates)
Potassium
Sodium
'Ammonium'

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NOTES FOR REVISION AND DISCUSSION

These notes have been found useful in class, not for giving information but for promoting discussion. Many of the subjects are deliberately chosen to challenge thought and to endeavour to compel the student to face difficulties and to prevent him from being satisfied with the shadow for the substance.

The danger in the use of this, as of all summaries, can be counteracted by the teacher using them in class for discussion only and not for explanation. Another danger to avoid, especially where points of doctrine and classification are discussed, is that of exalting the doctrine and the classification. Classification is made for man not man for classification. I believe the notes, when so used, will make for clearness of understanding and for logical insight.

References are given to pages in the text.

NOTES FOR REVISION AND DISCUSSION

I.

Every substance is recognised by definite properties.

An **Element** is a substance which has never been made to yield of itself two or more other substances; and of which there is no evidence that such an action is possible. [See p. 40.]

When one simple substance can be changed quantitatively into one other substance, these two substances are called ALLOTROPES of the same element. The meaning of this can be conveyed clearly only by an example. Take *Carbon*. Pure charcoal can be dissolved in (or combined with) liquid iron, and much of it will solidify or separate as *graphite*. *Diamond* when heated changes into graphite. Graphite and charcoal dissolved in iron have been made to yield a little diamond. Diamond, graphite and charcoal when burnt in oxygen yield the same proportion of carbon dioxide. Hence these three very unlike substances are allotropes of the element carbon. The change of one allotrope into another is accompanied by loss or gain of energy (and, perhaps, by change in molecular complexity). Diamond, graphite and charcoal differ not only physically, but even chemically in their action towards a heated mixture of nitric acid and chlorate. Similarly *Oxygen* and *Ozone* are allotropes of one element (there is no special name here to distinguish the element from one of the allotropes).

Apart from conversion of one allotrope to another, elements form new substances by combination only. [See pp. 37, 84, 117, 251, 270.]

A **Compound** is a substance which has been made to yield of itself *two* or more other substances (excluding allotropes); or of which there is evidence that such an action is possible. [See p. 37.]

The evidence of the compound nature of Calcium fluoride is indirect. Calcium oxide can now be synthesised from its elements, but its action with gaseous hydrogen chloride proved it a compound. It was regarded as a metallic oxide by analogy with caustic soda when Davy had electrolysed the latter. Chlorine, on the other hand, was shown by Davy to be an element, whereas, by analogy, it had been regarded as a non-metallic oxide. (Study also Uranium.)

The analysis of any sample of a given compound, whatever its origin, shows that it is composed of definite elements in definite proportions by weight. (Law of fixed Ratios.) [See pp. 48, 124.]

The weight of any sample of a given compound is equal to the sum of those of its components. (Law of Conservation of Mass.)

Since a compound is a substance wholly different from its components its properties also are wholly different from those of its components.

When a compound is formed, there is, almost without exception, a loss or gain of energy to the system. This usually appears as heat energy.

The energy change is definite in amount for a definite mass of compound formed or decomposed. [See p. 265.]

The most useful means for effecting decomposition are high temperature and the electric current.

A **Mixture** consists of more than one substance. [See p. 37.]

A mixture may *appear* to be *one* substance only (for instance air or brass).

A mixture may consist of elements only (for instance 'detonating gas'), or of compounds only (for instance granite), or of both elements and compounds (for instance air). Notice here that a mixture of allotropes is possible (for instance of red and yellow phosphorus, or of oxygen and ozone).

The properties of a substance are usually unaltered or only slightly modified in a mixture.

In this connection consider the cases of brass and of blue vitriol. Plot a curve showing the relation of the tensile strength of brass to its constitution.

It is evident that the relative masses of the constituents of a mixture may vary to a small or large degree. The physical properties such as density, colour, are then found to change gradually in accordance.

Some mixtures may be separated into their constituents by *mechanical* methods, particularly gaseous and solid mixtures where the densities of the constituents differ considerably. More often physical methods are necessary, just as for compounds, while in many cases (for instance with alloys) chemical methods only are efficient.

Contrast the ease with which nitrogen trichloride and dry copper carbide are decomposed by slight *shock*.

Consider the arguments advanced to prove the nature of air—

Mechanical separation by *diffusion*.

Mechanical and physical separation by *liquefaction* followed by *distillation*.

'Physical' separation by *solution in water* followed by boiling.

(The proof does not depend so much on completely separating the elements by diffusion and by solution, as on the fact that the relative amounts of the elements dissolved or diffused are what can be calculated from a knowledge of their relative densities and solubilities *and* the assumption that they are only mixed.)

Doctrinal arguments—the relative proportions vary slightly (so also would an oxide mixed with varying proportions of either element)—formation and properties of artificial air—no simple formula—denial of Avogadro's theory, $4N_2 + O_2 :::: 2N_4O$—are all cases of argument in a circle; and they are fortunately unnecessary.

Notice that the five undoubted oxides have properties quite different from those of the elements.

N.B. Apothecaries in many cases use the word 'compound' where we must use 'mixture.' And this use is common and proper in *English*, which is perhaps the reason why some boys are confused, and when they should be talking *Chemistry* may even speak of a mixture as a 'kind of compound.' Unfortunately ambiguity still lurks in the language of chemistry, for we often speak of the 'composition' of a mixture.

II.

LAWS OF CHEMICAL COMBINATION.

1. Law of Definite Proportion. (Proust, 1800.)

The proportion by weight of the components of a chemical compound never varies.

This proportion is independent of the mode of formation of the sample considered.

This law is also called the law of 'Fixed Ratios,' and 'Constant Composition.' [See p. 48.]

Proust used the carbonates of copper, and the oxides and sulphides of various metals for establishing the proof of the law. Stas used ammonium chloride.

The most suitable substance for laboratory illustration is black copper oxide: It can be made synthetically, for which purpose the copper may be produced by electrolysis, by reduction, or by displacement by another metal. The oxide itself may be prepared from the native ore melaconite, from the native carbonates azurite and malachite and artificial carbonates corresponding to them, from the nitrate, the hydroxide, and the red oxide. [See p. 124.]

2. Law of Multiple Proportions. (Dalton, 1802.)

If the same two elements are found in more than one compound, the different quantities of one of the elements which are combined with any given quantity of the other element can be represented as a ratio of small integral numbers. [See p. 81.]

Notice that a definite mass of one of the elements *must* be chosen in order to expose the relation. Proust missed the discovery because he represented composition by percentages only.

Avoid this type of error—of saying that 'there is twice as much oxygen in lead peroxide as in litharge' when you mean the ratio of oxygen (for any given mass of lead) is 2 : 1.

Take the case of the oxides of mercury which yield 3·84 per cent. and 7·40 per cent. of oxygen respectively. Dalton experimented with the oxides of nitrogen and the hydrides of carbon. His experimental work was poor. Stas's work on the oxides of carbon was perfect. [See pp. 119, 121, 123.]

