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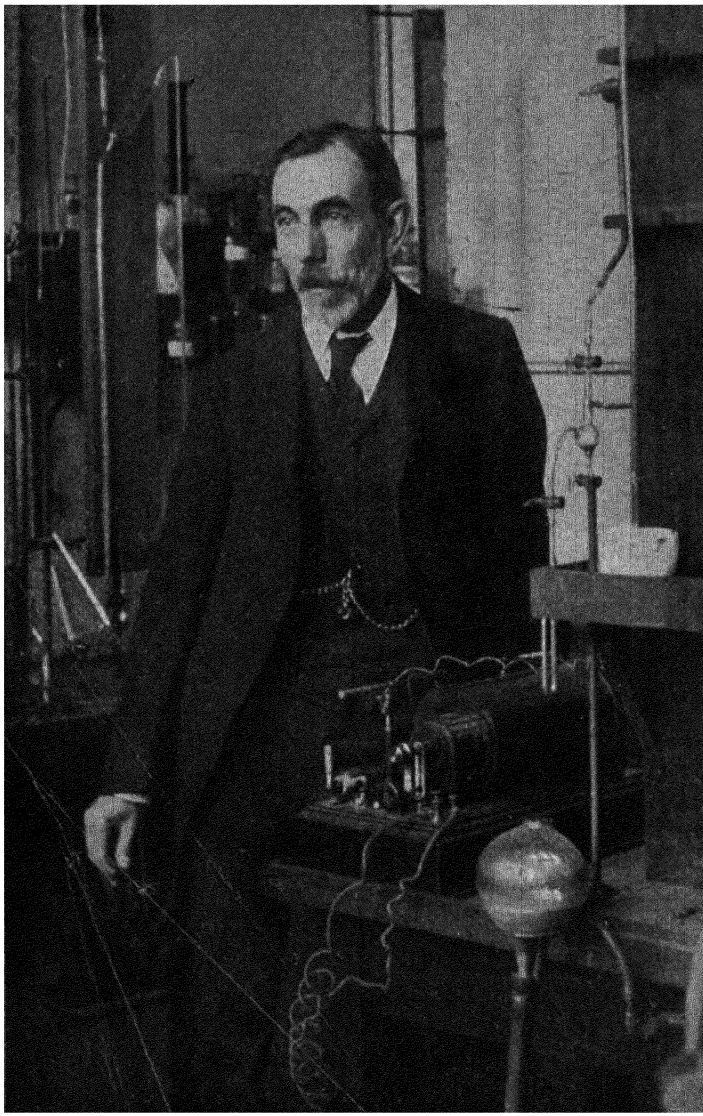
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SIR WILLIAM RAMSAY IN HIS LABORATORY

TEXT BOOK OF INORGANIC CHEMISTRY

A TEXTBOOK FOR COLLEGES AND SCHOOLS

BY

E. J. HOLMYARD, M.A., M.Sc., D.Litt., F.I.C

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FOREWORD

By CYRIL NORWOOD, M.A., D.Litt.,

Late Headmaster of Harrow School

Science has now been taught for many years in the bulk of the schools of this country, and for nearly a generation it has been an integral part of the education which the Board of Education approves. The somewhat paradoxical result has been that there is perhaps less respect for the scientist than in the days of Huxley and Tyndall, when science had no footing in the schools at all. Few would be bold enough to hazard the assertion that there are signs in any class of British society of the scientific habit of mind.

The cause cannot lie in the teaching of Classics to the boys of the Public Schools, for these form but a limited class, and for a good many years have enjoyed access to science teaching. I suggest that the causes rather lie in the strong reaction provoked by the extraordinarily one-sided results produced in the specially aided schools, which devoted themselves to Science in the last years of the reign of Victoria, and to the narrow formalism of much of the teaching. It was discovered that man cannot live and grow on science alone, and the revolt perhaps went too far, until the Great War forcibly reminded the nation that things were not well.

It ought to be possible to think out a general education in which all will be able to gain some elementary insight into the workings of the physical universe and to come to understand the meaning of scientific method, and the point of view of the scientist. So much is necessary if in the future

we are all to understand one another. It ought to be possible also so to teach Science that those who learn it do not become intolerant and unsympathetic, but realize that, though it is a necessary part, it is only a part of the modern citizen's outfit for life.

This book is written by one who has realized this, and who knows how to teach with breadth and without exclusiveness. Its pages give information and provoke curiosity; at many points they suggest that there are other realms of knowledge of a quite different sort. This characteristic, which may offend the purist, seems to me all to the good, and I hope that the work may find its way into the hands of many.

CYRIL NORWOOD.

PREFACE TO FIRST EDITION

If Science is to retain the honourable place it has won in the educational system of this country, I believe we shall have to recognize that it is the greatest of the " humanities," and deliberately abandon the so-called " utilitarian " standpoint. There are signs that this fact is being realized, and that schoolmasters are becoming alive to the vital truth recently re-expressed by Dr. Singer, " Science is a method and not a collection of facts."

The present book is an attempt to present to students of the School and Higher Certificate standards a logical course of chemistry which shall acquaint them with modern ideas and give them an insight into the problems, methods and achievements of the science. I have emphasized the physical point of view as a ready means of building a framework, but I have, I hope, not sacrificed the useful (and entertaining) parts of the usual school inorganic chemistry in doing so. I have not hesitated to mention uncommon substances where they are likely to thrill the youthful imagination, and I have included many biographical and historical facts, the psychological value of which as an aid in fixing the attention, assisting the memory and arousing the enthusiasm of the student is well known to every teacher.

It is my pleasant duty to record my heartiest thanks for much help received in the preparation of this book. I am especially indebted to Dr. H. J. H. Fenton, F.R.S., who generously undertook to read the whole of the proofs and whose suggestions have been of the greatest value. If I have caught a little of the spirit of his own *Outlines of Chemistry* my aim will have been amply achieved.

My thanks are also due to Dr. W. A. Knight, of Marlborough College, who read the proofs and gave me much invaluable advice ; to Professor Soddy, F.R.S., for reading and criticizing the chapter on the Structure of the Atom ; to the Master of Marlborough for writing the foreword ; to A. C. K. Toms, Esq., M.A., of Clifton College, who read the proofs and whose trenchant criticism was of much assistance ; and to some of my senior students, B. E. Berry, D. M. Stern, C. P. Wright and S. R. M. Porter, for preparing and checking the calculations.

I have also to thank Professor Sir Ernest Rutherford, F.R.S., for allowing me to quote from his Bakerian Lecture, 1920 ; Messrs. G. Bell & Sons, Ltd., for the loan of blocks ; and Messrs. Longmans, Green & Co., Messrs. J. & A. Churchill, and Mr. John Murray, for kind permission to quote from Stewart's *Recent Advances in Inorganic Chemistry*, Molinari's *Chemistry*, and Soddy's *Interpretation of Radium* respectively.

In conclusion, perhaps I may be allowed to say that this is the third generation of Clifton chemical textbooks published by Messrs. Edward Arnold & Co.—I hope that the connection may continue to be successful !

E. J. HOLMYARD.

CLIFTON COLLEGE.

PREFACE TO SECOND EDITION

In the nine years that have elapsed since the first edition of this book was originally published, many advances have been made in both pure and applied chemistry. Such of these advances as lie within the present limits have been incorporated, but care has been taken to preserve the character and individuality of the book with as little change as was consistent with the necessary additions. In particular, the temptation to include much more theoretical matter has been withstood, and it is hoped that readers will recognize in the new edition not a new book recast on a different basis, but an up-to-date form of the original edition.

The author's warmest thanks are due to those very numerous correspondents who, since 1922, have written to him pointing out difficulties or inaccuracies and making suggestions for improvements. To all of them he believes that he has replied personally, but he would now take the opportunity of renewing his thanks. Not the least of the benefits that the book has brought him is a large number of personal friends.

The author desires to express his thanks to Mr. R. B. Pilcher for permission to reproduce the portrait of Gay-Lussac and to Mr. F. W. Clifford of the Chemical Society for those of Faraday and Berzelius.

E. J. HOLMYARD.

CLIFTON COLLEGE.

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PART I

GENERAL THEORY

CHAPTER I

HISTORICAL

Many suggestions have been made as to the origin of the word Chemistry, but that which has most to support it derives the word from the ancient name for Egypt, *khem* or *chem*, which means " black," and was given to Egypt on account of the dark soil of that country. Whether this be the true derivation or not, it is at least certain that the ancient Egyptians were acquainted with more chemical operations than any other nation of antiquity, and that therefore the " Egyptian Science " as a name for chemistry is very appropriate. Egypt, however, had no monopoly of chemistry, for the Chaldeans, Chinese and Hindoos had acquired much chemical knowledge of an empirical nature, and it seems very probable that each nation of the ancient world contributed its share to the development of the science.

The kind of chemical knowledge possessed by men in those remote times is very much what we should expect, although we may be inclined to underestimate it. Metallurgy, glass-making, dyeing, the manufacture of pigments and poisons, soap-making and embalming, together with the preparation of drugs for medicinal purposes, were the principal subjects that engaged the attention of the ancient chemists. Chemistry was, therefore, mainly practical and empirical;

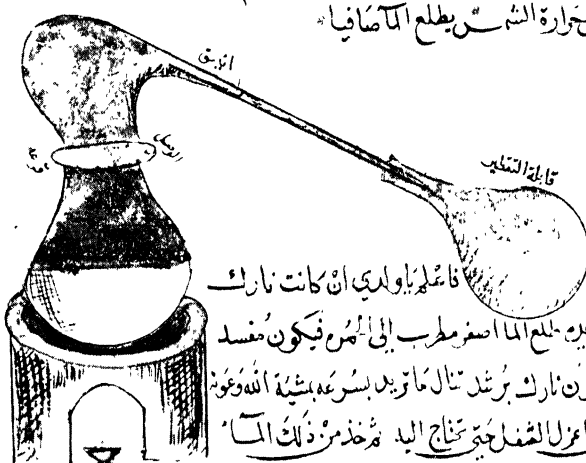
theory lagged behind and was neither closely connected with practice nor supported by experiment.

The first theoretical chemistry of importance—so far as our records go—was that of the Greek chemists. PYTHAGORAS, HERACLITUS, HIPPOCRATES, DEMOCRITUS, PLATO, ARISTOTLE, DIOSCORIDES and ZOSIMUS, as well as many more, covering a period of about 1,000 years from 600 B.C., all made chemical speculations and occasionally practical chemical observations as well. It appears, however, that the empirical chemical facts amassed by the Greeks were largely obtained by obscure men whose names have not come down to us. It might, indeed, be very naturally expected that they were craftsmen —metal-workers, dyers, and the like—and it is well known that the educated Greek had a marked distaste for experimental work, which did not appeal to his national genius.

The Greek theories of the structure of matter made the transmutation of the metals seem to be quite possible, and observations of the deposition of copper on an iron blade placed in a solution of vitriol, and many similar effects, must almost inevitably have been interpreted as actual examples of transmutation. If transmutation was possible, it was obviously a fact of supreme importance, for gold then, as now, was the sinews of war and the passport to ease and luxury. It is not surprising, therefore, to find that the problem of converting " baser " metals into gold soon began to occupy a prominent place in chemistry and finally engrossed so much of the attention of chemists that " chemistry " became practically synonymous with " gold-making."

When the empires of Byzantium and Persia were overthrown by the armies of Islam (seventh century A.D.), the Muslim conquerors, after they had settled down, began to encourage learning, and to that end had translations made of all such important Greek works as were available to them. These translations were made either directly from Greek into Arabic, or more often—at least at first—from Greek into Syriac and then into Arabic. Greek chemistry was thus introduced to the Arabs, who soon developed a passion for the science, and as they were also masters of Egypt they

ثم اغرزه في الوسط وركب الفطا عليها وطينها واجعلها في بنيه مثل عمل
النشادر واوقد عليه بنار لينه نصف يوم حتى يذهب الرطوبه ثم قوي
عليها النار تمام ثلاثة ايام بلياليها ثم اضعها يبرد يوما خر وافتحها تجد
قد صعد على الوجه جوهرا كانه الخثيثة البيضا فخذها واعلم انك قد حزت
ملك الدنيا فاخزنها في اناء زجاج واحكم الوصل بكلما تقدر عليه فان
الحكمه بالشد الجيد ليلا يروح وينقص منك واعلم ذلك ثم خذ
من الحجر الاول الحري فاغسله واجعله في قرعه وانبيق الى ثلثها او نصفها بلا زياده
وركب عليها الانبيق الواسع المزراب واحكم وصلها واوقد عليها بنار لينه
مثل حرارة الشمس يطلع المائيا



فاعلم يا ولدي ان كانت نارك
شديده طلع الماء اصفر مطرب الى الحمرة فيكون مفسد
فيكون نارك برشد تنال ما تريد بسرعه بمشية الله وعونه
حتى امزل القفل حتى تحتاج اليه ثم خذ من ذلك الماء
الابيض عشر دراهم التي منها ثلاثة دراهم ونصف من ذلك النشادر فانه يحل فيه
ويصير في اشد بياض من اللبن الحليب وهو الذي يقال له لبن العذرى فاجعله في
قدح العقد واحكم وصلها باللطف ثلاثة ايام بلياليها بالين ما تقدر عليه وعلامة
انعقاده ليس يطلع في القدح الفوقاني عرق البته فاعلم انه انعقد ثم ضعه

FIG. 1.—Page of Arabic Chemical MS., dealing with distillation.

were able to effect the necessary union of the theory of Greece with the practice of Egypt. This in itself was a great advance. The art of experiment was practically unknown in Greece, and the correlation of it with theory—and therefore the establishment of scientific method—is the great achievement of the chemists of Islam.

Traces of Arabic influence on chemistry are still to be found in many of our chemical terms—*alchemy*, for example, is merely "chemistry" with the prefix *al-*, the Arabic word for "the", while *alembic*, a kind of retort, *aludel*, a peculiarly shaped receiver, and *alcohol*, from the Arabic *al-khul*, all remind us of the days when the Muslims were the first chemists of the world. *Al-kuhl* was the name given to the black powder with which the Muslim ladies blackened their eyebrows and eyelids—possibly lead and antimony sulphides: its transference to spirit of wine is a strange fact for which PARACELSUS is responsible.