Suitable laboratory illustrations: reduction of the oxides of lead. The carbonic anhydride obtained from unheated and heated samples of sodium bicarbonate. [See p. 170.]

3. Law of Reciprocal Proportions (in a restricted sense by Richter, 1790).

Simplified statement.

When two elements severally combine with (or displace) a third, the separate masses of those two which combine with (or displace) any given mass of the third, are in the ratio in which these two elements combine together (or in some simple multiple of the ratio). [See pp. 70, 126.]

This is one of the startling truths of chemistry.

The relationship should always be expressed by the triangle. Hydrogen, magnesium and oxygen; and lead, sulphur and oxygen afford laboratory illustrations.

A specially interesting case is shown by Aluminium. It is corroded by dilute sulphuric acid, the hydrogen is collected, the sulphate is obtained and heated strongly and the residual oxide weighed. In a second experiment the hydrogen is burnt, and the water formed collected and weighed.

This law leads to and is included (with that of multiple ratios) in the following generalisation :—

The Law of Combining Weights.

'The proportions by weight in which all chemical combinations take place can be expressed in terms of small integral multiples of fixed numbers called *combining weights*, one for each element.

You should make sure that you clearly understand how these laws are explained by Dalton's Atomic Theory. [See pp. 128, 130.]

The 'combining weights' actually used to-day are the 'atomic' weights.

Methods of obtaining atomic weight.

I. By arbitrary choice of 'simplest' formula for a compound. Based on the results so obtained are the Law of Isomorphism and the Law of Atomic Heat, which caused certain corrections to be made (cf. e.g. selenium, chromium, vanadium and silver, respectively). [See pp. 141, 317.]

II. By the 'vapour density' method, which is based on Avogadro's molecular theory. Cannizaro developed the method. [See pp. 134—141].

III. By the Periodic Classification (Mendeléef) cf. Beryllium, Indium, Radium. [See p. 385.]

IV. The inert elements which form no compounds have been assigned atomic weights by deduction from the kinetic theory of gases, namely by the wave lengths of sound in them (see books on Physics).

4. The Law of Combination of Gases by volumes.

(Gay Lussac, 1808.)

The volumes of gases which appear or disappear in a given chemical reaction may be represented by a ratio of small integral numbers.

See that you grasp the immense importance of this generalisation to that development of the Molecular theory called Avogadro's Theory, and to the distinction between the 'atom' and the 'molecule.' [See pp. 131 *et seq.*]

Make a list of examples, including the synthesis of phosgene gas, and the series carbon + hydrogen ⟶ acetylene ⟶ ethylene ⟶ ethane.



The **equivalent weight** of an element is that weight of it which will combine with or displace *one* gram of hydrogen (or, by the law of reciprocal ratios 8 grams of oxygen or 35·5 grams of chlorine, &c.).

Pure substances must be obtained; direct methods are generally to be preferred.

Important historical determinations are those of Stas for Silver, Chlorine, Potassium (p. 232): Oxygen and Hydrogen (pp. 147 and 249): Carbon (p. 119).

Laboratory methods: displacement of hydrogen (pp. 61—63), reduction of oxide (p. 47), oxidation by nitric acid and decomposition of the nitrate (p. 230), displacement of one metal from its salt by another metal (p. 113).

Other methods: electrolysis, indirect methods such as decomposition of salts, $CaCO_3 \rightarrow CaO$ (for calcium) (p. 177), or by exchange of acid radicle, $CaF_2 \rightarrow CaSO_4$ (for fluorine).

III.

ACIDS.

Definition.

An acid is a special type of hydrogen compound which tends to exchange the hydrogen for an equivalent of metal. The compound so produced is called a salt. [See p. 69.]

The element or group of elements common to an acid and its salts is called the **acid radicle.** [See pp. 91, 110, 163, 331.]

The acid radicle is regarded as having no independent existence. Thus the sulphite radicle (SO_3) of sulphurous acid H_2SO_3, is not to be confused

with sulphuric oxide, SO_3, the anhydride of sulphuric acid. The radicles of binary hydracids (haloid acids, hydrogen sulphide) and of hydrogen cyanide are likewise not to be confused with the free element, or with cyanogen.

The same formula in several cases does duty for more than one acid radicle $(MnO_4)''$ for manganate and $(MnO_4)'$ for permanganate, and $(FeC_6N_6)''''$ and $(FeC_6N_6)'''$ for ferrocyanide and ferricyanide respectively.

When an acid reacts directly with a metal, the displaced hydrogen is in the 'nascent' condition: it may go free or it may reduce some acid present (in some cases it is used to reduce substances foreign to the immediate reaction—for instance ferric to ferrous salts). On 'nascence' consult page 227.

When an acid reacts with a metallic oxide, the hydrogen of the acid and the oxygen of the base yield water.

Do not fall into the error of saying that an acid 'combines' with a basic oxide: the reaction is one of exchange of radicles

$$Zn\ O + H_2\ SO_4 = Zn\ SO_4 + H_2\ O.$$

Most acids have a sour taste; and nearly all turn blue litmus red.

Strength.

The 'acid property' is salt formation, and acids are relatively 'strong' or 'weak' as they display this power. To compare the strengths of acids we must allow them to compete in salt formation under strictly equal conditions. [See p. 295.]

The strongest acids are hydrochloric and nitric: hydrogen sulphide is one of the weakest. The terms 'strong' and 'weak' are very commonly, and unfortunately, used for 'concentrated' and 'dilute' respectively. Concentration and strength are not to be confused in chemistry.

Extra-acid properties.

Acids may have other than the 'acid' property. Concentrated sulphuric acid is a most valuable *hygroscopic* agent, and in addition will cause many substances to decompose with production of water (thus oxalic acid $C_2O_4H_2 \longrightarrow CO_2 + CO + H_2O$) Several acids are good *oxidising* agents, particularly nitric acid. Others are *reducing* agents (H_2S, H_2SO_3, H_3PO_3, HI). Picric acid is used as a dye and as an explosive (lyddite). Hydrocyanic acid (HCN) is an intense poison; Salicylic acid is used as a remedy for rheumatism and as an antiseptic; Sulphurous acid is a bleaching agent; and so on.

Classification.

Acids are classified into **oxyacids,** which are compounds of oxygen, and **hydracids,** which are not compounds of oxygen. Most oxyacids may be formed by the *combination* of an acidic oxide with water ($SO_3 \longrightarrow H_2SO_4$; $SO_2 \longrightarrow H_2SO_3$; $N_2O_5 \longrightarrow HNO_3$; &c.) Such oxides are also called **acid anhydrides** (or acidic oxides).

Chloric acid and some others have no known anhydride. Nitrous oxide is *not* an acidic oxide, but it may be regarded as the anhydride of hyponitrous acid. (Consider the case of carbon monoxide with reference to formic acid.) [See p. 354.]

A further classification of oxyacids is necessary when an acid anhydride by combining with more than one proportion of water produces more than one acid, all of which are regarded as at the same stage of oxidation, namely that of the anhydride. The best case is given by phosphoric anhydride

P_2O_5, which yields not only *meta* phosphoric acid, HPO_3, and *ortho* phosphoric acid, H_3PO_4, but also *pyro* phosphoric acid, $H_4P_2O_7$. The last acid represents the **'condensed' type of acid,** that is, one whose molecule is formed together with water from more than one molecule of the *ortho* acid. Pyrophosphoric acid is a *di*-acid—formed from two ortho molecules, so also is pyrosulphuric, $H_2S_2O_7$. Dichromates ($K_2Cr_2O_7$) are condensed chromates (K_2CrO_4). Borax is a tetra borate ($Na_2B_4O_7$ from HBO_2).

Basicity.

When the molecule of an acid has only *one* replaceable hydrogen atom it is said to be *monobasic*, thus Hydrochloric acid, HCl. Hypophosphor*ous* acid, H_3PO_2, affords an example of a monobasic acid which has other hydrogen atoms which are *not* replaceable (the acid radicle is therefore H_2PO_2'). Sulphuric acid is *dibasic*; ortho phosphoric acid is *tribasic*; pyrophosphoric acid is tetrabasic.

For methods of determining the basicity of acids see p. 283.

You must note carefully that the basicity is not determined by the total number of the atoms of hydrogen per acid molecule but by the number of the *replaceable* atoms.

Normal solutions.

For volumetric analysis 'standard' solutions are necessary. For diminishing the labour of calculation to a minimum the 'normal' solution has been adopted as the basis of such solutions. It is such that 1 litre yields 1 gram of *replaceable* hydrogen[1]. A better name would be 'equivalent-per-litre.' It is evident that a normal solution of any acid contains

$$\frac{\text{molecular weight of acid}}{\text{basicity of acid}} \text{ grams per litre of solution.}$$

Thus Sulphuric $\frac{98}{2}=49$; Hydrochloric $\frac{36{\cdot}5}{1}=36{\cdot}5$;

Phosphoric $\frac{98}{3}=32{\cdot}67$; Oxalic $\frac{90}{2}=45$.

Stability.

Acids differ in their 'stability' under ordinary conditions. Thus sulphurous and carbonic acids are stable only in cold dilute solution. Concentrated solutions of them cannot be obtained, and if even these 'dilute' solutions are heated the acid decomposes and the acid anhydride is evolved. With nitrous acid, HNO_2, the acid anhydride (N_2O_3) is evolved, which is then oxidised in the air (NO_2). Nitric acid is stable in solution, and is obtainable as a vapour. But it is unstable when pure and exposed to light, breaking down to water, nitric peroxide and oxygen. Hydriodic acid is stable as a vapour at moderate temperatures, but when heated decomposes into its elements; and so on. Sulphuric acid is stable as 98 per cent. acid up to 338° C.: it then decomposes into water and the anhydride, but the latter further decomposes to the dioxide and oxygen (compare nitric acid). Metaphosphoric acid is very stable.

[1] [1 c.c. of $\frac{N}{1}$ acid does *not* correspond to 1 c.c. of free hydrogen at S.T.P. but to 1·11 c.c.]

Notice that a stable acid may be weak (phosphoric and hydrofluoric) or strong (hydrochloric) and an unstable acid may be weak (carbonic) or strong (nitric and chloric).

The arguments advanced in favour of the existence of carbonic acid are as follows:—

1. Its salts are well known (but so are those of the much less certain thiosulphuric acid).

2. Its solution affects litmus, and it reacts with powdered magnesium to yield hydrogen.

3. We can give a series of acids from those which, though unstable, can readily be isolated. $HClO_4$, HNO_3, $HClO_3$, H_2SO_3 (H_2CO_3) [H_2S].

Volatility and solubility.

Some acids are gaseous or easily volatilised, three haloid acids and nitric acid for instance, which are very 'strong' acids, and hydrogen sulphide and hydrogen fluoride, which are very weak, while phosphoric acid (a weak acid) is not volatile. Some acids are very soluble in water, for instance the haloid acids and sulphuric acid; boric acid is much less soluble, and benzoic acid is almost insoluble in water.

Historical.

The name acid, in the earlier days (before Lavoisier), was given to substances which corroded metals, dissolved 'calces,' had a sour taste, and changed the colour of certain vegetable pigments. Lavoisier taught that all acids are compounds of oxygen. This is called the **oxygen theory of acids.** According to this view the acid anhydride is *the* acid. Berzelius adopted this view, but afterwards modified it slightly in his **dualistic theory,** where he represented the acid as a hydrate thus, $H_2O.SO_3$, for sulphuric acid; to him a salt was therefore a compound of basic and acidic oxide: $BaO.SO_3$ for barium sulphate. When Davy proved that hydrochloric acid is not a compound of oxygen, the **hydrogen theory of acids** displaced the oxygen theory, and the definition which stands at the head of this article expresses this theory. As a consequence the idea of the acid radicle crystallised. [See pp. 91, 244.]

Oxyacids are regarded as hydroxides by Williamson's Theory. [See p. 159.]

Notice that in a sense quite unexpected by Lavoisier, oxygen does have an influence towards acidity, for of some elements (Manganese, Chromium, Tin) the lower oxides are markedly basic, the higher are markedly acidic, and the intermediate oxides exhibit the change from one condition to the other. This also is interesting from the hydroxide theory.

Methods of preparation of acids.

There are several more or less general methods of preparing acids. Many acids can be prepared by more than one of them.

A. From their salts—by exchange of radicles.

General equation $HY + XR' = XY + HR'$.

i. When HY is less volatile than HR' this is a common case. The cheapest acid reagent is sulphuric acid (for HCl, HNO_3, $HClO_4$), but it is also an oxidising agent and cannot be used for preparing hydriodic and hydrobromic acids. For these however phosphoric acid will do.

Even the very weak stable and non-volatile phosphoric acid will dispossess the very strong nitric acid. The method is, of course, quite unsuitable for volatile but unstable acids.

ii. (*a*) When *HR'* is less soluble and volatile it is evolved (H_2S, HCN), but when it is also unstable its anhydride will be set free (SO_2, CO_2).

(*b*) If the new formed acid is insoluble (H_2SiO_3: see p. 369) or relatively insoluble so that its solution may become saturated (HBO_2 from borax and HCl) it separates out.

Notice that the reaction occurs if the strong acid is dilute, but it may be necessary to use a saturated solution.

(*c*) Some unstable acids are prepared by choosing *XY* insoluble or non volatile. Thus chloric acid from barium chlorate and sulphuric acid solution, formic acid from the lead salt and gaseous hydrogen sulphide. (Compare preparation of hydrogen peroxide.)