The greatest of the Arabic chemists were JĀBIR IBN HAYYĀN, whose name has been westernized to GEBER, and who lived in the eighth century A.D., ABU BAKR MUHAMMAD IBN ZAKARIYYA AL-RAZI (died A.D. 925), ABU'L-HASAN ʿALĪ AL-ANDALUSĪ, sometimes known as IBN ARFAʿ RA'S (died A.D. 1197), ABU'L-QĀSIM MUHAMMAD IBN AHMAD AL-ʿĪRAQĪ (thirteenth century), and ʿIZZ AD-DĪN AIDAMIR IBN ʿALI AL-JILDAKĪ (died A.D. 1361 or thereabout). Of these, Jabir has the greatest reputation, but AL-RAZI (known to the West as Rhazes) was perhaps a better practical chemist. Jabir is said to have written some 500 treatises on chemistry, of which only a few are now known to exist. Ibn Arfaʿ Ra's wrote a long chemical poem, known as *Particles of Gold*, of which many copies are preserved in our museums, while Abu'l-Qāsim al-ʿIrāqi wrote the important work *Al-Muktasab*, or, to give it its full title in English, *Knowledge Acquired Concerning the Production of Gold*, in which we find a very full account of the chemical theory of the day and the experimental work that the author had carried out in connection therewith

The westernmost province of the Muslin Empire was Spain, and it was here that chemistry first took firm root in Europe.

Fostered by the Muslim rulers, science in Spain flourished, and chemistry might at the present day have been in a much higher stage of development if the great disaster of the defeat of the Muslims by CHARLES THE HAMMER at Tours in A.D. 732 had not taken place. This triumph of the forces of reaction was a great blow to science in general and chemistry in particular, and although the Moorish power in Spain was not finally overthrown until 1492, irreparable damage had been done.

From Spain, the study of chemistry gradually spread over the rest of Europe, and the European chemists of the Middle Ages frankly admitted their debt to the Muslims. They did not, however, realize what they owed to the Greeks until after the Renaissance, when Greek manuscripts were first directly available. It was then possible to see the modifications of Greek chemistry produced by its passage through Islam.

When chemistry became thoroughly established in Europe rapid advance took place, largely owing to the more systematic mind of the European as compared with that of the Asiatic. The faculty of correlation is not highly developed among Eastern nations, and this faculty is of course a very essential one for scientific progress. We find that the Latin works of European origin of the thirteenth and fourteenth centuries show a marked advance in systematic arrangement, and this, with the scientific method developed by the Muslims, soon bore fruit.

The great chemists of the Middle Ages in Europe were ROGER BACON (1214–1292) and PARACELSUS (1493–1541). By the time of Paracelsus, the obsession of metallic transmutation was on the wane, but the change was not altogether one for the better, for chemistry became temporarily the handmaid of medicine, and the efforts of chemists were mainly directed to the preparation and investigation of drugs. This was the period of *Iatrochemistry*, or medical chemistry, and may be taken as covering roughly the years A.D. 1500–1700.

Towards the end of this time appeared the famous ROBERT BOYLE (1627–1691), who lived in the reign of Charles II and

was one of the founders of the Royal Society. Boyle was a scientist of the first rank, and his book *The Sceptical Chymist* (1661) was an extremely valuable contribution to chemical theory. In it he insists upon a rigid observance of scientific method, experiment, observation and inference ; he questions the truth of the old theory of the constitution of matter, which regarded Fire, Air, Earth and Water as the four " elements," and defines an element as a substance that cannot be split up into other substances ; and finally he suggests that matter is composed of small particles of different shapes and sizes called *atoms*, combination and separation of which take place in chemical changes.

Boyle was, however, in advance of his age, and his ideas had not the immediate great effect which might have been expected. Chemists were very much engrossed at this time, and for a hundred years after, in the study and expansion of a theory of combustion. JOHANN JOACHIM BECHER (1635–1682) suggested in his *Physica Subterranea* (1669) that the process of combustion was a decomposition of the burning substance into its constituents. All substances that would burn he assumed to contain a fatty substance, the *terra pinguis*, and supposed that on combustion this substance was lost. The residue after combustion represented the remaining constituent or constituents of the original body. GEORG ERNST STAHL (1660–1734) developed this theory and named the substance that was lost on combustion *phlogiston*, the " principle of fire," a word that had been previously used by Boyle but not in so clear and definite a way. The Phlogiston Theory offered a simple and coherent explanation of many facts of combustion, and we shall return to it later (p. 410). It will be sufficient here to say that the Phlogiston Theory may well be regarded as the first theory of Modern Chemistry, and greatly helped the advance of the science.

Towards the end of the eighteenth century the Theory of Phlogiston was overthrown, to some extent by the work of PRIESTLEY (1733–1804) (quite unintentionally on his part, for he was a confirmed phlogistian), but chiefly by the work of ANTOINE LAURENT LAVOISIER (1743–1794). It had for long

been known that the residue left after the combustion of a metal weighed more than the metal taken originally, but the knowledge was not general and its importance not perceived. Lavoisier, however, after many years of patient and brilliant experimental work, was able to convince the chemical world that, probably in all cases of combustion and certainly in most, an *increase* of weight occurred, whereas according to the Theory of Phlogiston a *decrease* would be expected. These observations made the Phlogiston Theory totter, and it fell when Lavoisier was able to show that Priestley's newly discovered gas, *dephlogisticated air*, was present in the atmosphere and, in all cases of combustion in air, combined with the burning substance, whence the increase in weight. He later called this gas *oxygen*. Lavoisier was guillotined during the French Revolution, in 1794.

A few years later JOHN DALTON (1766–1844) made the greatest step in the history of chemistry by his work on the Atomic Theory. We shall consider this in some detail in the next chapter and therefore need say no more here than that with the aid of this theory and the new theory of combustion just perfected by Lavoisier, the nineteenth century opened for chemistry under the happiest auspices. During the next 130 years an advance was made that can modestly be described as marvellous.

The history of chemistry since 1800 cannot be adequately treated in the present book, and has already been excellently described by many distinguished chemists to whose books (some of which are mentioned at the end of the chapter) the reader is referred for further information. The most noteworthy features, however, are the development of organic chemistry by LIEBIG, KEKULÉ, EMIL FISCHER and many others of scarcely less celebrity; the rise of stereochemistry, due largely to the labours of PASTEUR, VAN'T HOFF and SIR WILLIAM POPE; the rapid progress of physical chemistry, in which the names of RAOULT, ARRHENIUS, OSTWALD and NERNST are perhaps the most prominent; the discovery of the rare gases of the atmosphere by SIR WILLIAM RAMSAY; the discovery of radioactivity by BECQUEREL and M. and

MME. CURIE; and the recent work on the structure of the atom and the nature of valency by SIR J. J. THOMSON, LORD RUTHERFORD, SODDY, LANGMUIR, BOHR, SCHROEDINGER, DIRAC, ASTON and many others.

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QUESTIONS

1. Write an account of the early history of chemistry.
2. Who were the chief Muhammadan chemists? What contributions to the development of chemistry were made by Islam?
3. Mention the chief landmarks in the progress of chemistry since the time of Boyle.
4. With what discoveries do you associate the names of (*a*) Becher; (*b*) Boyle; (*c*) Priestley; (*d*) Lavoisier; (*e*) Dalton?
5. Estimate the probable advance of chemistry in the next fifty years.

CHAPTER II

THE ATOMIC THEORY

The idea that matter is composed of extremely minute particles, the various kinds and arrangements of which give rise to the many forms that matter assumes, was first elaborated by the Greek philosophers, an excellent account of whose work is to be found in *The Study of Chemical Composition* by the late Miss FREUND. In the ancient world, however, theories of the constitution of matter could be nothing more than speculations—or, to put it plainly, guesses —entirely unsupported by experimental, if not by observational, evidence. We do not call MOTHER SHIPTON the inventor of the motor-car, although she prophesied that some day carriages would move without horses, and in just the same way we do not regard the Greek philosophers as the founders of the Atomic Theory. That position is occupied by JOHN DALTON (1766–1844).

Dalton was a Quaker schoolmaster, born at Eaglesfield in Cumberland. Like all other scholars of the time he was given a classical education (although he studied mathematics as well), and was probably therefore acquainted with the classical ideas on the structure of matter. He seems to have pondered over these, and the more definite ideas of the atomic nature of matter suggested by NEWTON, and finally reshaped the theory in such a form that it explained certain facts already known and was also capable of experimental proof or disproof, partial if not complete. It is important to note that Dalton did not arrive at the Atomic Theory from a consideration of experimental results already gained; he

thought out the theory first and then made experiments to test it.

The main points of the Atomic Theory as formulated by Dalton are as follow :—

1. Matter is composed of a great number of extremely small particles, called *atoms*. [The word *atom* means " indivisible," and was given to these particles because they were considered to be incapable of further division, in the case of elements. The " compound atoms " of compounds on division, of course, would give atoms of elements, and therefore in this sense a compound atom is also indivisible, or is at least the smallest particle of the compound of which one can conceive.]

2. All the atoms of the same element are identical in all respects, and different from those of other elements.

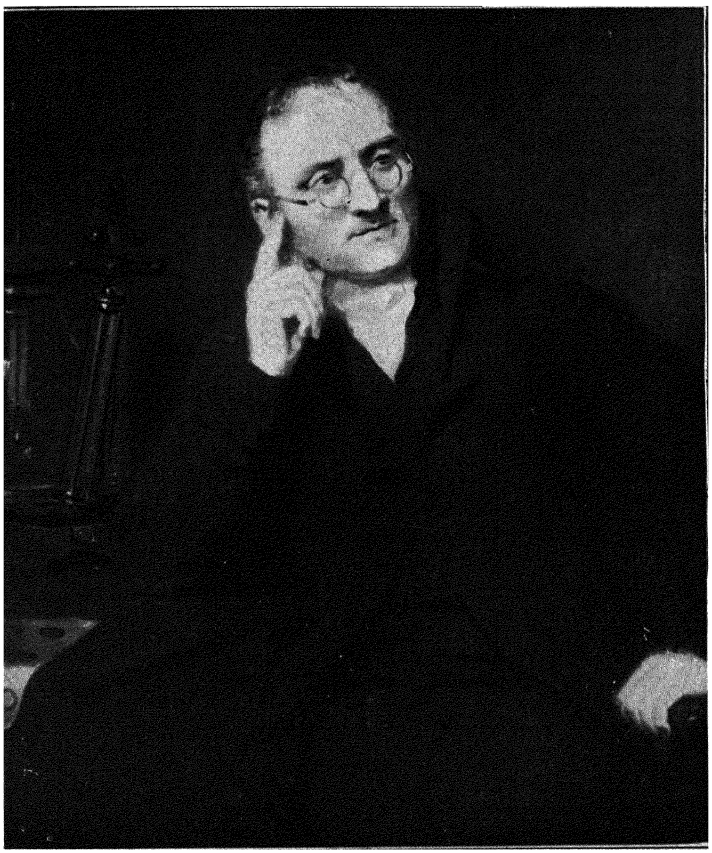
3. Atoms are indestructible and cannot be created.

4. In the formation of compounds, combination occurs between *small* whole numbers of atoms of the elements concerned.

5. All the " compound atoms " of a compound are exactly alike.

From these postulates (they were at that time nothing more) it is possible to deduce certain conclusions that can be tested by experiment. This at once put the Atomic Theory on a sound scientific basis, and explains the fact that chemists universally consider Dalton to be the Founder of the Theory. No scientific theory is of any use unless it can be tested experimentally, either directly or indirectly. In spite of this fact, which should be sufficiently obvious, we shall find that many " untestable " theories have been suggested.

The first deduction to be made from the Atomic Theory is called the **Law of Constant Composition,** viz., *that the same chemical compound always consists of the same elements combined together in the same proportion by weight.* This follows from 2, 4, and 5 above. As this is the first " Law " of chemistry we have met with, it will be well for us to consider exactly what we mean by the word *law* in this connection. It has clearly a quite different meaning from that



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JOHN DALTON

implied in the phrase " penal law," for it would be ridiculous to suppose that up to the time of Dalton chemical compounds led a free and easy existence, and that water, for example, could consist of tin and lead, if it so desired, at one time, and of hydrogen and oxygen at another. It would be equally foolish to imagine that if a chemical compound had the temerity to break the " law " of constant composition it could be punished in any way (although many chemists of the middle of the nineteenth century must have heartily wished they could sentence nitric oxide to a term of hard labour for its effrontery in refusing to obey the Law of Even Numbers). We have discovered, therefore, what a chemical " law " is not, but we still have to decide what it is. We can easily do this if we take a simpler example. It is a " law " of Nature that every man has two eyes. Now this does not prevent a man from plucking out his eye if it offend him, neither does it follow that a man may not have a third (glass) eye in his waistcoat pocket, and indeed he has a third rudimentary eye in the top of his head, so zoologists tell us. It does, however, imply that, *as a matter of fact and observation*, men *do* have two eyes. It is a short way of saying " A has two eyes, B has two eyes, C, D, E, and 1,900,000,000 more human beings have each two eyes." It is, in fact, a *summary of experience*, and this is true of chemical laws. The Law of Constant Composition means simply this : that *up to the present no compound has been discovered of a variable composition.* If such compounds were ever discovered, the " law " would vanish, and here again we see the difference between a penal law and a chemical law, for if I am fined £1 for allowing a dog to stray, I find that after the infraction the law against the straying of dogs is quite unharmed.

Let us now examine the relation between the Law of Constant Composition and Dalton's Atomic Theory. In essence it is this : if the Atomic Theory be true, then, as a matter of fact and observation, the composition of any one chemical compound should always be the same. How far is the converse true ? Does it follow that if, by experiment, we find that the composition of a certain chemical compound

is constant, therefore the Atomic Theory is true ? A little reflection will convince us that this is not so. Suppose a man to be going by train ; well, we can form a Travel Theory about him. We should, as a matter of fact, expect him to come along the road to the station, to buy a ticket, to arrive at the station before the scheduled time of departure of the train, to hurry if he were late, and possibly to carry a bag. Now, suppose we see a man walking towards the station. Does it follow that he is going by train ? Of course it does not ; he may be going to meet a friend, or to claim damages for a broken article, or for many other reasons. But the fact that he is going towards the station does *agree with* the theory that he is going by train ; it by no means *proves* it. Suppose, however, that he is running as well, that it is nearly time for a train to go, that he is carrying a bag, and that he goes to the booking-office and buys a ticket—is the theory proved now ? No, for he may be acting for the cinematograph or he may be mad ; we cannot be absolutely certain that he *is* going by train until we have seen him get into it and go off in it. But the above evidence would make it extremely probable, and the Travel Theory would be much more reasonable than the Cinematograph or Insanity Theories, and we should be justified in accepting it in the absence of definite evidence for either of the others.

This is exactly the position that the Atomic Theory was in all through the nineteenth century. No one, so to speak, had seen the man get into the train and go off, but the circumstantial evidence was very strong indeed. There were no " eye-witnesses " until the early years of the present century.

The fact that, in practice, the Law of Constant Composition is found to be true, is then in accordance with the truth of the Atomic Theory, but it does not *prove* it. It is circumstantial evidence. Now the value of circumstantial evidence increases, as LORD DARLING has pointed out, not in arithmetical but in geometrical progression, so that if we find the next deduction from the Theory to be borne out in practice, the probability of the truth of the Theory will be greatly increased ; and if several deductions are tested and

found satisfactory the probability will become a practical certainty.

Before we pass on to the next deduction from the Atomic Theory there is another point to be considered. One is sometimes asked how to *prove* the truth of the Law of Constant Composition, or of other chemical laws. The answer is that the question is badly expressed. It is clearly impossible to *prove* a law of chemistry in the general sense, for to " prove " the Law of Constant Composition, for example, we should have to analyse all the specimens of all the compounds that exist now, have ever existed, and will exist in the future in the whole universe. The most we can do is to show that it is true in certain cases, and to tell the sceptic that if he knows of an exception, to produce it.

Incidentally, it has to be remarked that all measurement is bound to be more or less inexact, and that we can therefore, even in a special case, demonstrate the truth of the Law *only within the limits of experimental error.*

The Law of Multiple Proportions is the next conclusion we can draw from the Atomic Theory. It is that *when two elements combine to form more than one compound, then the weights of one of those elements which combine with a constant weight of the other are in a simple ratio to one another*, and is a logical inference from 2 and 4 (" *small* " whole numbers). Suppose, for example, that the elements A and B unite together to form two different compounds. The simplest imaginable case will be when in one of the compounds 1 atom of A combines with 1 atom of B, and in the other compound 1 atom of A combines with 2 atoms of B. Since, in one " compound atom " of each of the two compounds there is 1 atom of A, it follows, from Dalton's assumption 2, that the weight of A is constant in these two " compound atoms." The weights of B, on the other hand, will be in the ratio of the number of atoms of B present in each " compound atom " : in this case, 1 : 2. This is a simple ratio, and if compounds are always composed of *small* numbers of atoms, the ratio always *must* be simple. It does not matter of which element we take the constant weight, nor what weight we

take as the constant weight, as long as we find the *ratio to one another of the weights of the other element* that have combined with this constant weight. Thus, suppose in the above instance we take the weights of A that have combined with a constant weight of B. Let 1 atom-weight of B be the constant weight of B. Then in the first compound we have 1 atom-weight of A combining with the given, constant, weight of B. In the second compound, 2 atom-weights of B combine with 1 atom-weight of A, therefore 1 atom-weight of B (the " constant " weight, or " reference " weight) would combine with $\frac{1}{2}$ an atom-weight of A. Now the ratio of 1 atom-weight of A to $\frac{1}{2}$ atom-weight of A is 2 : 1.

Having deduced the Law, Dalton's next care was to test it experimentally. He worked on certain compounds of carbon and hydrogen and found that he obtained the expected results. It is, however, easier to illustrate the truth of the Law with other compounds, such as the oxides of lead or copper. To make quite certain of understanding the Law it is best to work through several numerical examples.

Examples.—(1) Phosphorus trichloride and phosphorus pentachloride contain 77·45 per cent. and 85·13 per cent. chlorine respectively. Show that these compounds illustrate the law of multiple proportions.

In the trichloride

77·45 gms. chlorine are combined with 22·55 gms. phosphorus.

In the pentachloride

85·13 gms. chlorine are combined with 14·87 gms. phosphorus.

therefore $\frac{85{\cdot}13}{14{\cdot}87} \times 22{\cdot}55$ gms. ,, ,, ,, 22·55 gms. ,,

129·1 gms. ,, ,, ,, 22·55 gms. ,,

Thus in these two compounds the weights of chlorine that are combined with a constant weight (22·55 grams) of phosphorus are 77·45 gms. and 129·1 gms. respectively ; these weights are in the ratio 3 : 5.

(2) Four oxides of titanium contain the following percentages of oxygen :

Monoxide .	24·96 per cent.	Sesquioxide .	33·29 per cent.
Dioxide . .	39·95 ,,	Trioxide . .	49·95 ,,

Show that these figures illustrate the law of multiple proportions.

In the monoxide
75·04 gms. titanium are combined with 24·96 gms. oxygen.
In the sesquoixide
66·71 gms. titanium are combined with 33·29 gms. oxygen
therefore $\frac{66·7}{33·29} \times 24·96$ gms. ,, ,, ,, 24·96 gms. ,,
50·02 gms. ,, ,, ,, 24·96 gms. ,,
In the dioxide
60·05 gms. titanium are combined with 39·95 gms. oxygen.
therefore $\frac{60·05}{39·95} \times 24·96$ gms. ,, ,, ,, 24·96 gms. ,,
37·52 gms. ,, ,, ,, 24·96 gms. ,,
In the trioxide
50·05 gms. titanium are combined with 49·95 gms. oxygen.
therefore $\frac{50·05}{49·95} \times 24·96$ gms. ,, ,, ,, 24·96 gms. ,,
25·01 gms. ,, ,, ,, 24·96 gms. ,,

Thus the weights of titanium combined with a constant weight (24·96 gms.) of oxygen are 75·04 gms., 50·02 gms., 37·52 gms., and 25·01 gms. respectively; these are in the ratio 6 : 4 : 3 : 2.

The Law of Reciprocal Proportions also follows as a corollary of Dalton's Atomic Theory. It states that *if an element A combines with an element B and also combines with an element C, then* if *B and C combine together, the proportion by weight in which they do so will be simply related to the ratio of the weights of B and C which (separately) combine with a constant weight of A.* For example, sodium will combine with chlorine in the proportion of 1 gram of sodium to 1·54 grams of chlorine. Sodium will also combine with iodine in the proportion of 1 gram of sodium to 5·52 grams of iodine. Therefore *if* iodine and chlorine combine together, the ratio of the weights in which they do so should be simply related to $\frac{5·52}{1·54}$, which is the ratio of the weights of these elements that combine with a constant weight of sodium. Now as a matter of experimental fact, it is found that iodine and chlorine *will* combine together, in the proportion of 1 gram of chlorine to 1·19 grams of iodine. Is the ratio $\frac{5·52}{1·54}$ simply related to

$\frac{1{\cdot}19}{1}$? If we simplify the ratio $\frac{5{\cdot}52}{1{\cdot}54}$ by dividing top and bottom by 1·54 we get $\frac{3{\cdot}58}{1}$, when it becomes apparent that $\frac{3{\cdot}58}{1}$ is to $\frac{1{\cdot}19}{1}$ as 3 is to 1—a simple ratio.

The logical necessity of this law will be obvious when it is remembered that Dalton postulated that (*a*) combination takes place between *small* whole numbers of atoms, to form a compound, and that (*b*) all the atoms of the same element are of exactly the same weight. Note that the Law does not state that the elements "B" and "C" *will* combine; it states only what will happen *if* they do.

A final deduction from the Atomic Theory is the **Law of the Conservation of Matter,** which states that *matter is uncreatable and indestructible.* This Law is clearly essential and fundamental for the development of chemistry as an exact science. Logical proof of the Law cannot, of course, be attempted; the most one can do is to show that in any special case of chemical change, the total weight of the products is exactly equal (within the limits of experimental error) to the total weight of the substances started with.

Careful experiments of this kind were carried out by LANDOLT (1909) and MANLEY (1912). Both were unable to detect the slightest change in weight during the chemical reactions they investigated.

We shall find later on (Chapter XVI) that Dalton's Theory has proved to be inexact in every particular, but that as a working guide for all but the most minutely accurate research it is not likely to be superseded. We have only to think of the wonderful development of chemistry during the nineteenth century to realize how useful the theory has been.

QUESTIONS

1. What are the main features of the Atomic Theory as formulated by Dalton ?
2. What do you understand by a *law* in chemistry ?

3. State the Law of Multiple Proportions and say how you would illustrate its truth.

4. Show that the laws of constant composition, reciprocal proportions and multiple proportions are direct corollaries of the Atomic Theory.

5. The three oxides of phosphorus contain the following percentages by weight of phosphorus :—

Pentoxide	43·668 per cent.
Tetroxide	49·212 ,,
Trioxide	56·365 ,,

Show that these figures illustrate the Law of Multiple Proportions.

6. 10 gms. stannous sulphide contain 7·877 gms. tin, while 8 gms. stannic sulphide contain 5·196 gms. tin.

Find the weight of sulphur combined with 1 gm. tin in each case and show that your results agree with the Law of Multiple Proportions.

7. Samples of the three chlorides of vanadium contained the following weights of the elements :—

	Vanadium.	*Chlorine.*
(i)	0·3643 gm.	0·5060 gm.
(ii)	1·6149 gm.	3·3638 gms.
(iii)	0·6580 gm.	1·8279 gm.

Calculate the weight of chlorine combined with 1 gram of vanadium in each case and show that the results illustrate the Law of Multiple Proportions.

8. Ferrous sulphate contains 36·76 per cent. iron and ferric sulphate contains 27·93 per cent. iron. Show from these figures that the law of Multiple Proportions is obeyed in the case of the sulphates of iron.

9. Samples of four oxides of lead contain the following weights of the elements :—

	Lead.	*Oxygen.*
Suboxide	4·144 gms.	0·160 gm.
Monoxide	1·036 gm.	0·080 gm.
Sesquioxide	5·2007 gms.	0·600 gm.
Peroxide	6·488 gms.	1·002 gm.

Show that these results illustrate the Law of Multiple Proportions.

10. 13·962 gms. of aurous chloride were taken and acted upon with water. This gave 7·888 gms. of gold together with some auric chloride. The auric chloride was then heated to 220° and the resulting metal was found to weigh 3·944 gms.

Find the weight of chlorine combined with 1 gram of gold in each of the chlorides and show that your answer illustrates the Law of Multiple Proportions.

11. Given a sample of iron wire, what experiments would you make to find whether iron oxides obey the Law of Multiple Proportions ?

CHAPTER III

EQUIVALENTS

"*Substances react only by definite weights.*"—AL-JILDAKĪ
(† *ca.* 1360 A.D.)

If we take a definite weight of pure sulphuric acid, say 10 grams, and dilute it with water, we shall find that it will act upon zinc. The zinc will dissolve and an inflammable gas, hydrogen, will be evolved. We shall also find that the *weight* of zinc that 10 grams of sulphuric acid will dissolve is limited and not indefinite. Experiment shows that 10 grams of sulphuric acid, when diluted with water, will dissolve 6·63 grams of zinc; if more zinc be added the excess will remain undissolved, and if less be used, some of the sulphuric acid will be left over. We therefore say that 10 grams of sulphuric acid are *equivalent* to 6·63 grams of zinc. The hydrogen, too, that is evolved when 6·63 grams of zinc are dissolved in 10 grams of sulphuric acid, diluted with water, is found always to weigh 0·204 grams; we may therefore say that 0·204 grams of hydrogen are *equivalent* to 10 grams of sulphuric acid or to 6·63 grams of zinc.

The same sort of thing is true for all other reactions, and this *constancy of reacting weights* of elements and compounds is one of the fundamental facts of chemistry. It was mentioned by AL-JILDAKĪ about 1360, and was re-discovered by CAVENDISH in 1766, who showed that the weights of sulphuric acid and nitric acid that would separately neutralize a definite weight of caustic potash, would also separately dissolve a (different) definite weight of marble. The weights of sulphuric acid and nitric acid he therefore called *equivalent* to one another; the weights of potash and

marble were also *equivalent* to one another and to the weights of the respective acids.

Chemists soon found it convenient to choose a standard weight of a suitable substance in terms of which the equivalent weights of all other elements and compounds could be expressed. For this purpose they fixed upon *one unit weight of hydrogen.* On this system of reference, the equivalent of sulphuric acid is 49, since when hydrogen is liberated from sulphuric acid, 49 grams of the acid always yield 1 gram of hydrogen; or when 49 ounces of the acid are used, they yield 1 ounce of hydrogen, and so on. We can therefore define the **Equivalent** of any element or compound as *that number of units of weight of it which will react either directly or indirectly with one of the same units of weight of hydrogen.* Note that the equivalent is a *number* only; it is incorrect to say that the equivalent of sulphuric acid is 49 *grams*—the equivalent is *not* 49 *grams* but just 49. When we say that the equivalent of sulphuric acid, then, is 49, we mean that 49 grams, grains, ounces, pounds or tons of it will react with evolution of 1 gram, grain, ounce, pound or ton respectively of hydrogen. Similarly, the equivalent of oxygen is the *number* of units of weight of it which will combine with one of the same units of weight of hydrogen. Thus, although the unit of weight commonly used in chemistry is the gram, the equivalent of a substance is a *number* only, and, in the words used by AL-'IRĀQĪ when speaking of another matter, "*Know this therefore, and ponder thereon, for verily it is one of the fundamental things of this Divine Science.*"

When we come to consider the equivalent of a metal, we could determine it by finding the *number* of grams of the metal that will liberate 1 gram of hydrogen from a dilute acid; but there are many metals that do not dissolve in acids with liberation of hydrogen. In these cases we attack the problem by an indirect method. Oxygen will combine directly with hydrogen and we can therefore easily determine its equivalent directly. Experiments have shown that 8 grams of oxygen will combine with 1 gram of hydrogen; hence the equivalent of oxygen is 8. Now, although it may

be impossible to get the metal to liberate hydrogen from a dilute acid, it is almost always possible to make it combine with oxygen, and the number of grams of it which will combine with 8 grams of oxygen is taken as its equivalent, since 8 grams of oxygen combine with 1 of hydrogen. In short, we assume that *the weights of two substances which are equivalent to a constant weight of a third are also equivalent to one another*, and this assumption has justified itself in practice.

Note that the term equivalent weight is not confined to elements ; equivalents of compounds may also be determined and are included in the same definition.

Methods of Determining the Equivalents of Elements. A. *Metals.*

(i) If the metal is soluble in a dilute acid (or in a solution of an alkali) with liberation of hydrogen, take a known weight of it, dissolve it in a suitable dilute acid (or alkaline solution) and find the weight of hydrogen evolved.

(ii) If the metal is not soluble in a dilute acid, convert a weighed quantity of it into its oxide, and find the weight of oxygen taken up (= increase in weight). Then calculate the number of grams of it which would combine with 8 grams of oxygen.

(iii) If neither of the above methods is suitable, convert a weighed quantity of the metal into its chloride. Weigh this and calculate the number of grams of the metal which would combine with 35·5 grams of chlorine, since 35·5 is the equivalent of chlorine. Methods ii and iii may also be used in the reverse way, that is, reduction of the oxide or chloride to the metal.

(iv) The equivalent of a metal may often be conveniently found by displacement of it from a solution of one of its salts by means of a weighed quantity of another metal of known equivalent. Then the equivalent of the first metal is that number of grams of it which is displaced by the equivalent in grams of the second.

(v) By electrolysis. It was shown by FARADAY that in electrolysis the weights of substances liberated at the electrodes were in the ratio of their chemical equivalents. By

measuring, therefore, the weight of a metal deposited in an electrolytic cell and the weight of hydrogen liberated by the same quantity of electricity, the equivalent of the metal may be found.