In certain cases when the weaker acid has an insoluble salt, it may 'displace' the stronger.

$2AgNO_3 + H_2S = Ag_2S + 2HNO_3$ (contrast ferrous sulphate).

B. 'Hydrolysis' of acid halide.

i. Thus phosphorous acid, H_3PO_3, from PCl_3.

ii. In the case of hydrobromic and hydriodic acids, HBr and HI, the haloid acid is the object, not the other acid. [See p. 292.]

C. By direct synthesis.

$H_2SO_4(S \longrightarrow SO_2 \longrightarrow SO_3 \longrightarrow H_2SO_4)$, $HNO_3(N_2 \longrightarrow NO_2 \longrightarrow HNO_3)$.
[See p. 233.]

Notice that the oxidation of iodine and phosphorus by nitric acid to iodic (HIO_3) and phosphoric acids respectively are also cases of this kind. So also any case where the acid radicle combines with water to produce the acid.

Formulae. You should understand how the composition of the commoner acids has been determined.

By volume relation of gases HCl (combination), H_2S (reaction with tin), HBr and HI (partially by reaction with sodium).

Synthetic $H_2SO_4(Ag \longrightarrow Ag_2S \longrightarrow Ag_2SO_4)$.

Nitric acid. $Pb(NO_3)_2$ decomposed by heat and the nitrogen oxides reduced by copper. [See p. 217.]

IV.

BASES.

Basic oxide is the term applied to a metallic[1] oxide which reacts with acids to produce a salt and water only.

Notice this action is one of exchange—not of combination.

Notice also that metallic peroxides yield salts corresponding to *lower oxides*, the rest of the oxygen appearing free or acting as an oxidising agent (manganese peroxide with sulphuric and hydrochloric acids respectively).

Some basic oxides (those of potassium, sodium, barium and calcium are the most important) react with water to give solutions which have an *alkaline* reaction, that is, which turn red litmus blue and have a soapy feeling to the skin. It is believed that these oxides combine with water to form metallic hydroxides ($CaO \longrightarrow Ca(OH)_2$; $K_2O \longrightarrow 2KOH$). Insoluble hydroxides of other metals may usually be obtained from corresponding soluble salts by the precipitation method. [See p. 155.]

Definition. It is to the metallic hydroxides, together with ammonia solution, that the term **base** is specially applied. The *soluble* hydroxides are distinguished as 'caustic bases,' sometimes as alkalis.

The number of replaceable hydroxide groups in the molecule determines the 'acidity' of a base. Compare the 'basicity' of acids.

In salt formation the hydrogen of the acid and the hydroxide of the base yield water.

$$Cu(OH)_2 + H_2SO_4 = CuSO_4 + 2H_2O$$
$$CuO + H_2SO_4 = CuSO_4 + H_2O$$

'Normal' solutions. Standard solutions of bases yield 8 grams of replaceable oxygen, or 17 grams of replaceable 'hydroxyl,' per litre. Hence 1 c.c. of any 'normal' base neutralises 1 c.c. of any 'normal' acid exactly (provided both are strong). It is also clear that 1 litre of normal base solution contains the equivalent weight of the metal.

Preparation. Some bases may be prepared by the action of the metal on water (sodium), but the method is of no practical value whatever. Slaked lime is prepared by the combination of quick lime and water. The soluble caustic soda was once prepared by interaction between slaked lime (milk of lime) and sodium carbonate: it is now prepared from brine by electrolysis. Most insoluble hydroxides are prepared by the action of a soluble base on a soluble metallic salt. Care must be taken to add sufficient base, otherwise basic salt may contaminate

[1] It will be noticed that the term 'metal' is used in the definitions of basic oxide and acid. It is very difficult, if not impossible, to avoid this 'question-begging,' for the term metal can best be defined as an element having a basic oxide.

the specimen of hydroxide. In certain cases, when the metallic hydroxide will also react as a weak acid [$Al(OH)_3$, $Zn(OH)_2$, $Cr(OH)_3$] towards a strong base, excess of the latter must be avoided. Ammonium hydroxide is most convenient for use—provided it does not give other reactions (as with silver, mercury, copper salts, &c.).

Certain substances will act *either* as acid or base ($Al(OH)_3$ &c.).

Mercury forms no hydroxide. Silver hydroxide is very unstable. Most metallic hydroxides decompose when heated (exc. caustic potash and soda).

Classification of oxides.

acidic N_2O_5 Al_2O_3 (MnO_2) Mn_2O_7, CrO_3

[N_2O_4 gives two acids corresponding to other oxides]

indifferent NO. (CO, N_2O)

[Fe_3O_4 gives two series of salts]

basic Fe_2O_3 Al_2O_3 MnO, Cr_2O_3

(Peroxides) Na_2O_2 MnO_2 (Cr_2O_3).

V.

SALTS.

Definition. A salt is the product of the interaction of a base (or basic oxide) and an acid. It is a compound of the metal and acid radicle. Water also is formed.

Notice that a salt may be prepared independently of either the base or acid; for instance by direct synthesis. Some salts exist the acid of which has never been prepared, for instance sodium thiosulphate, $Na_2S_2O_3$. [See p. 311.]

Water of hydration or 'crystallisation.' Many salts crystallise from solution with water of hydration. Definite compounds are so produced, represented by definite formulae; thus blue vitriol is more than copper sulphate—it is the penta hydrate $CuSO_4.5H_2O$. Usually this water may be expelled at increased temperatures; in some cases, however, a more decided chemical reaction takes place in which the free acid and the metallic oxide or basic salt are formed: in these cases the anhydrous salt cannot be prepared merely by heating the hydrated salt. [See p. 153.]

Do not suppose that all crystalline salts have water of crystallisation—the commonest of all soluble salts, sodium chloride, is anhydrous (NaCl).

Formulae. The formula of a salt follows as a necessity from those of the base (or basic oxide) and acid, since in the formation of water $O = H_2$ and $OH = H$.

$$Fe_2O_3 + 6HCl = 2FeCl_3 + 3H_2O$$

$$2Fe(OH)_3 + 3H_2SO_4 = Fe_2(SO_4)_3 + 6H_2O, \quad \text{and so on.}$$

It is easy to remember the correct formula for any salt if you learn the following by rote: [See p. 143.]

Oxides of the X_2O type are K_2O(KOH); Na_2O(NaOH); Ag_2O; Hg_2O (mercur*ous* salts); Cu_2O (cupr*ous* salts) [NH_4OH].

Remember that copper salts commonly in use are cup*ric* (CuO) salts, and that mercuric salts (HgO) are as common as mercurous.

Oxides of the X_2O_3 type are Al_2O_3; Bi_2O_3; Cr_2O_3 (chrom*ic* salts); Mn_2O_3 (mangan*ic* salts); Fe_2O_3 (ferr*ic* salts).