(vi) A compound of the metal with an element of known equivalent may be converted into another compound of the metal with other elements of known equivalents. From the weights of the two compounds the equivalent of the element may be determined. For example, calcium chloride, containing the metal calcium, whose equivalent is desired, and chlorine, equivalent 35·5, is converted into calcium sulphate, containing calcium, sulphur and oxygen. We know from experiments with sulphuric acid that the equivalent of the "sulphate" group is 48. Suppose we took 1·000 grams of calcium chloride and obtained 1·225 grams of calcium sulphate. Then if x be the equivalent of calcium we have $\frac{x + (35{\cdot}5)}{x + (48} = \frac{1{\cdot}000}{1{\cdot}225}$

$$\therefore 1{\cdot}225x + (35{\cdot}5)\ (1{\cdot}225) = x + (48)$$

$$\therefore 0{\cdot}225x = 48 - 43{\cdot}488 = 4{\cdot}512$$

$$\therefore x = \frac{4{\cdot}512}{0{\cdot}225}$$

$$= 20{\cdot}06.$$

B. *Non-Metals.*

The determination of the equivalents of non-metals, while equally simple in theory, is usually more difficult in practice, since so many of the non-metallic elements are gases that need more skill in manipulation.

(i) By direct combination of the element with hydrogen, when the equivalent may be calculated from the weight of the element taken and the weight of the product.

(ii) By formation of the oxide or chloride.

(iii) By method vi as given for metals.

Details of the determination of the equivalents of various non-metallic elements will be found in the descriptive part of this book.

The exact determination of equivalents is of great importance, since upon it mainly depend the values of the *atomic*

weights of the elements (Chapter VI). It is usual at the present day to take as standard not 1 unit of weight of hydrogen but 8 units of weight of oxygen. If the hydrogen unit be taken, the equivalent of oxygen is not exactly 8, but 7·94, hence equivalents on the oxygen standard are $\frac{8}{7{\cdot}94}$ times the equivalents on the hydrogen standard. The oxygen standard is preferred, since the numbers it gives are more often or more nearly whole numbers than those on the hydrogen standard. There is also theoretical justification for the oxygen standard, but the matter is too advanced to be discussed here.

Equivalents of Compounds.—The equivalent of a compound is determined by making use of some reaction in which the compound takes part. Thus, the equivalent of sulphuric acid is the number of grams of the acid which will yield 1 gram of hydrogen on treatment with zinc. If the equivalent of sulphuric acid be known, then the weight in grams of caustic soda which the equivalent in grams of sulphuric acid will neutralize is the equivalent of caustic soda. By continuing this process, the equivalent of any compound may be discovered. It follows that, if two substances react together, they will do so in the proportion by weight of their equivalents, since their equivalents have been determined in this way. This property is made use of in volumetric analysis, where a *normal solution* of a substance is one that contains the equivalent in grams of the substance in one litre of solution. Hence, *equal volumes of all normal solutions are exactly equivalent to one another.* Thus 10 c.c. of N-hydrochloric acid will neutralize exactly 10 c.c. of N-caustic soda or N-caustic potash; and 25 c.c. of $\frac{N}{2}$ or half-normal hydrogen peroxide will decolourize exactly 25 c.c. of $\frac{N}{2}$ potassium permanganate, and so on. It is as a rule possible to find the equivalent of a compound from an inspection of its formula (Chapter VII), but you should carefully avoid the mistake of imagining that the equivalent of a compound is always the sum of

the equivalents of its constituent elements. It often is and often is not.

It should be noted that the equivalent of a substance may sometimes have different values for different reactions or in different compounds, but these values are always simply related to one another. Thus the equivalent of copper in black copper oxide is 31·8, while in brown copper oxide it is 63·5, the ratio of the two being 1 : 2. The explanation of this phenomenon we shall discuss later.

QUESTIONS

1. Define *equivalent*. What methods are available for determining the equivalents of metals ?

2. 0·461 grams of a metal on oxidation gave 0·503 grams of its oxide. What is the equivalent of the metal ?

3. 1·342 grams of the chloride of a metal were reduced in a current of hydrogen. The metal thus produced weighed 0·753 grams. Calculate its equivalent.

4. On dissolving 0·36 grams of a metal in a dilute acid, 0·013 grams of hydrogen were evolved. Find the equivalent of the metal.

5. What do you mean by a *normal solution* ? How many c.c. of N/10 hydrochloric acid would be required to neutralize 19·3 c.c. of N/3 caustic soda ?

CHAPTER IV

THE GAS LAWS

Changes of temperature and pressure alter the volume of a gas, and the laws expressing the relation between temperature, pressure and volume have been formulated by BOYLE and CHARLES.

In 1662 Boyle stated that *the volume of a given mass of gas varies inversely as the pressure upon it, if the temperature is constant.* This is known as **Boyle's Law,** and may be written shortly as

$$V \propto \frac{1}{P} \text{ if T is constant.}$$

Gas pressure is measured in terms of the length of a column of mercury which the pressure could support; thus, "a pressure of 100 mm." means a pressure that would support a column of mercury 100 mm. high. For higher pressures, a larger unit, the "*atmosphere,*" is used; this is equal to the average pressure of the earth's atmosphere at sea-level, viz., 760 mm. The pressure of 760 mm. is also called *Normal* or *Standard* Pressure.

Assuming Boyle's Law, if we know the volume of a gas at one pressure, we can calculate what volume it would occupy at another, if the temperature remain constant. Suppose a gas to occupy 100 c.c. at 500 mm. pressure. What volume would it occupy at 760 mm.? Since the pressure will be greater, the volume will be less, and therefore we must put the larger pressure at the bottom in the expression

$$\text{New volume} = \frac{100 \times 500}{760}$$
$$= 65{\cdot}7 \text{ c.c.}$$

If you always ask yourself first whether the final volume will be greater or smaller, and arrange the factors of your expression accordingly, you will never go wrong.

Charles' Law states that, provided the pressure is constant, *a gas will expand* $\frac{1}{273}$ *of its volume at* 0° *C. for every rise in temperature of* 1° *C. and will contract* $\frac{1}{273}$ *of its volume at* 0° *C. for every fall in temperature of* 1° *C.* If we have 1 c.c. of gas at 0° C. the volume, v, at t° C. will therefore be $1 + \frac{t}{273}$ c.c., or if we have x c.c. at 0° C., at t° C. the new volume x' will be equal to $x\left(1 + \frac{t}{273}\right)$ c.c. Suppose $t = -273$° C., what will the volume of the gas be at this temperature? For every fall of 1° in temperature, the gas contracts $\frac{1}{273}$ of its volume at 0° C., therefore at -273° it will have contracted $\frac{273}{273}$ of its volume at 0°, that is, it will have no volume at all. This is shown too by the formula, where x' will now equal $x\left(1 + \frac{-273}{273}\right)$ or $x(0) = 0$. If therefore we could cool a gas to -273° C. it would vanish. As a matter of fact, all gases evade the issue by changing to liquids before this temperature, called *absolute zero*, is reached. The lowest temperature yet recorded is 0·75° above absolute zero, or $-272{\cdot}25$° C. It can be shown theoretically that at absolute zero every substance would be perfectly devoid of heat; hence a lower temperature is inconceivable.

The *Absolute Scale of Temperature* uses the same degrees as the Centigrade Scale (i.e., there is a difference of 100° between the melting-point of ice and the boiling-point of water), but its zero is 273° below the Centigrade zero. To convert



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ROBERT BOYLE

temperatures C. into temperatures Absolute all that we have to do is to add 273. Thus 15° C. is 273 + 15° Absolute, or 288° Abs. From these considerations it can easily be shown that *the volume of a given mass of gas is directly proportional to the Absolute Temperature, provided that the pressure is constant.* Suppose a gas to occupy x c.c. at 0° C., and x' c.c. at t° C., then from the above formula,

$$x' = x\left(1 + \frac{t}{273}\right)$$

$$\therefore \frac{x}{x'} = \frac{1}{1 + \frac{t}{273}} = \frac{273}{273 + t}.$$

Suppose now that the gas occupies x″ c.c. at t'° C. Then

$$\frac{x}{x''} = \frac{273}{273 + t'}$$

whence

$$\frac{x'}{x''} = \frac{273 + t}{273 + t'}$$

or, in other words, the volume of a gas is directly proportional to the temperature in ° C. + 273, that is, to the *temperature absolute.*

When correcting the volumes of gases for changes in temperature the first necessity, then, is to express the temperature in ° Absolute, by adding 273 to the temperature in ° C. A famous chemist used to put a private mark in his books on a certain page, for identification purposes. When asked upon what page he put the mark, he replied, "On what other page *could* a chemist put his mark than 273 ?"

Charles' Law may be written shortly as

$$V \propto T \text{ (Absolute) if } P \text{ is constant.}$$

or

$$\frac{v}{v'} = \frac{T}{T'} \therefore vT' = v'T.$$

Example.—A gas occupies 72 c.c. at 15° C. What will be its volume at − 10° C. ?

Change the temperatures to degrees absolute first. 15° C. = (273 + 15)° Abs. = 288° Abs. and − 10° C. = (273 − 10)° Abs. = 263° Abs. The original temperature is higher than the final, therefore the gas

is to be cooled and therefore will contract. Hence the larger of the two temperature numbers must go at the bottom in the expression

$$\text{New volume} = \frac{72 \times 263}{288}$$
$$= 65{\cdot}5 \text{ c.c.}$$

Or, by means of the formula, $\frac{72}{x} = \frac{288}{263}$

$$\therefore\ x = 65{\cdot}5 \text{ c.c.}$$

In all calculations it is much better to work from first principles than to use the formula. *Never use a formula until you know its meaning thoroughly and can work it out for yourself.*[1]

Normal or Standard Temperature is 0° C. or 273° Abs. N.T.P. or S.T.P. are contractions for Normal or Standard Temperature and Pressure, 0° C. 760 mm.

Correction of Volumes of Gases for Temperature and Pressure Simultaneously.—This presents no difficulty. Correct for Temperature first and then for Pressure, e.g.,

A gas occupies 180 c.c. at 87° C. and 1,000 mm. pressure. What volume will it occupy at N.T.P. ?

Temperatures in ° Absolute : 87° C. = 360° Absolute.
0° C. = 273° ,,

The gas is therefore to be cooled, ∴ the new volume

$$x = \frac{180 \times 273}{360}.$$

This volume has now to be corrected for pressure. Original pressure 1,000 mm., final 760 mm., ∴ the pressure is to be lowered, ∴ the gas will expand, ∴ the new volume

$$y = \frac{180 \times 273}{360} \times \frac{1{,}000}{760}$$
$$= 179{\cdot}6 \text{ c.c.}$$

The final volume at N.T.P. is therefore 179·6 c.c.

A Third Gas Law may be deduced from those of Boyle and Charles, and is therefore nameless. It is that *the pressure*

[1] If you use a formula in a mechanical way you will never make any advance, and, to look at the matter from a very low point of view, any examiner can very easily set you a question in which slavish use of the formula will lead you hopelessly astray. To find out whether the candidate understands his work properly or has merely absorbed formulae is, indeed, one of the few cases in which an examiner may legitimately set traps.

of a given mass of gas varies directly as the Absolute Temperature if the volume is constant, or $P \propto T$ if V is constant.

For, from Boyle's Law,

$$V \propto \frac{1}{P}$$

and from Charles' Law

$$V \propto T \textit{ abs.}$$

Combining these two expressions, $V \propto \frac{T \textit{ abs.}}{P}$

$$\therefore P \propto \frac{T \textit{ abs.}}{V}$$

and if V is constant, $P \propto T$ *abs.*

Or, alternatively, the pressure exerted by a gas increases by $\frac{1}{273}$ of its value at 0° C. for every rise in temperature of 1° C., if the volume is kept constant.

These three laws may be combined into one expression, $\frac{PV}{T}$ = a constant. This constant is usually called R, so that the *gas equation* becomes

$$PV = RT.$$

A value can be calculated for R by taking definite values for P, V and T.

Suppose we take P = 76 cm. of mercury, V = 22,400 c.c.* (the reason for this will be seen later, p. 65), and T = 273° Absolute. Expressing the pressure in dynes per square cm. we should have $P = 76 \times 13{\cdot}5 \times 981$, since 13·5 is the specific gravity of mercury. The equation then is

$$\frac{76 \times 13{\cdot}5 \times 981 \times 22{,}400}{273} = R$$

$$\therefore R = 8{\cdot}3 \times 10^7 \text{ ergs per } 1° \text{ C.}$$

If we divide this by the mechanical equivalent of heat,

$$1 \text{ calorie} = 4{\cdot}18 \times 10^7 \text{ ergs},$$

we shall get the value of R in thermal measure $= \frac{8{\cdot}3 \times 10}{4{\cdot}18 \times 10^7}$

$$= 2 \text{ calories.}$$

Correction of the Volume of a Moist Gas.—If a gas is collected over water, it takes up some water vapour with it. The gas collected therefore is not pure, but mixed with water vapour. In a mixture of gases it was found by DALTON in 1801 that *each gas exerts the same pressure that it would exert if it were alone in the same volume.* This is called the Law of **Partial Pressures,** and may be alternatively stated as "*In a mixture of gases, the total pressure is equal to the sum of the partial pressures of the gases present.*"

The total pressure exerted by a gas that is saturated with water-vapour will therefore be made up of two pressures, (*a*) the pressure of the gas itself, and (*b*) the pressure of the water-vapour. Now the pressure of water-vapour in contact with liquid water is found to be constant at a constant temperature. Tables have been drawn up giving the "pressure of aqueous vapour," or "vapour pressures of water" at different temperatures, and by reference to them we can at once find the partial pressure of the water-vapour in a gas saturated with the latter at a known temperature. If the gas is collected under atmospheric pressure, the real pressure of the gas itself will be the atmospheric pressure *minus* the pressure of water-vapour at the temperature concerned.

Example.—Suppose we have 100 c.c. of a moist gas at 15° C. when the barometer reads 770 mm. What will be its volume *dry* at N.T.P. ? First, look up the pressure of water-vapour at 15° C. This is found to be 12·7 mm. Therefore the true pressure of the gas is 770 − 12·7 = 757·3 mm. The rest of the correction is then made in the usual way.

QUESTIONS

1. Find the volume at 300° C. of a gas that occupies 1,000 c.c. at 10° C. (Pressure constant.)

2. Find the volume at 3½ atmospheres of a gas that occupies 10 litres at 740 mm. (Temperature constant.)

3. At what temperature will a gas, that occupies 100 c.c. at 15° C., occupy 321 c.c., if the pressure remains constant ?

4. Find the volume at N.T.P. of a gas that occupies 3,000 c.c. at 12 mm. pressure and 79° absolute.

5. What will be the volume, dry, at N.T.P. of a gas occupying 23·4 c.c. at 18° C. 755 mm., collected over water ?

6. State (*a*) Boyle's Law, (*b*) Charles' Law. What is the *gas equation* ?

CHAPTER V

MOLECULAR WEIGHTS

Having assumed the existence of atoms of elements and of "compound atoms" of compounds, Dalton's scientific curiosity led him on to try to determine the weights of these minute particles. It was clearly ridiculous to try to express their weights in *grams*, since the gram is so enormously larger than an atom. In the Middle Ages, the Schoolmen used gravely to discuss the problem of the maximum number of angels who could dance on the point of a needle, and concluded that there was probably room for 10,000. Atoms are so small that 10,000 of them would find as much room on the point of a needle as 10,000 people would on the continent of Europe; we know now, in fact, that the weight of an atom of hydrogen is 0·00000000000000000000000165 grams [i.e. $1{\cdot}65 \times 10^{-24}$ grams].

Dalton therefore contented himself with the lesser problem of finding the *relative* weights of atoms, choosing the lightest atom, that of hydrogen, as unit. But even this was a task stupendous in its magnitude, although it has now become so commonplace a thing that we are often apt to forget the sublime genius of the chemists who first successfully solved the problem.

Before we proceed, it is necessary for us to get more precise ideas of "atoms" and "compound atoms," so that we may know exactly what we propose to do. The gradual crystallization in the minds of chemists of the conceptions of these tiny particles is to be found elsewhere; it will be sufficient here to give the modern definitions.

For our purpose, then, we may take the *atom* to be *the smallest, chemically indivisible, particle of an element that can take part in a chemical change.* Physicists have shown that atoms are divisible, but no one has yet succeeded in splitting up an atom by chemical means, so that our definition is sound.

The smallest particle of an element or compound that can normally lead a separate existence is called a **molecule.** It is evident that our term *molecule* includes Dalton's "compound atoms," but it also includes the ultimate particles of elements that can exist in a state of freedom. For example, the smallest particles of hydrogen that can lead a separate existence each consist of 2 *atoms* of hydrogen; these *diatomic* particles are called *molecules* of hydrogen. But the atoms of argon, one of the rare gases of the atmosphere, normally, and indeed always, lead a solitary existence. Here the atom of argon is also the molecule, and the molecule is said to be *monatomic* in this case. Similarly, the molecule of ozone is *triatomic*, that of phosphorus vapour is *tetratomic*, while in sulphur vapour *hexatomic* and *octatomic* molecules are found. The vapours of most non-metallic elements are *diatomic*, while the vapours of metals are generally *monatomic* so far as they have been investigated.

The smallest number of atoms that the molecule of a compound can contain is obviously two, since a compound must contain at least two elements, and the smallest number of atoms of each element that its molecule can contain is 1. There is no upper limit to the number of atoms the molecule of a substance may contain. Thus the starch molecule contains at least 10,000 atoms, and that of albumen probably a much larger number. Such molecules are said to be *polyatomic.*

The weights, then, of atoms and molecules are expressed in terms of the weight of the hydrogen atom, which is taken as 1. Hence the **Atomic Weight** *of an element is the number of times its atom is heavier than the atom of hydrogen, and the* **Molecular Weight** *of an element or compound is the number of times its molecule is heavier than the ATOM of hydrogen.*

As in the case of Equivalents, Atomic and Molecular Weights

are *ratios*, and tell us nothing of the actual weight in grams of the atom or molecule. All the information they give us is that *if* the hydrogen atom weighs x grams, then the atom of oxygen, for example, weighs $16x$ grams, and the molecule of marble $100x$ grams, and so on. This conception is very useful in practice, for if we know the relative numbers of atoms or molecules taking part in a reaction, and also know their atomic or molecular weights, we shall know also the *relative weights in grams* (or in any other units) of the substances concerned. Thus, suppose we knew that one molecule of caustic potash is neutralized by one molecule of hydrochloric acid, and that the molecular weight of caustic potash is 56 while that of hydrochloric acid is 36·5, we could then say that when caustic potash and hydrochloric acid react they do so in the proportions by weight of 56 to 36·5 in any units we cared to choose, probably grams, but equally truly in pounds or ounces.

The first step on the road to molecular weight determination was taken by the brilliant French chemist JOSEPH-LOUIS GAY-LUSSAC, who in 1808 formulated the **Law of Gaseous Volumes,** or as it is more generally now known, **Gay-Lussac's Law :** *When gases react together their volumes are simply related to one another and to the volumes of the products if these are gaseous.*

For example, assuming all measurements to be made at the same temperature and pressure,

(i) 1 vol. of hydrogen combines with 1 vol. of chlorine to form 2 vols. of hydrochloric acid gas.

(ii) 2 vols. of carbon monoxide combine with 1 vol. of oxygen to form 2 vols. of carbon dioxide.

(iii) 2 vols. of hydrogen combine with 1 vol. of oxygen to form 2 vols. of steam.

(iv) 1 vol. of nitrogen combines with 3 vols. of hydrogen to form 2 vols. of ammonia.

Although Gay-Lussac himself did not conclude from these, and other results of a similar nature, that the ratio of the volumes of reacting gases must bear a simple relation to the ratio of the numbers of "atoms" in those volumes of the

gases, the Swedish chemist BERZELIUS saw the implication and somewhat rashly suggested that "equal volumes of gaseous elements contain equal numbers of atoms," and this was afterwards extended to include all gases, not merely the elementary ones. Dalton and Gay-Lussac, however, both pointed out that this statement led to grave inconsistencies. Thus, 1 volume of hydrogen, containing say n atoms, will combine with 1 volume of chlorine, also containing n atoms (according to the above hypothesis), to form 2 volumes of hydrochloric acid. Now, if in this process 1 atom of hydrogen combines with 1 atom of chlorine to form 1 particle of hydrochloric acid, it follows that n particles of hydrochloric acid will be formed. But these occupy 2 volumes, therefore 1 volume will contain $\frac{n}{2}$ particles, or only half as many as the same volume of hydrogen or chlorine. Berzelius' suggestion had therefore to be abandoned, but two years previously, namely in 1811, the Italian scientist AMEDEO AVOGADRO had already put forward a hypothesis which fully explained the difficulty.

Avogadro's Hypothesis was that *Equal volumes of all gases, under the same conditions of temperature and pressure, contain the same number* of **molecules** (not *atoms* as Berzelius had supposed).

If the Atomic Theory is the main arch of chemistry, Avogadro's hypothesis is the keystone of the arch. Not only did it clear up the difficulties which had puzzled (and even, it is said, created bad feeling between) Dalton, Berzelius and Gay-Lussac, but it gave also a ready access to the determination of molecular weights. Yet, strange as it may seem to us, the hypothesis was scarcely regarded at the time and lay almost forgotten for nearly half a century, until this Sleeping Beauty was rediscovered by a Prince Charming in the person of Avogadro's countryman CANNIZZARO, who in 1858 (two years after Avogadro's death) recalled the attention of chemists to the invaluable jewel they had neglected. How much the progress of chemistry was delayed by lack of appreciation of Avogadro's Hypothesis it would be difficult to say. One has only to read some of the text-books of chemistry

of the first half of the nineteenth century to realize the confusion that reigned in the minds of chemists regarding the true values of atomic and molecular weights.

Let us first see how Avogadro's Hypothesis explains the volume changes in the reaction of hydrogen and chlorine. One vol. of hydrogen combines with 1 vol. of chlorine to form 2 vols of hydrochloric acid; that is experimental fact. According to Avogadro, we can say "therefore, *n molecules* of hydrogen combine with *n molecules* of chlorine to form *2n molecules* of hydrochloric acid, ∴ 1 *molecule* of hydrogen combines with 1 *molecule* of chlorine to form 2 *molecules* of hydrochloric acid." In other words, since, by the Atomic Theory, all the molecules of hydrochloric acid must be identical, *the hydrogen and chlorine molecules must each have been halved.* Now atoms are, *ex hypothesi*, indivisible, therefore *the molecules of these gases must contain an even number of atoms*, at least two. It does not follow that they do not contain more than two.

The density of a gaseous substance, that is, its mass per unit volume, is always very small, so chemists prefer to express the density of such substances in terms of the density of hydrogen taken as unity. This applies not only to substances which are normally gaseous, but to the vapours of all substances which can be vaporized. Hence the VAPOUR DENSITY of a substance is the relative density of its vapour in terms of that of hydrogen as unity, or *the number of times a certain volume of its vapour is heavier than the same volume of hydrogen under the same conditions of temperature and pressure.*

We shall arrive at an important conclusion if we consider this definition in the light of Avogadro's Hypothesis. We have, at constant temperature and pressure,

$$\text{Vapour Density} = \frac{\text{weight of a certain volume of vapour}}{\text{weight of the same volume of hydrogen}}$$

$$\therefore \text{ by Avogadro, V.D.} = \frac{\text{weight of } n \text{ molecules of the vapour}}{\text{weight of } n \text{ molecules of hydrogen}}$$

$$= \frac{\text{weight of 1 molecule of the substance}}{\text{weight of 1 molecule of hydrogen}}$$



By kind permission of R. B. Pilcher, Esq., of the Institute of Chemistry of Great Britain and Ireland.

JOSEPH-LOUIS GAY-LUSSAC

In other words, *the number that expresses the vapour density of a substance is also the number of times the molecule of the substance is heavier than the molecule of hydrogen.*

If we combine this with the definition of molecular weight, we shall make another important step, for

$$\text{M.W.} = \frac{\text{weight of 1 molecule of the substance}}{\text{weight of 1 } \textit{atom} \text{ of hydrogen}}, \text{ and}$$

$$\text{V.D.} = \frac{\text{weight of 1 molecule of the substance}}{\text{weight of 1 } \textit{molecule} \text{ of hydrogen}}$$

Therefore **the molecular weight of a substance is as many times its vapour density as there are atoms in the molecule of hydrogen.**

Now we are beginning to see our way to the determination of molecular weights, and can realize the importance of Avogadro's Hypothesis. If only we can find how many atoms ("x") there are in the molecule of hydrogen we shall be able to find the molecular weight of any gaseous or volatile substance simply by measuring how many times a certain volume of the gas or vapour is heavier than the same volume of hydrogen under the same conditions of temperature and pressure, and then multiplying this number by "x."

Atomicity of the Hydrogen Molecule.—We have already found that the molecule of hydrogen must contain at least two atoms, and if more than two, still an even number. We can get further evidence from a study of the behaviour of acids. All acids consist of two parts, of which one is hydrogen. In a great many acids all the hydrogen can be replaced by a metal, the products being called *salts*. Suppose that the molecule of one of these acids contains one hydrogen atom, and that we call the rest of the molecule X. We could then represent the acid by Fig. 2.

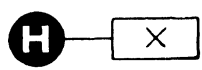


FIG. 2.

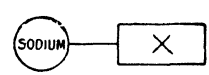


FIG. 3.

If we now act upon this acid in such a way as to form its

sodium salt, it is clear that the hydrogen can be replaced in *one stage only*, for it is impossible to split an atom. The sodium " X-ate " would be represented by Fig. 3.

But suppose the molecule of an acid contains two atoms of hydrogen ; it will then be possible to replace the hydrogen by sodium in two stages, forming first the compound represented by Fig. 4, then that of Fig. 5.

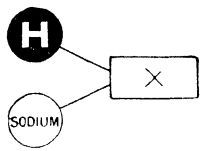


FIG. 4.

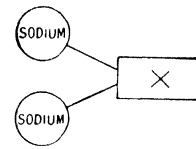


FIG. 5.

The first of these two compounds is half an acid and half a salt ; it is called an *acid salt*. The second is the *normal* sodium salt of that acid. Continuing the process, if the molecule of an acid contains n hydrogen atoms (let us represent it by H_nX), that acid will form n sodium salts, viz.,

Sodium H_{n-1} X ; Sodium Sodium H_{n-2} X, and Sodium Sodium Sodium H_{n-3} X

and so on, up to Sodium Sodium ... Sodium H_{n-n} X or $Sodium_nX$.

In other words, *the number of sodium salts that an acid will form is the number of hydrogen atoms contained in its molecule.* Now, hydrochloric acid will form one sodium salt, and one only. Hence its molecule contains *one* hydrogen atom ; but we have already shown (p. 36) that its molecule contains *half a molecule* of hydrogen.

∴ Half a molecule of hydrogen = 1 atom of hydrogen

∴ *the molecule of hydrogen contains* 2 *atoms.*

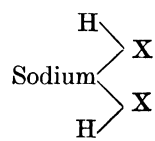
Probably while you have been reading it you have had an uneasy feeling that all is not well with this argument, and

you may even have arrived at some definite criticisms of it. See if they agree with the following—

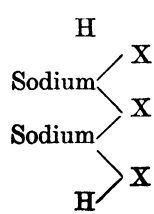
1. How do we know that hydrochloric acid is one of those acids *all* of whose hydrogen is replaceable by a metal ? The answer to this criticism is that no one has yet succeeded in preparing any sodium chloride containing hydrogen. (This can easily be tested by analysis.)

2. Are we not pledging the future by assuming that, because no one has yet prepared an acid sodium chloride, no one ever will ? Here the answer is that until some one does so, we are entitled to believe that it is impossible, especially after a hundred and fifty years of systematic chemistry.

3. How do we know that *one* atom of sodium will replace *one* atom of hydrogen ? This seems to be a much more formidable problem, for there seems no valid reason *a priori* why one atom of sodium should not be capable of replacing say two atoms of hydrogen. Suppose, for the sake of argument, that it does. How is the " proof " of the diatomicity of the hydrogen molecule affected ? If the acid contains one atom of hydrogen *per* molecule, it is not affected at all, for the sodium salt *must* be $\boxed{\text{sodium}}\!<\!\begin{matrix}\text{X}\\\text{X}\end{matrix}$; no other is possible. If the acid molecule contains two atoms of hydrogen, the following sodium salts would be possible—

Sodium X, 

but so would salts of the type



etc.

However, these facts are really irrelevant, *since however many atoms of hydrogen one atom of sodium will replace*, it is obvious from the above that an acid containing *one* atom of hydrogen per molecule will form only *one* sodium salt, while any acid whose molecule contained more than one atom of hydrogen could always form more than one sodium salt. We are therefore justified in assuming that if hydrochloric acid will form only one sodium salt, its molecule contains only one atom of hydrogen.

It must, however, be admitted that this proof of the diatomicity of the hydrogen molecule is not altogether satisfying, especially for a fact of such basic importance. It rests on *negative* results, namely, the impossibility of preparing acid chlorides, and can therefore never be as satisfactory as a *positive* proof. Fortunately, other evidence is forthcoming, and although a strictly logical proof cannot be given in this place, the following confirmatory facts may set at rest the mind of a doubting Thomas.