Remember that ferrous salts (FeO) are also commonly in use; that manganous salts (MnO) are more common than manganic; and that chromous salts (CrO) are not used because they are too readily oxidised.

All the other important oxides are of the **XO** type.

Take notice also that isomorphous salts have analogous formulae.

Classification. Salts are classified into three groups—Normal, Acid (or hydrogen), and Basic

Notice that two or more salts may enter into a *mixed crystal*, but their character is not changed; or we may have crystals of *double salts*, which have a definite composition. The properties of the solution of a double salt are those of their components independently. But its crystalline form, colour, solubility differ from those of its components. Certain salts, however, with the same acid radicle, will combine in such a manner that not only colour, form, &c. differ in the new compound but also it has properties different from its components in solution. It behaves as a simple salt of a new acid radicle. Such are called complex salts. [See pp. 315, 317, 361, 363.]

A **Normal salt** is formed when acid and base react so that all the replaceable hydrogen of the acid and the hydroxide of the base (or oxygen of basic oxide) form water. The normal salt has neither Many salts can of course be prepared synthetically, or by other methods without the use of acid or base.

Some people speak of a normal salt as a 'neutral' salt. It must not be forgotten that many normal salts are *alkaline* in solution (Na_2CO_3) and many others are *acidic* in solution ($FeCl_3$). [See p. 165.]

An **Acid salt** (or Hydrogen salt) has replaceable hydrogen; it may be regarded as one which has been formed by the *partial* substitution by metal of the replaceable hydrogen of the acid. Hence an 'acid salt' is truly an acid, and can react like an acid with bases

An 'acid salt' is not necessarily *acidic* in solution; it may even be alkaline. monohydrogen sodium phosphate, HNa_2PO_4, is slightly alkaline to litmus and sodium hydrogen carbonate ($NaHCO_3$) is neutral to phenolphthalein, but alkaline to litmus.

Acid salts are commonly referred to as *bi*-salts, thus sodium *bi*carbonate, $NaHCO_3$, and potassium bisulphate, $KHSO_4$. It is an unfortunate affix, for it has been made to do duty to three distinct types of compound (for instance, $Ca(HCO_3)_2$, $FeCl_3$, $K_2Cr_2O_7$), and it was given from a discarded idea of the composition of hydrogen salts.

A **Basic salt** may be regarded as one which has been formed by the *partial* substitution by the acid radicle of the hydroxide of the base (or the oxygen of the basic oxide). It has replaceable oxygen or hydroxyl. It is therefore a base because it acts with an acid to produce a salt (normal salt) and water.

Basic salts are usually insoluble in water. The composition of some must be represented by such complex formulae that the point of our definition is obscured. Basic ferric sulphate, $Fe(OH)SO_4$, from $Fe(OH)_3$, and basic bismuth chloride, BiOCl, from Bi_2O_3, have quite simple formulae and so has clay

$$2[Al(OH)Si_2O_3] . H_2O.$$

Malachite has the formula $CuCO_3 . Cu(OH)_2$, a basic carbonate. [See pp. 172—174.]

Hydrolysis. The alkalinity or acidity of normal salts is due to chemical reaction with water in which the free acid and free base are formed (or an acid or basic salt may be formed). [See p. 165.]

$$Na_3PO_4 + HOH = Na_2HPO_4 + NaOH.$$
$$FeCl_3 + 3HOH = Fe(OH)_3 + 3HCl.$$

Whether the solution is acidic or alkaline depends upon the relative effect upon the indicator of the products of the hydrolysis.

General Methods of Preparation. i. By the direct action. Specially useful for some anhydrous chlorides. Sulphides can be oxidised to sulphates (or sulphates reduced to sulphides).

ii. Action of acids on metals. When two series of salts are possible the lower is produced if hydrogen is set free.

iii. Reaction between base or basic oxide and acid. According to the proportion, the normal, acid, or basic, salt is formed.

$$\left.\begin{array}{l} NaOH + H_2SO_4 = NaHSO_4 + H_2O \\ 2NaOH + H_2SO_4 = Na_2SO_4 + 2H_2O \end{array}\right\}$$
$$\left.\begin{array}{l} CuO + H_2SO_4 = CuSO_4 + H_2O \\ 2CuO + H_2SO_4 \rightarrow Cu(OH)_2 . CuSO_4. \end{array}\right\}$$

iv. Reaction between a salt and its own acid or base.

$$CuSO_4 + Cu(OH)_2 = CuSO_4 . Cu(OH)_2$$
$$2FeSO_4(OH) + H_2SO_4 = Fe_2(SO_4)_3 + 2H_2O$$
$$Na_2SO_4 + H_2SO_4 = 2NaHSO_4$$
$$Ca(HCO_3)_2 + Ca(OH)_2 = 2CaCO_3 + 2H_2O.$$

v. Action of an acid upon the salt of another acid.

This method is adopted when the salt reacting is that of either a *more volatile* or a *less stable* acid than the attacking acid and provided the salt is soluble Or, a *salt* which is *insoluble* in a moderate excess of acid may be precipitated from solution. The rule has many exceptions The most convenient salts to use are the carbonates.

vi. Insoluble salts are also prepared by the so-called method of Double Decomposition (exchange of radicles).

Solutions of two soluble salts are mixed, one having the metal and the other the acid radicle. The second salt formed must be soluble.

$$BaCl_2 + Na_2SO_4 = BaSO_4 + 2NaCl.$$

Decomposition by heat. Just as many oxyacids are decomposed into water and acid anhydride at high temperatures, so also are most salts of these acids similarly decomposed: and in this case also if the acid anhydride is unstable under the conditions of the experiment its decomposition products are formed. Of all the salts the carbonates and

nitrates are most readily decomposed (silicates—for instance glass—are very stable).

$$CaCO_3 = CaO + CO_2\ ;\ 2Pb(NO_3)_2 = 2PbO + 4NO_2 + O_2$$
$$2Al_2(SO_4)_3 = 2Al_2O_3 + 6SO_2 + 3O_2.$$

Notice that in the cases cited we have the commercial method of obtaining quicklime, and the laboratory method of preparing nitrogen peroxide.

Notice that the *salts of the alkali metals* (sodium and potassium) are usually stable at all temperatures to be obtained by our furnaces.

Exceptions to this rule are hydrogen salts

$$2NaHCO_3 = Na_2CO_3 + H_2O + CO_2\ ;$$
$$2KHSO_4 = K_2S_2O_7 + H_2O\ ;$$

also $K_2S_2O_7 = K_2SO_4 + SO_3 (\longrightarrow 2SO_2 + O_2)$;

the nitrate and chlorate

$$2KNO_3 = 2KNO_2 + O_2.\ \begin{cases} 2KClO_3 = 2KCl + 3O_2 \\ 4KClO_3 = 3KClO_4 + KCl. \end{cases}$$

The *ammonium salts* behave in various ways. For *chloride* see p. 208; for *sulphate* p. 210; for *nitrate* p. 223; for *nitrite* p. 224; for *dichromate* p. 347.