(i) In the reactions of hydrogen with other gases, it is common to find that one volume of hydrogen gives two volumes of the gaseous product, but *never more*. If the molecule of hydrogen contained more than two atoms, we might expect that occasionally one volume of hydrogen would give more than two volumes of a gaseous product. This is *negative* evidence again, but is nevertheless extremely significant.

(ii) Considerations of the specific heats of gases lead to the conclusion that the molecule of hydrogen is diatomic. The specific heat of a substance is the number of calories required to raise the temperature of 1 gram of a substance through 1° C. (A calorie is the amount of heat required to raise the temperature of 1 gram of water through 1° C. Be careful to avoid saying "to raise 1 gram of the substance through 1° C."—it is not the substance that you "raise," but its *temperature*.) Now if a gas is heated, it expands, and in doing so will perform work, as in the expansion of the gases in the cylinder of a motor. The energy necessary for the performance of this work is taken from the heat supplied, and to raise the temperature of 1 gram of a gas through 1° C. will therefore

require more heat if the gas be allowed to expand and do external work than if the gas be kept at constant volume and hence prevented from doing external work. *A gas therefore has two specific heats*, the specific heat at *constant volume*, and the specific heat at *constant pressure* (when it is allowed to expand); and the latter will be the greater. Now if the molecules of a gas are monatomic, all the heat supplied to the gas will go to increase the *speed of translation* of the molecules, that is, the speed with which they move about; but if the molecules of the gas contain more than one atom, part of the heat supplied will go as before to increase the speed of translation of the molecules, but a part will be used in increasing the *speed of vibration of the atoms within the molecule.* It can be shown theoretically that in the latter case the ratio $\frac{\text{specific heat at constant pressure } (C_p)}{\text{specific heat at constant volume } (C_v)}$ is always less than for a gas whose molecule is monatomic, and the greater the number of atoms in the molecule the smaller the value of $\frac{C_p}{C_v}$. For a monatomic gas, $\frac{C_p}{C_v} = 1{\cdot}67$; diatomic gases give the approximate value of 1·4, and so on. The value for hydrogen is 1·408.

(iii) No hydrogen compound yet discovered contains less hydrogen than that found in an equal volume (as gas) of hydrochloric acid.

(iv) No facts have yet been discovered that do not harmonize with the assumption that the molecule of hydrogen contains two atoms.

Note, however, that not one of the above arguments is a *logical proof* that the molecule of hydrogen is diatomic. The diatomicity of hydrogen *has* been conclusively proved by physical means, but even if it had not, the above evidence would justify us in assuming it until something turned up to disprove it.

We may therefore now say that the **Molecular Weight of a substance is twice its Vapour Density,** since the molecule of hydrogen contains two atoms (see p. 38).

Methods of Determining Vapour Densities.

A. **Gases.** The principle of this method is very simple, but to get accurate results many precautions have to be taken and corrections made. A glass or metal globe, fitted with a stopcock, is evacuated by means of an air-pump and then weighed (w gms.). It is then filled with the gas and weighed again (m gms.). Weight of gas $= m - w$ gms. The globe is now evacuated once more and then filled with hydrogen and weighed (n gms.). Weight of hydrogen $= n - w$ gms.

$\therefore$ V.D. $= \frac{m - w}{n - w}$ if the temperature and pressure have remained constant throughout.

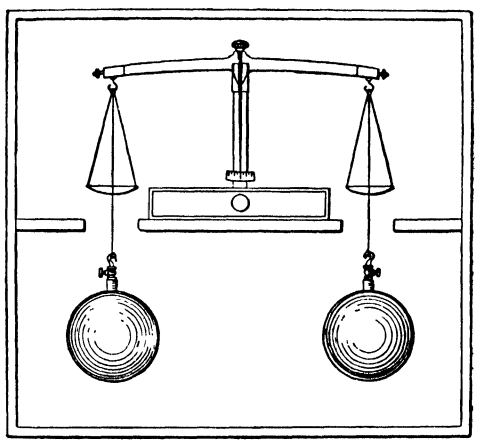


FIG. 6.—Regnault's Vapour Density Apparatus.

In accurate work, great care has to be taken to see that all the measurements are carried out at exactly the same temperature and pressure, or at known temperatures and pressures if they are different, when a correction has to be made according to the laws of Boyle and Charles. It is also important to note that the *real* weight of the globe, that is, its weight *in vacuo*, is its apparent weight in air + the weight of air displaced. Although the difference between the real

weight and the apparent weight is very small, it is sufficient to affect the results if not allowed for. Moreover, the weight of air that the globe displaces will depend upon the temperature, pressure and relative humidity of the air, and owing to the water-vapour present in the air there is always a film of moisture on the surface of glass, porcelain and metal. To make the necessary corrections for all these things would be very tedious and, probably, the corrections would not be very accurate when made. Regnault solved the problem by using a second similar globe which he hung on the other arm of the balance. The errors due to the above conditions now balanced one another, so that the corrections were unnecessary. A final correction, suggested by Lord Rayleigh, deals with the shrinkage in volume of the globe on evacuation. This has to be found by experiment, and allowed for.

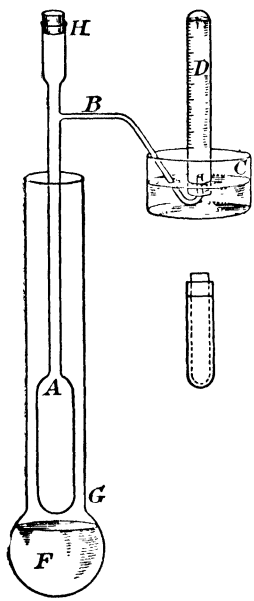


FIG. 7.—Victor Meyer Vapour Density Apparatus.

B. **Volatile Liquids (and Solids).** (i) *Victor Meyer's Method.*—Victor Meyer and his pupils used to make large numbers of new compounds, and wanted a method of determining their vapour densities (and thence their molecular weights) which should be simple, quick and reasonably accurate. Meyer therefore devised the following method, which is much more convenient than that of Dumas (ii).

The apparatus consists of an inner tube A, the lower end of which is enlarged into a cylindrical bulb, while the upper end is enlarged to carry a rubber stopper H. Towards the upper end of the tube A there is a side-neck B communicating with a pneumatic trough C. The inner tube is surrounded by a wider outer tube or jacket G, at the bottom of which is a bulb F in which are placed 70–80 c.c. of a liquid whose

boiling-point is at least 30° higher than that of the liquid whose vapour density is required. The apparatus is set up as shown, except that the graduated tube D is not yet placed over the end of the side-neck. The liquid in F is boiled and the heating continued until the temperature of the inner tube is constant, that is, when no more bubbles of air escape from the end of the side-neck and no water is sucked back. When this is so, the graduated tube, filled with water, is placed in position (as is shown in the figure).

Meanwhile a small bottle, of such a size that it slips easily down the tube A, is weighed empty and is then filled with the liquid whose V.D. is required, and weighed again. Next, the cork is removed, the weighed bottle and contents dropped in, and the cork replaced—all as quickly as possible. The bottle falls to the bottom of the inner tube, where a little mercury may be placed to break its fall. The liquid in the small bottle now finds itself in a place which is at a temperature some 30° higher than its boiling-point. It therefore vaporizes *very rapidly* and blows the stopper out of the bottle ; and the vapour, advancing up the tube *en masse*, drives its own volume of air over into the graduated tube D. The graduated tube is then transferred to a deep jar full of water, in which it is lowered until the levels of the water inside and outside the tube are the same, and the volume of the air read. This process of "levelling" is necessary in order to get the moist air in the tube at atmospheric pressure.

The height of the barometer is then read, and the temperature of the water in the pneumatic trough taken. This temperature will be the temperature of the moist air in the graduated tube, since the air has passed through the water. (Of course, if the volume of air is not read off at once, it would be more accurate to take the temperature of the air surrounding the tube.) We now have the following data—

Weight of bottle + liquid $= x$ gms.
Weight of bottle $= y$ gms.
$\therefore$ Weight of liquid $= x - y$ gms.

Barometer = say 770 mm. Temperature = say 15° C.

Volume of moist air after levelling = m c.c.

1 litre of hydrogen at N.T.P. weighs 0·09 gms.

From these data we can calculate the Vapour Density of the liquid. All gases obey the same gas-laws, therefore *the volume of air in the graduated tube is equal to the volume which $x - y$ gms. of the substance in the state of moist vapour would occupy if it could exist under the same conditions of temperature and pressure.* The whole point of the method is the ingenious way in which the vapour of the liquid is made to drive over its own volume of air, which remains gaseous under conditions in which the vapour itself could not. The reason for having the temperature of the outer jacket so much higher than the boiling-point of the liquid under experiment will now be clear: it is to ensure that the vapour of the liquid shall come off with a rush, and therefore drive the air over before diffusion of the vapour into the air can take place. If diffusion occurred, the gas driven through the side-neck would consist partly of air and partly of vapour, and as the latter would condense in the water of the trough, the experiment would be useless, since the volume of air collected would no longer be equal to the volume of vapour produced. The shape of the inner tube also helps to prevent diffusion.

The result is calculated as follows:—

Volume of moist air at 770 mm. 15° C. = m c.c.

Vapour pressure of water at 15° C. = 12·7 mm.

$\therefore$ true pressure of the air = 770 − 12·7 mm. = 757·3 mm.

Temperature = 15° C. = 288° Absolute.

$$\therefore \text{ Volume of air, dry, at N.T.P.} = \frac{m \times 757{\cdot}3 \times 273}{760 \times 288}$$

$$= n \text{ c.c.}$$

$\therefore$ n c.c. of the vapour at N.T.P. would weigh $x - y$ gms. But n c.c. of hydrogen at N.T.P. weigh $n \times 0{\cdot}00009$ gms.

$$\therefore \text{ Vapour density} = \frac{x - y}{n \times 0{\cdot}00009}$$

and the Molecular Weight of the substance will be twice this.

For liquids that boil up to 70° C., water may be used in the outer jacket. For those with higher boiling-points suit-

able substances to use in the outer jacket are aniline, B.P. 182° ; nitrobenzene, B.P. 208° ; sulphur, B.P. 444°, etc.

(ii) *Dumas' Method.*—A glass globe provided with a long neck drawn out to a point (see Fig. 8) is weighed, and then a few grams of the liquid whose V.D. is required are introduced. This is done by dipping the end of the neck into some of the liquid in a crucible and then gently warming the globe. The air inside expands, and some is driven out, so that on allowing the globe to cool a small quantity of the liquid is drawn in. The globe is then immersed in a bath the tem-

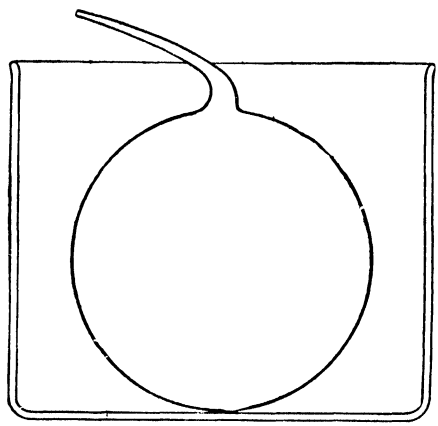


FIG. 8.—Dumas Vapour Density Globe.

perature of which is constant and at least 30° above the boiling-point of the liquid. This temperature is recorded. When vapour ceases to be expelled from the globe (which is easily ascertained by holding a clean piece of glass opposite to the neck—when the glass is no longer dimmed, the vapour has stopped coming out), and the last drop of liquid has volatilized, the end of the neck is sealed in the blowpipe flame.

The globe, which is now full of vapour, is removed from the bath, dried, cooled and weighed. The end is then broken off under freshly-distilled (i.e., air-free) water, when the globe fills with water. It is dried on the outside and weighed

again, together with the end of glass broken off. Generally a small bubble of air is left in the globe ; this is air which the vapour has not expelled, and a correction must be made for it.

The capacity of the globe is found by subtracting the weight of the globe full of air from its weight when filled with water, since the weight of the air may be neglected in comparison with the weight of the water. The weight of the water in grams is therefore equal to the capacity of the globe in c.c.

From this volume, the weight of the air filling the globe at the observed temperature and pressure can be calculated, since 1 c.c. of air at N.T.P. weighs 0·00129 grams. The weight of the globe filled with air *minus* the weight of the air gives the weight of the globe empty. Subtracting this from the weight of the globe full of vapour gives the weight of the vapour. Thus we know the weight of vapour which occupies a known volume at known temperature and pressure, and hence the vapour density can be calculated, since 1 litre of hydrogen at N.T.P. weighs 0·09 grams.

Although this method is capable of giving more accurate results than that of Victor Meyer, it is much more tedious to carry out and more troublesome in calculation, and hence is rarely used except in special cases.

The result may be worked out as follows :—

Weight of globe filled with air at temperature $t°$ and pressure $p = x$ gms.

,, ,, ,, ,, vapour ,, $t'°$ and pressure $p = y$ gms.

,, ,, ,, ,, water $= z$ gms.

$\therefore$ Capacity of globe in c.c. = weight of water in grams

$= z - x$.

$z - x$ c.c. of air at $t°$ C. p mm. pressure become

$$\frac{(z - x)273.p}{(273 + t)760} \text{ c.c. at N.T.P.}$$

$\therefore$ weight of the $z - x$ c.c. of air at $t°$ C. p mm. pressure

$= \frac{(z - x).273.p}{(273 + t).760} \times 0{\cdot}00129$ grams, since 1 c.c. of air at N.T.P. weighs 0·00129 gms.

$\therefore$ weight of globe empty $= x - \left[\frac{(z - x).273.p}{(273 + t)760} \times 0{\cdot}00129\right]$ gms.

$= m$ grams

$\therefore$ weight of $z - x$ c.c. of vapour at $t'°$ and p mm. $= y - m$ grams.

If $y - m$ grams of vapour occupy $z - x$ c.c. at $t'°$ and p mm., they will occupy

$$\frac{(z - x) \times 273 \times p}{(273 + t') \times 760} \text{ c.c. at N.T.P.}$$

$= n$ c.c.

But n c.c. of hydrogen at N.T.P. weigh $0{\cdot}00009 \times n$ gms.

$$\therefore \text{ Vapour Density} = \frac{y - m}{n \times 0{\cdot}00009}$$

and the molecular weight will be twice this.

(iii) *Hofmann's Method.*—Certain substances decompose when heated to their boiling-points under atmospheric pressure, but will vaporize without decomposition under lower pressures. It is evident that Victor Meyer's method and Dumas' method are inapplicable here, and Hofmann's method is used in these cases. The principle is to vaporize the substance at a temperature and pressure such that it is not decomposed, and then to find the volume of a given weight of vapour.

The apparatus consists of a wide barometer-tube which is graduated on one side from the bottom upwards in millimetres, and on the other from the top downwards in cubic centimetres. This tube is filled with mercury and inverted in a trough of mercury, thus giving rise to a Torricellian vacuum.

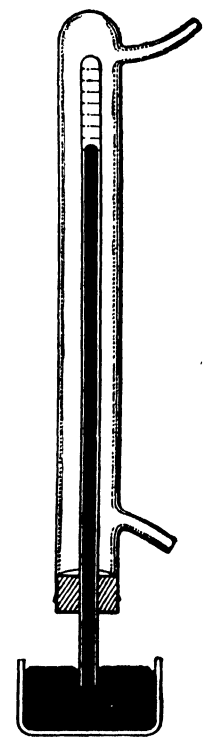


FIG. 9.—Hofmann Vapour Density Apparatus.

The tube is now surrounded by a jacket through which the vapour of a liquid that boils at a suitable temperature may be passed. The vapour passes out at the bottom of the jacket and may be condensed, if desired, by means of a Liebig condenser.

A small quantity of the liquid whose vapour density is

required is weighed out in a tiny bottle similar to that used in the Victor Meyer method, and this bottle is introduced into the barometer tube, when it rises to the top of the mercury and enters the vacuum. Here, owing to the low pressure, the liquid volatilizes at the temperature of the vapour in the jacket, which may be much below that of its boiling-point under atmospheric pressure.

The vapour of the boiling liquid in the flask is passed through the jacket for some time until the level of the mercury, which has fallen, remains constant. The height of the mercury column is then read off on the millimetre scale, and the difference between this height and the original height of the mercury gives the pressure on the vapour. The temperature is taken as that of the boiling-point of the liquid in the flask. The volume of the vapour is read from the c.c. scale.

Weight of liquid (and therefore of vapour) = m gms.
Original height of mercury column = a mm.
Final ,, ,, ,, ,, = b mm.
$\therefore$ pressure of vapour = $(a - b)$ mm.
Temperature = $t°$ C. Volume of vapour = v c.c.

Now v cc. at $t°$ C. and $(a - b)$ mm. pressure become

$$\frac{v.273\ (a - b)}{(273 + t).760} \text{ c.c. at N.T.P.}$$
$$= d \text{ c.c.}$$

But d c.c. of hydrogen at N.T.P. weigh $d \times 0{\cdot}00009$ gms.

$$\therefore \text{ Vapour Density} = \frac{m}{d \times 0{\cdot}00009}$$

and the molecular weight will be twice this.

For other methods of determining Molecular Weights see Chapter XI.

Questions

1. Define *atom*, *molecule*, *atomic weight*, *molecular weight*.
2. State Avogadro's Hypothesis and explain its importance in chemistry.
3. Suppose that Avogadro's Hypothesis were proved to be untrue. What do you think would be the effect upon chemistry ?
4. Define *vapour density*. What is the relationship between the molecular weight and the vapour density of a substance ?

5. Prove, as far as you can, that the molecule of hydrogen contains two atoms.

6. Describe Victor Meyer's method of determining vapour densities.

7. Describe Dumas' and Hofmann's methods of finding vapour densities. Under what circumstances is Hofmann's method especially useful ?

CHAPTER VI

ATOMIC WEIGHTS

In the last chapter we saw how it was possible to determine the molecular weights of those elements and compounds that can be obtained in the state of gas or vapour. Our next task is to find *atomic* weights, that is, those numbers which express the ratio of the weight of an atom of an element to the weight of an atom of hydrogen. It so happens that the molecules of many elements that are normally gaseous consist of two atoms, hence *in these cases, and purely by chance*, the vapour density, being half the molecular weight, is numerically equal to the atomic weight of the element. This occurrence misled the chemists of the first half of the nineteenth century into the error of supposing that the vapour density of an element was *always* equal to its atomic weight. It is clear, however, that this equality occurs only in those cases where the molecule of the element is diatomic. If, for example, the molecules of an element are monatomic, as is the case with argon and the other gases of the argon group, the molecular weight and atomic weight will be identical, and therefore the vapour density will here be *half* the atomic weight. In short, from the vapour density alone it is impossible to determine the atomic weight of an element. Other methods are fortunately not lacking.

(i) The smallest number of atoms of an element which can be present in the molecule of any compound of that element is 1, since atoms are indivisible. That is, the smallest *weight* of any element which can be present in the *molecular weight* of any of its compounds is the *atomic weight* of that element.

Note that it does not follow that the smallest weight of the element which *is* present in the molecular weight of any of its compounds is necessarily the atomic weight of the element, since it is possible to conceive that certain elements might not form compounds containing less than 2 or 3 or n atoms of those elements per molecule. Here again, however, we are justified in taking as the atomic weight of an element *the smallest weight of that element which is found in the molecular weight of any of its compounds*, until we find some fact or other that is not in accordance with the value we have obtained. If the values we get for atomic weights are supported by other evidence, and nothing is discovered which shows that these values are incorrect, then we may assume that they are the true values.

Our first method, then, involves two processes—(*a*) the preparation of a great many compounds of the element concerned, and the determination of their molecular weights, and (*b*) quantitative analysis of these compounds in order to determine the weight of the element present in the molecular weight of each. The smallest weight of the element that is ever found in the molecular weight of any of its compounds is then taken to be the atomic weight of that element.

In general, it will be most convenient to take volatile compounds of the element, since the molecular weights of these will be easily determinable by vapour-density methods.

As an example, let us consider the case of carbon. This element forms many volatile and gaseous compounds, some of which give the following data by the above method :—

	Mol. Wt.	*Parts by Wt. of Carbon in Mol. Wt.*
Acetylene	26	24
Ethylene	28	24
Methane	16	12
Carbon monoxide	28	12
Benzene	78	72
Alcohol	46	24

From these figures it is concluded that the atomic weight of carbon is 12.

If, at some future date, a carbon compound were discovered which contained only 6 parts by weight of carbon in its molecular weight, we should then have to admit that the number 12 as the atomic weight for carbon is incorrect. But, as in many other cases in chemistry, collateral evidence concerning atomic weights can be obtained, and when all the evidence for any one atomic weight points to the same conclusion we may feel confident that this conclusion is correct.

Dulong and Petit's Law (1819) has proved a valuable instrument for atomic weight determinations. These two chemists found that *in a great many cases the atomic weight of a metal* × *its specific heat* = 6·4 *approximately.* Hence, if we wish to find the atomic weight of a certain metal, we could determine its specific heat and divide it into 6·4 ; the quotient would give us an *approximate* value for the atomic weight. It may be asked of what use an approximate value for the atomic weight is ; surely we want to know atomic weights as accurately as possible ? To answer this question we shall have to consider the question of valency.

Valency.—The subject of valency is a very large one, and whole books have been written on it—it has, in fact, been defined as " that subject of which freshmen at the University think they know everything and of which mature chemists realize that they know nothing." Fortunately for our immediate purpose we do not need to study it in detail, and can easily arrive at a definition of valency that will meet our requirements.

The atoms in a molecule are not merely lying side by side ; they are bound together by *chemical force.* It is the question of the nature of this force that introduces the difficulties of valency ; here, therefore, we will simply accept it as a fact, and will leave the closer discussion of it for a more advanced course.

Chemists have found, however, that the power which any atom of a given element has of combining with atoms of hydrogen is always the same. Thus any atom of oxygen is capable of combining with 2 atoms of hydrogen ; an atom of chlorine can combine with 1 atom of hydrogen ; that of

phosphorus with 3 of hydrogen; and that of carbon with 4 of hydrogen. No element is known which will combine with hydrogen in such a way that there is a smaller proportion of hydrogen in the compound than 1 atom of the element to 1 of hydrogen; in other words, there is no known element of such small combining power that 2 or more atoms of it are required to hold 1 atom of hydrogen in combination.

For this reason, chemists have taken as the unit of combining power of an atom the ability to hold in combination 1 atom of hydrogen. *The number of atoms of hydrogen with which 1 atom of an element will combine is called the VALENCY of that element.*[1] Some elements, however, will not combine with hydrogen, but will do so with other elements. It is evident that in such cases the valency of the element cannot be *directly* measured, but if we remember that ability to hold in combination 1 atom of hydrogen is merely the "unit of combining power," we shall be able to measure the valency in an indirect way. For example, zinc will not combine with hydrogen, but it will do so with oxygen, in such a way that 1 atom of zinc combines with 1 atom of oxygen. Now 1 atom of oxygen will combine with 2 atoms of hydrogen; we therefore assume that if zinc and hydrogen could be made to combine they would do so in the proportion of 1 atom of zinc to 2 of hydrogen, and therefore say that the valency of zinc is *two*. Similarly, gold will not combine with hydrogen, but will combine with chlorine in such a way that 1 atom of gold combines with 3 of chlorine. Since 1 atom of chlorine will combine with 1 of hydrogen, we say that the valency of gold is 3.

Atoms are chemically indivisible, therefore *the valency of an element must always be a whole number.*

We shall now be able to see that there is an intimate relationship between the three numbers that represent respectively the valency, atomic weight and equivalent of an element. Suppose that 1 atom of an element, of atomic weight, say, 20, combines with 1 atom of hydrogen.

[1] This, of course, is only one of the conceptions of valency. There are many others.

We could represent the molecule of the compound so formed (Fig. 10) as—

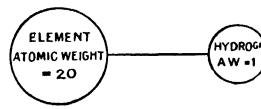


FIG. 10.

What is the equivalent of this element? We know that the equivalent of an element is the number of units of weight of it that will combine or otherwise react with 1 of the same units of weight of hydrogen. Let the unit of weight chosen in this case be the weight of 1 atom of hydrogen. Then since the atomic weight of the element is 20, 20 units of weight of it have combined with 1 unit of weight of hydrogen, $\therefore$ its equivalent = 20. But the atomic weight of the element is also 20, $\therefore$ in this case $\frac{\text{Atomic Weight}}{\text{Equivalent}} = 1$. But 1 atom of the element has combined with 1 atom of hydrogen, therefore the valency of the element = 1,

$\therefore$ here, at any rate, $\frac{\text{Atomic Weight}}{\text{Equivalent}} = \text{Valency}$.

Now let us suppose that 1 atom of the element combines with 2 atoms of hydrogen; the molecule will be as in Fig. 11.

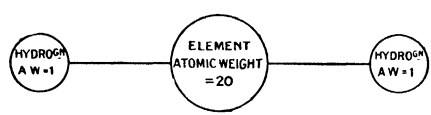


FIG. 11.

What is the equivalent of the element here? Choosing the same unit as before, namely, the weight of 1 atom of hydrogen, it is clear that 20 units by weight of the element have combined with 2 units by weight of hydrogen, $\therefore$ the equivalent of the element $= \frac{20}{2} = 10$. The atomic weight of the element = 20, $\therefore$ $\frac{\text{Atomic Weight}}{\text{Equivalent}} = \frac{20}{10} = 2$.

But 1 atom of the element has combined with 2 of hydrogen, therefore the valency is 2, and here again

$$\frac{\text{Atomic Weight}}{\text{Equivalent}} = \text{Valency.}$$

Similarly, if 1 atom of the element combines with n atoms of hydrogen, a figure will show that the equivalent $= \frac{\text{Atomic Weight,}}{n}$ or $\frac{\text{Atomic Weight}}{\text{Equivalent}} = \text{Valency.}$ This is a very important conclusion, for the equivalent of an element may easily be determined with a high degree of accuracy, and we know from the above that if we can find the valency (which must be a whole number) we shall be able to get the atomic weight, since atomic weight = equivalent × valency.

It is here that Dulong and Petit's Law becomes of value. Suppose that you were fortunate enough to discover a new metal; how would you determine its atomic weight? There is still (1931) one metal or so to be discovered, so the question is not of mere theoretical interest!

The first thing to do would be to obtain the metal in a state of purity. When this has been done, the next step is to determine the equivalent as accurately as possible by one of the methods previously described. If we knew the valency we could obtain the atomic weight by multiplying the equivalent and valency together. The next stage, therefore, is to find the valency. This is done by means of Dulong and Petit's Law. The specific heat of the metal is found by the method of mixture or by means of Bunsen's Ice Calorimeter, and if the number so obtained is divided into 6·4 the quotient will be the *approximate* atomic weight. If we now divide the approximate atomic weight by the equivalent, we shall get the approximate valency. But the valency must be a *whole* number, therefore the nearest whole number to the approximate valency is taken to be the true valency. This multiplied by the exact equivalent will give the true atomic weight.

What if the approximate valency came out to, say, 2·5? Which is the true valency, 2 or 3? The procedure in such

circumstances is first to feel annoyed and immediately after to tackle the problem in another way.

MITSCHERLICH, in 1819, from a study of the shape of the crystals of a great many compounds, came to the conclusion that *compounds of the same class that have analogous constitutions crystallize in the same form.* This statement is sometimes known as the **Law of Isomorphism,** or **Mitscherlich's Law.** (Two substances are said to be *isomorphous* when they crystallize in the same form.)

Applied in the reverse way, this law is useful in the determination of atomic weights, for it is assumed that compounds of the same class that crystallize in the same form have analogous constitutions. For example, suppose we were investigating the atomic weight of chromium, and that we had already determined its equivalent. We should then be trying to find its valency. Now when potassium sulphate and aluminium sulphate, in the proportion of 1 molecule of one to 1 of the other, are dissolved in water together, and the solution evaporated to crystallization, they combine together and crystallize out as a compound called *alum*, which forms beautiful crystals whose form can be very easily measured. If potassium sulphate and chromium sulphate are mixed in solution and the solution then evaporated to crystallization, it is possible to get crystals of a " chrome alum " which are isomorphous with those of ordinary alum. According to Mitscherlich's Law, we should be able to conclude that since chromium has replaced aluminium in alum, giving rise to an isomorphous chrome alum, chromium and aluminium have the same valency, otherwise the constitutions of these two isomorphous compounds of the same class would not be analogous. Hence, if we know that the valency of aluminium is 3, we may justifiably conclude that the valency of chromium is 3, and from this and the equivalent weight we can get the atomic weight.

The **Periodic System** also is useful in fixing atomic weights. (See Chapter XV.)

In the case of those gases or vapours the ratio of whose specific heats shows them to consist of monatomic molecules,

it is, of course, possible to get their atomic weights from their vapour densities only. For their molecular weights = their vapour densities × 2, and since the molecules are monatomic their molecular weights = their atomic weights.

To sum up, we may say that in most cases atomic weights are determined by (i) finding the equivalent weight, then (ii) obtaining as much evidence as possible to show what multiple of the equivalent weight the atomic weight is.