Students of Organic Chemistry should recall behaviour of ammonium salts to heat in giving acid amides, and of ammonium cyanate in yielding urea. [See p. 360.]

Oxalates decompose after the fashion of the acid

$$CaC_2O_4 = CO + CaCO_3 (\longrightarrow CaO + CO_2).$$

Lead oxalate yields both oxides of carbon and litharge, and also lead—probably because some carbon monoxide reduces the litharge.

The nitrates of a lower of two series yield the higher oxide and no oxygen.

$$\underset{(ous)}{HgNO_3} = \underset{(ic)}{HgO} + NO_2.$$ [See p. 231.]

VI.

OXIDATION AND REDUCTION.

1. The simplest idea of **oxidation** is the combination of a substance with *oxygen*: the substance is said to be oxidised, and the greater the proportion of oxygen with which it combines the more highly oxidised it is said to be. The removal of oxygen from a substance is called **reduction**: the substance so deprived is reduced.

Of course the *increase* in the percentage of the other element to an oxide has the same effect as the removal of oxygen

$$CO_2 + C = 2CO \text{ and } CO_2 + Zn = CO + ZnO.$$

2. By analogy the idea of oxidation is extended to include cases where a substance reacts with oxygen without increasing its oxygen proportion.

Thus hydrogen chloride is 'oxidised' to chlorine, ammonia is 'oxidised' to nitrogen $4HCl + O_2 = 2Cl_2 + 2H_2O$.

3. The idea of oxidation and reduction is now still more comprehensive, for the addition of *hydrogen* to a substance is regarded as reduction and its removal as oxidation.

4. Ideas of oxidation and reduction are, to a considerable extent, influenced by the phenomena of electrolysis, thus one gram of hydrogen is held to have an equal effect in reducing as eight grams of oxygen have in oxidising; so that the addition or removal of hydrogen *and* oxygen *in equivalent quantities* (1 : 8), as in water, is said not to alter the stage of oxidation from that of the original substance.

Thus a given oxyacid and its salts are regarded as at the *same* stage of oxidation as their acid anhydride.. $SO_3 + H_2O = H_2SO_4$. Sulphuric acid represents a higher stage of oxidation than sulphurous acid or hydrogen sulphide; and as we know, it may be reduced to these stages.

$$\begin{array}{ccc} SO_3 & \longrightarrow & SO_2 \\ \downarrow & \searrow & \\ H_2S & & S \end{array}$$

Hence ortho acids and condensed acids (or their salts) are at the *same* stage of oxidation. H_3PO_4 and $H_4P_2O_7$: K_2CrO_4 and $K_2Cr_2O_7$; HBO_2 and $Na_2B_4O_7$.

But the stage of oxidation of salts may be considered from another point of view—namely that of the basic oxide. Their method of formation from acid and basic oxide, with simultaneous formation of *water* allows us to regard all the salts of a given base as at the same stage of oxidation as that base.

$$\begin{aligned} X_2O + H_2SO_4 &= X_2SO_4 + H_2O \\ X_2O + H_2SO_3 &= X_2SO_3 + H_2O \\ X_2O + H_2S &= X_2S + H_2O \\ X_2O + 2HCl &= 2XCl + H_2O \end{aligned}$$

Thus all mercurous salts are at the stage represented by Hg_2O, and all the mercuric salts at the HgO stage. And—from *this* point of view—mercur*ic* sulph*ide* (HgS) is at a higher stage of oxidation than mercur*ous* sulph*ate* (Hg_2SO_4).

It follows that a normal, acid and basic salt of a given acid and base are at the same stage of oxidation, *e.g.*, K_2SO_4 and $KHSO_4$: $MgCO_3$; $Mg(HCO_3)_2$; $Mg(OH)_2 . 2MgCO_3$. Discuss the change $CuSO_4 + Na_2S = CuS + Na_2SO_4$.

From the foregoing remarks the following definition will be better appreciated.

Definition. Oxidation takes place when a substance representing a lower stage of combination with oxygen is made to yield one representing a higher stage of combination with oxygen. This may occur either by combination

with oxygen, or by the addition of any electronegative element or radicle; or it may occur by the removal of hydrogen or of any electropositive element or radicle.

An oxidising agent is one which will produce the above effects.

A definition of Reduction may easily be constructed by the small necessary alterations in the above definition.

Types of oxidation and reduction.

Oxidation may be **direct** or **indirect**, that is, the agent may itself yield the oxygen or radicle, or, by reacting with a third substance, make the oxygen or radicle available. Similarly reduction may be either direct or indirect.

$SnCl_2 + Cl_2 = SnCl_4$ (direct oxidation)

but $PbO + OH_2 + Cl_2 = PbO_2 + 2HCl$ (indirect oxidation)

and $2FeCl_3 + H_2S = 2FeCl_2 + 2HCl + S$ (direct reduction)

but $Fe_2(SO_4)_3 + 2H_2O + SO_2 = 2FeSO_4 + 2H_2SO_4$ (indirect reduction).

The bleaching actions of sulphurous acid are probably due to indirect reduction.

A type of reaction which, judged from our present point of view is decidedly curious, is that undergone by hypochlorites when warmed.

$$3KClO = 2KCl + KClO_3.$$

It will be seen that the salt hypochlorite has decomposed into two other salts, one representing a more highly oxidised, the other a less highly oxidised stage than itself. [Condition of Cl_2O to condition of HCl and Cl_2O_5.]

Similar cases are represented by the following equations:

$$2NO_2 + H_2O \text{ (very cold)} = HNO_2 + HNO_3$$

[$N_2O_3 + N_2O_5$ condition]

$$3NO_2 + H_2O \text{ (ordinary temperature)} = NO + 2HNO_3$$

$$4KClO_3 = 3KClO_4 + KCl$$

$$4H_3PO_3 = 3H_3PO_4 + PH_3$$

and the action of alkalis on halogens and on phosphorus.

A moment's consideration makes it clear that an oxidising agent is reduced when it oxidises another substance, and that a reducing substance is oxidised when it reduces another substance, so that one should be oxidised and the other reduced. A few reactions, however, occur where this may be argued as not strictly true; for instance the production of lead from galena

$$2PbO + PbS = 3Pb + SO_2$$

and

$$PbSO_4 + PbS = 2Pb + 2SO_2.$$

Certain unstable oxidising substances mutually decompose each other.

$$5H_2O_2 + 2KMnO_4 \text{ (acidified)} \rightarrow 5H_2O + 5O_2 + 2Mn(SO_4) + K_2(SO_4) + 3(H_2O).$$

$$H_2O_2 + Ag_2O = 2Ag + O_2 + H_2O.$$

Oxidation and Reduction in Nature and daily life.

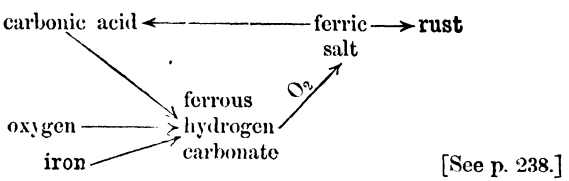
Oxidations of immense importance take place in nature directly or indirectly with the oxygen of the air. Thus the respiration of animals and plants is essentially a slow combustion of the body in order to supply the energy necessary for the vital processes of growth and movement (p. 373). On the other hand the formation of sugar and starch from carbon dioxide and water by

the protoplasm of green plants is essentially reduction, the energy for which is absorbed from the sun's rays (p. 376). When wood and animal tissues decompose, bacterial influence leads to oxidations and reductions: as one result coal is formed from plant remains, and this is burned in our grates and furnaces to carbon dioxide mainly; or from it are obtained coke and illuminating gas which also are burned. In the mines, marsh gas (CH_4), one of the products of the decomposition of plant remains, is set free, and this, with the oxygen of the mine air, may lead to devastating explosions.

The formation of nitrates in the soil from decomposing animal and vegetable remains, or excretions, or from the nitrogen in the soil air, is due to oxidation by bacterial agency (pp. 239 and 381). Calcium nitrate is now being made in Sweden for manures by exposing air to the heat of the electric arc and passing the oxides over slaked lime.

Certain of the older rocks of the earth's crust are suffering oxidation during their weathering; ferrous compounds to ferric; natural sulphides to sulphates, or to oxides and sulphur.

The rusting of iron is of particular interest since the oxidation can so easily be shown to be due to quite a complicated series of reactions. These may be shortly indicated thus



[See p. 238.]

Oxidising agents.

Gaseous oxygen is used in the laboratory and in the industries for oxidising purposes. Amongst instances of the latter are

(i) $BaO \longrightarrow BaO_2$ (Brin's process).

(ii) Chrome iron ore $\longrightarrow$ chromate.

(iii) $MnO_2 \longrightarrow K_2MnO_4 \longrightarrow KMnO_4$.

(iv) Weldon's process. $MnO \longrightarrow MnO_2$.

(v) $FeS_2 \longrightarrow SO_2 \longrightarrow H_2SO_4$ (lead chamber process).

(vi) $SO_2 \longrightarrow SO_3 \longrightarrow H_2SO_4$ (contact process).

(vii) Roasting of ores (blende, galena, &c.).

Gaseous oxygen is used in the eudiometric methods of analysing gaseous mixtures; of finding composition of carbon monoxide, ammonia, carbon dioxide, sulphur dioxide, water, &c.

To 'nascent' oxygen are due many of the oxidations of the laboratory

$$Cl_2 + H_2O + PbO = PbO_2 + 2HCl.$$

Consider the production of persulphate from acid sulphates at the anode. [See p. 309.] $KHSO_4 \longrightarrow KSO_4$
and of chlorate. [See p. 264.]

Peroxides.

Examples:

$4H_2O_2 + PbS = PbSO_4 + 4H_2O$

Na_2O_2 and $Cr(OH)_3 \longrightarrow Na_2CrO_4$ } used in Qual.

Na_2O_2 and $Mn(OH)_2 \longrightarrow MnO_2$. } Anal., Group III.

MnO_2 (acidified) $+ C_2O_4H_2 \longrightarrow 2CO_2 + H_2O + Mn(SO_4)$.

$MnO_2 + 4HCl = MnCl_2 + 2H_2O + Cl_2$.

Oxyacids and their salts.

Use of chlorates and nitrates in pyrotechny.

Potassium nitrate in gunpowder. [See p. 228.]

In the dry methods of making chromate and manganate.

Permanganate

for oxidising organic matter,
in volumetric analysis.

$$2KMnO_4 + 3H_2SO_4 \begin{cases} \text{Oxalic acid} \longrightarrow 2CO_2 + H_2O \\ \text{Ferrous salts} \longrightarrow \text{ferric salts} \end{cases} + \begin{matrix} K_2SO_4 \\ 2MnSO_4 \\ 3H_2O. \end{matrix}$$

$2KMnO_4 + \text{Alcohol} \longrightarrow (\text{aldehyde, \&c.}) + 2KOH + 2MnO_2$.

Dichromate.

$$K_2Cr_2O_7 + 8HCl + \begin{cases} \text{ferrous salts} \longrightarrow \text{ferric salts} \\ \text{iodide} \longrightarrow \text{iodine} \\ \text{sulphite} \longrightarrow \text{sulphate} \end{cases} \begin{matrix} 2KCl \\ + \ 2CrCl_3 \\ 4H_2O. \end{matrix}$$

Note.—Decinormal solutions of oxidising agents used in volumetric analysis for oxidising purposes yield ·8 gram of 'available' oxygen per litre of solution; thus $\frac{2KMnO_4}{10 \times 10}$ or $\frac{K_2Cr_2O_7}{6 \times 10}$ grams per litre. Calculation can be made accordingly.

Conc. **Sulphuric acid.**

$S + 2H_2SO_4 \longrightarrow 2H_2O + 3SO_2$.

H_2SO_4 and $HBr \longrightarrow Br_2$ and SO_2 and S.

H_2SO_4 and $HI \longrightarrow I_2$ and H_2S.

$2H_2SO_4 + C = 2H_2O + 2SO_2 + CO_2$.

$H_2SO_4 + H_2S = 2H_2O + SO_2 + S$.

Hence conc. Sulphuric acid cannot be used for drying hydrogen sulphide or for preparing *all* the haloid acids.

Nitric acid is one of the most valuable of oxidising agents in the laboratory. Iodine is oxidised to Iodic acid (HIO_3); phosphorus to phosphoric acid (H_3PO_4); sulphur to sulphuric acid; sulphides and sulphites to sulphates; charcoal to carbon dioxide; graphite to graphitic acid (in this case chlorate also is used); tin to stannic acid (by heating, SnO_2 is obtained); sugar to oxalic acid, &c., &c., &c.

The reduction products of nitric acid in the above reactions are mainly nitrogen peroxide NO_2 and nitric oxide, NO.

Hypochlorites are excellent oxidising agents. **Bleaching powder** which yields hypochlorite in solution

$$2Ca(OCl)Cl \longrightarrow CaCl_2 + Ca(ClO)_2$$

is commonly used (see p. 263).

Halogens.

All the halogens react with caustic alkali.

$$2KOH \text{ (cold)} + \begin{cases} Br_2 \\ Cl_2 \end{cases} = \begin{matrix} KBr \\ KCl \end{matrix} + \begin{matrix} KBrO + H_2O \\ KClO + H_2O \end{matrix}$$

$$6KOH \text{ (hot)} + 3X_2 = 5KX + KXO_3 + 3H_2O$$

(The production of the KXO_3 compound is probably secondary to KXO.)

$$X_2 + H_2S = S + 2HX.$$

$$Na_2SO_3 + OH_2 + X_2 = Na_2SO_4 + 2HX \quad \text{(used in qual. and vol. analysis).}$$

Chlorine will oxidise iodine to iodate (HIO_3) and periodate (HIO_4).

Hence the necessity of avoiding excess of chlorine in testing for iodides by the carbon disulphide and chlorine test.

$$2K_2MnO_4 + Cl_2 = 2KCl + 2KMnO_4.$$

'Nascent' Chlorine liberated at the anode is used in electrolytic commercial methods of manufacturing chlorate; and in the preparation of iodoform (iodide electrolysed in alcohol).

Some oxides.

Several oxides other than peroxides are important; the most useful is black copper oxide, at red heat, for finding composition of *water*, *carbon monoxide*, *ammonia*, organic compounds generally.

Silver oxide reacts in suspension in water very readily.

Reducing agents.

Gaseous **hydrogen** is used in the laboratory for reducing certain metallic oxides. 'Nascent' hydrogen liberated at the kathode is now used in the commercial preparation of certain organic compounds, notably aniline. Nascent hydrogen, formed in reaction between acids and metals and between sodium amalgam and water, is used in reduction. The reduction of acids which react on metals may be imputed to nascent hydrogen, nitric acid being reduced even to N_2O, N_2, NH_2OH (by tin) and NH_3; sulphuric acid even to S and H_2S.

Metals. Copper is used in the laboratory for reducing all the oxides of nitrogen . it will *not* reduce steam or carbon dioxide. The use of aluminium in thermite and in the Goldschmidt method of preparing metals difficult of fusion are important examples. Magnesium will reduce silica and boron oxide. [See pp. 189, 365.]

Carbon and coal are the great *cheap* reducing agents of manufacturing chemists. Coke, for making the so-called 'water gas.' [See pp. 196, 267.]

$$H_2O + C = CO + H_2 \text{ and } 2H_2O + C = 2H_2 + CO_2.$$

In furnaces they are used for reducing oxides. See that you understand when and why the following types of furnace are used: Muffle (Zinc), Reverberatory (Tin), Blast (Iron), Electric (phosphorus, silicon and calcium and silicon carbides).

Hydrides.

Hydrogen Sulphide.

Ferric to ferrous salts.

Iodine to hydriodic acid.

Sulphurous oxide to sulphur.

Hydriodic acid.

Hydrogen peroxide to water.

Sulphuric acid to hydrogen sulphide.

Greatly used in reducing alcohols, &c.

Lower series of salts act as reducing agents; ferrous salts, stannous chloride (Group II., Qual. Anal.); etc.

Carbon monoxide is important in the blast furnace. It reduces many metallic oxides.

Substances which react both ways.

Some substances may be reduced or oxidised somewhat readily according to circumstances, consequently they can act either as oxidisers or reducers. Such are **hydrogen nitrite.** This compound may be *reduced* to nitric oxide, hence it will oxidise hydriodic acid to iodine (test); sulphurous acid to sulphuric acid; ferrous salts to ferric. Nitrites are readily *oxidised* to nitrate, hence they reduce permanganate.

Sulphur dioxide (or rather sulphurous acid) is *oxidised* to sulphuric acid, it reduces nitric acid, dichromate, iodate to iodine.

$$2HIO_3[I_2O_5] + 5SO_2 . H_2O = I_2 + 5H_2SO_4 + H_2O.$$

[The commercial method of preparing iodine is essentially the same

$$2NaIO_3 + 5NaHSO_3 = I_2 + 2Na_2SO_4 + 3NaHSO_4 + H_2O.]$$

Potassium dichromate (yielding chrome alum)

$$K_2Cr_2O_7 + H_2SO_4 + 3H_2SO_3 = \underbrace{K_2SO_4 + Cr_2(SO_4)_3} + 4H_2O$$

crystallises as $K_2SO_4 . Cr_2(SO_4)_3 . 24H_2O$.

Sulphur dioxide is *reduced* to sulphur by tin, and by hydrogen sulphide; on these, therefore, it acts as oxidiser.

$$2H_2S + SO_2 = 3S + 2H_2O.$$

Iodine may be *reduced* to hydriodic acid; hence much of its use in volumetric analysis (sulphite, hydrogen sulphide).

It may also be *oxidised* to iodic acid by nitric acid and to iodic and periodic acids by chlorine. Both of these it reduces (to NO_2 and HCl respectively).

VII.

TYPES OF CHEMICAL REACTION.

1. Change of one substance into one other.
   - *a.* One allotrope into another. Oxygen $\leftrightarrow$ Ozone.
   - *b.* One compound into another of the same molecular weight. Urea $\leftrightarrow$ Ammonium cyanate. [See p. 360.]
   - *c.* Polymerisation. Acetylene $\longrightarrow$ benzene. [See p. 194.]
2. Direct combination, of elements or compounds
3. Decomposition.
   - *a.* As with potassium chlorate and Nitrogen chloride.
   - *b.* Dissociation—where reversal of conditions allows recombination. $2BaO_2 \rightleftarrows 2BaO + O_2$. [See p. 253.]
   - *c.* The special cases where a second substance causes the decomposition, thus conc. sulphuric acid with sugar gives carbon and water; with oxalic acid $\longrightarrow$ CO, CO_2, H_2O (and diluted sulphuric acid).
4. Simple displacement.
   - *a.* $2HCl + Zn \longrightarrow ZnCl_2 + H_2$. $CuSO_4 + Zn \longrightarrow ZnSO_4 + Cu$.
     $2Al + Fe_2O_3 \longrightarrow Al_2O_3 + 2Fe$.
   - *b.* Substitution. $CH_4 + Cl_2 = CH_3Cl + HCl$.
5. Double exchange.
   - *a.* In salt formation particularly.
   - *b.* *Hydrolysis* is a special case—the opposite of salt formation where a salt is concerned—when water reacts on a substance dissolved in it.

The term is made to include several cases not of the type of salt hydrolysis

Starch + water $\rightarrow$ maltose.

Cane sugar + water $\rightarrow$ glucose + fructose.

The case of organic cyanides is very peculiar in that the nitrile yields an acid and a base unrelated to those from which it is derived.

The following are not regarded as cases of hydrolysis :—

$CuSO_4 + 5H_2O = CuSO_4 . 5H_2O$, $P_2O_5 + H_2O = 2HPO_3$,
$Ca_3P_2 + 6H_2O = 3Ca(OH)_2 + 2PH_3$, $CaO + H_2O = Ca(OH)_2$.

6. Oxidation and reduction.

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