Questions

1. Explain why the determination of molecular weight generally has to precede the determination of atomic weights.

2. State Dulong and Petit's Law. Of what use is it?

3. Explain shortly what you understand by *valency*.

4. Prove that the atomic weight of an element is equal to its equivalent multiplied by its valency.

5. Suppose you were to discover a metal that is still unknown. How would you determine its atomic weight?

6. State the Law of Isomorphism and explain its application.

7. 1·081 gms. copper displace 3·670 gms. silver from a solution of silver nitrate. Find the equivalent of copper, given that that of silver = 107·88.

8. 0·4717 gms. zinc when dissolved in sulphuric acid give 171 c.c. hydrogen, collected over water, at 12° C. and 760·5 mm. pressure. Calculate the equivalent of zinc.

9. 2·5537 gms. copper oxide heated in a current of hydrogen gave 2·0391 gms. copper. Find the equivalent of copper. (Oxygen equivalent = 8.)

10. 0·2178 gms. magnesium, when dissolved in hydrochloric acid, gave 218·2 c.c. hydrogen collected over water at 17° C. and 754·5 mm. pressure. The specific heat of magnesium is 0·245. Find the atomic weight of magnesium.

11. 4·323 gms. nickelous chloride are found to contain 1·956 gms. nickel. The specific heat of nickel is 0·1092. Find the atomic weight. The equivalent of chlorine is 35·5.

12. The iodide of a metal is found to contain 55·86 per cent. iodine. The specific heat of the metal is 0·033. Find its atomic weight. The equivalent of iodine is 126·92.

CHAPTER VII

FORMULÆ AND EQUATIONS

It is convenient to use symbols to represent atoms and molecules. DALTON used a symbolic notation of circles—plain, containing a dot, containing a cross, blacked in, and so on—to represent the atoms of various elements; "compound atoms" [molecules] were represented by groups of these circles. Some of Dalton's symbols are shown in Fig. 12. A "compound atom" of water (which he believed to



FIG. 12.

consist of one atom of hydrogen and one of oxygen) was represented as follows:—



FIG. 13.

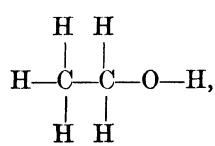
This system, however, had many drawbacks and in 1811 BERZELIUS suggested the system that we now use. He represented an atom of an element by the initial, or initial and another characteristic letter, of the name of the element, sometimes using the Latin (or pseudo-Latin) name in cases where two or more elements had names with the same initial letter. The following table gives some examples:—

Element.	"Latin" Name.	Symbol for One Atom.
Sulphur	—	S
Phosphorus	—	P
Oxygen	—	O
Hydrogen	—	H
Potassium	*Kalium*	K
Mercury	*Hydrargyrum*	Hg
Iron	*Ferrum*	Fe
Radium	—	Ra
Platinum	—	Pt
Bromine	—	Br
Sodium	*Natrium*	Na

For a complete table of symbols and atomic weights see p. 574.

A molecule of hydrogen consists of 2 atoms; the formula for this is H_2. 2H stands for 2 atoms of hydrogen not combined together. $2H_2$ stands for 2 molecules of hydrogen each consisting of 2 atoms. $3O_2$ means 3 molecules of oxygen each consisting of 2 atoms, while $2O_3$ means 2 molecules of ozone each containing 3 atoms of oxygen.

The formulæ for compounds are written similarly. Thus H_2SO_4 stands for 1 molecule of sulphuric acid, consisting of 2 atoms of hydrogen combined with 1 of sulphur, and 4 of oxygen. If we wish to represent the way in which the atoms of a molecule are arranged, we use *structural* or *graphic formulæ*. The molecule of alcohol is C_2H_6O, but this tells us nothing of the way in which the atoms are arranged; if, however, it is important to express this we write the formula in the following way:—



where the lines represent "valencies" or unit combining powers. Such a formula evidently gives us much more information than an ordinary formula.

It is most important to note that H_2O, for example, does

NOT stand for "water." The symbol 1*d.* does not stand for "wealth," but for a single, minute and practically indivisible particle of wealth. In exactly the same way, H_2O stands for *one MOLECULE of water*, and not for "water" in general. If, therefore, you say "I dissolved the substance in H_2O," you are, actually, saying that you dissolved the substance in 1 *molecule of water*, which you probably do not mean. It is, of course, permissible to use formulæ instead of names in writing rough notes, and so on, but it is incorrect and should always be avoided if possible.

The Professor, indeed, who now is—

> ". . . . . no more,
> For what he thought was H_2O
> Was H_2SO_4"

must have died from some other cause, since it is difficult to imagine a constitution so delicate that 1 molecule of sulphuric acid could upset it!

In the same way that formulæ are used to represent atoms and molecules, equations are used to represent reactions between atoms and molecules. What information, for example, does the equation

$$Zn + H_2SO_4 = ZnSO_4 + H_2$$

give us? It tells us—

(i) That *under certain conditions not specified*, zinc and sulphuric acid will react together in such a way that hydrogen is displaced from the acid and zinc takes its place.

(ii) That 1 atom of zinc will react with 1 molecule of sulphuric acid, containing 2 atoms of hydrogen, 1 of sulphur and 4 of oxygen, to give 1 molecule of zinc sulphate, containing 1 atom of zinc, 1 of sulphur and 4 of oxygen, and 1 molecule of hydrogen, containing 2 atoms.

(iii) That the valency of zinc is 2, and that the valency of the SO_4 group of atoms is 2.

If we know the atomic weights of the elements concerned (Zn = 65; H = 1; S = 32; O = 16) it tells us—

(iv) That 65 units of weight of zinc will react with 98 units of weight (= 2 + 32 + 64) of sulphuric acid to give 161



BARON BERZELIUS

units of weight of zinc sulphate and 2 units of weight of hydrogen.

What information about the reaction does it not give us, information that perhaps we should like to have ?

(i) It does not tell us whether the reaction is accompanied by evolution or absorption of heat.

(ii) It tell us nothing of the physical states of the substances concerned.

(iii) It does not tell us whether it is necessary to dilute the acid or not.

(iv) It does not tell us whether it is necessary to apply heat or not.

(v) It tells us nothing of the *time* taken by the reaction.

(vi) It does not tell us whether the action is reversible or not.

An equation, therefore, gives us a good deal of information about the reaction which it represents, but leaves almost as much untold. An equation, however, is very useful since the information that it does give is *definite* and is also that which as a rule it is most important to know. We shall see, too, from the following considerations, that if gases appear in a reaction, the equation tells us what *volume* of those gases will be used or formed for a known weight of material.

It is found by experiment that 2 grams [1] of hydrogen at N.T.P. occupy 22·4 litres, i.e. n molecules of hydrogen at N.T.P. occupy 22·4 litres. Now 22·4 litres of any other gas at N.T.P. would also contain n molecules, by Avogadro's hypothesis ; therefore the ratio—

$$\frac{\text{weight of 22·4 litres of a gas at N.T.P.}}{\text{weight of 22·4 litres of hydrogen at N.T.P.}} =$$

$$\frac{\text{weight of } n \text{ molecules of the gas}}{\text{weight of } n \text{ molecules of hydrogen}} = \text{the number representing the vapour density (A).}$$

But in this case, n is the number of molecules of hydrogen that weigh 2 grams, $\therefore$ the weight in grams of n molecules of the gas must be the molecular weight in grams, to get the necessary result (A) that—

[1] Actually 2·016 grams, since the standard of atomic weights is now taken as O = 16, upon which H = 1·008. The difference may be neglected at this stage.

$$\frac{\text{weight of } n \text{ molecules (= M.Wt. in grams) of the gas}}{\text{weight of } n \text{ molecules of hydrogen (= 2 grams)}}$$

should give the number representing the vapour density.

In other words, *the molecular weight in grams* (sometimes called the G.M.W. or Gram-Molecular-Weight or Gram-Molecule) *of any gas at N.T.P. occupies* 22·4 *litres* (sometimes called the G.M.V. or Gram-Molecular-Volume). By means of the gas laws it is of course now possible to calculate what volume the G.M.W. of a gas would occupy at any other temperature and pressure.[1]

Hence, in the equation—

$$\underset{\text{Marble}}{CaCO_3} + \underset{\text{Hydrochloric acid}}{2HCl} = \underset{\text{Calcium chloride}}{CaCl_2} + \underset{\text{Carbon dioxide}}{CO_2} + \underset{\text{Water}}{H_2O},$$

we know that 2 × (1 + 35·5) grams of hydrochloric acid will give (12 + 32) grams of carbon dioxide, since Cl = 35·5 and C = 12. But (12 + 32) or 44 grams of carbon dioxide is the G.M.W. of this gas. Therefore at N.T.P. it will occupy the G.M.V. or 22·4 litres. Suppose we wished to know what weight of hydrochloric acid we must use in the above reaction to obtain 20 litres of dry carbon dioxide at 37° C. 700 mm. pressure. First find what volume this would be at N.T.P.—

$$\frac{20 \times 273 \times 700}{310 \times 760} = 16{\cdot}22 \text{ litres.}$$

Now 22·4 litres of carbon dioxide are obtained by using 73 grams of hydrochloric acid,

∴ 16·22 litres are obtained by using

$$\frac{73 \times 16{\cdot}22}{22{\cdot}4} = 52{\cdot}9 \text{ grams.}$$

Calculation of a Formula from Percentage Composition.—In determining the formula of a compound, one usually begins by analysing the compound quantitatively, the results of the analysis being expressed as a percentage

[1] Bear in mind that the molecular weight is simply a RATIO, whereas the gram-molecular-weight is a definite WEIGHT of the substance.

composition ; thus the quantitative composition of calcium carbonate is

Calcium 40 per cent., Carbon 12 per cent., and Oxygen 48 per cent. by weight.

Does the percentage composition enable us to calculate the formula of a substance ? The percentage by weight of an element present in a given compound is obviously directly proportional to (*a*) the number of atoms of that element per molecule of compound, and (*b*) the atomic weight of the element. It is therefore proportional to the product of these two things, or

Percentage of Element A in the compound C varies as atomic weight of A × number of atoms of A in 1 molecule of C.

∴ No. of atoms of A in 1 molecule of C

is proportional to $\frac{\text{Percentage of A in C}}{\text{Atomic weight of A}}$

Similarly, the number of atoms of the element B in 1 molecule of the compound C is proportional to $\frac{\text{Percentage of B in C}}{\text{Atomic weight of B}}$, and so on.

$$\therefore \frac{\text{No. of atoms of element A in 1 molecule of compound C}}{\text{No. of atoms of element B } \quad \text{,,} \quad \text{,,} \quad \text{,,} \quad \text{,,} \quad \text{,,}} = \frac{\text{Percentage of A in C}}{\text{Atomic weight of A}} : \frac{\text{Percentage of B in C}}{\text{Atomic weight of B}}.$$

That is, *the ratio of the numbers of atoms of the elements* A, B, *etc., which are present in the molecule of a compound* C *is the same as the ratio of the numbers obtained by dividing the percentages of* A, B, *etc., in the compound* C *by their respective atomic weights.*

If, for instance, taking the above example, we divide the percentages of the elements calcium, carbon and oxygen in calcium carbonate by the atomic weights of these elements, we have

$$\% \text{ of calcium} = 40 \; ; \; \text{At. Wt. of calcium} = 40 \; ; \; \frac{\%}{\text{At. Wt.}} = 1$$

$$\% \text{ of carbon} = 12 \; ; \; \text{At. Wt. of carbon} = 12 \; ; \; \frac{\%}{\text{At. Wt.}} = 1$$

$\%$ of oxygen $= 48$; At. Wt. of oxygen $= 16$; $\frac{\%}{\text{At. Wt.}} = 3$

From these results we conclude that the ratio of the numbers of atoms of Calcium, Carbon and Oxygen present in a molecule of calcium carbonate is 1 : 1 : 3.

Again, the percentage composition of alcohol is C = 52·2 per cent. ; H = 13·0 per cent. ; O = 34·8 per cent. Applying the same method, the ratio of the numbers of carbon, hydrogen and oxygen atoms present in the molecule of alcohol is $\frac{52{\cdot}2}{12} : \frac{13{\cdot}0}{1} : \frac{34{\cdot}8}{16} = 4{\cdot}35 : 13{\cdot}0 : 2{\cdot}17$. Simplifying this ratio by dividing each number by the highest common factor (in this case, 2·17 is the highest common factor), it becomes 2 : 6 : 1. Therefore the atoms of carbon, hydrogen and oxygen present in the molecule of alcohol are in the ratio of 2 of carbon to 6 of hydrogen to 1 of oxygen.

This ratio is fulfilled in all the following formulæ :—

C_2H_6O ; $C_4H_{12}O_2$; $C_6H_{18}O_3$; etc. up to $C_{2n}H_{6n}O_n$.

In other words, the percentage composition alone of a substance is not sufficient to give us the *true* formula of that substance. It gives us the simplest or *empirical* formula only, and the true formula is n times this, where n is a whole number since atoms are indivisible. Thus in the case of alcohol, the empirical formula is C_2H_6O, but the true formula is $[C_2H_6O]n$, and n we have still to discover. What further evidence is necessary to give us n, and therefore the true formula ? We can soon think of this by considering two or three possibilities for the true formula for alcohol, e.g. :—

(i) C_2H_6O ; (ii) $C_4H_{12}O_2$; and (iii) $C_6H_{18}O_3$. The molecular weight of (i) is 46, that of (ii) is 92, and that of (iii) is 138. It is therefore possible to decide what multiple of the empirical formula of a substance is the true formula, by observing which gives a molecular weight corresponding to the *observed* value of the molecular weight. The vapour density of alcohol, calculated by Victor Meyer's method, is 23 ; therefore its molecular weight = 46. Now a molecular

weight of 46 corresponds to formula (i) above, and will not agree with any other ; hence here $n = 1$ and the empirical formula happens to be the true one also. This is not always the case. The empirical formula for grape-sugar is CH_2O, but the molecular weight of this compound is found to be 180. The molecular weight of $CH_2O = 12 + 2 + 16 = 30$; therefore $n = \frac{180}{30} = 6$, and the true formula for grape-sugar is $C_6H_{12}O_6$.

It should be mentioned that we are ignorant of the molecular weights of many solid compounds, and in these cases we assume the true formula to be the same as the empirical formula until facts are discovered which show us that our assumption is untenable. Thus we write NaCl for solid common salt, but for all we know to the contrary its true formula might be $Na_{1000}Cl_{1000}$ or Na_5Cl_5, etc. As we have no evidence either way, it is preferable to choose the simplest of these formulæ. Modern work seems to show that, in such electrolytes (p. 94) as sodium chloride, etc., any single crystal, however large, may be regarded as a single molecule. For substances of this nature, the empirical formula is consequently the only one of practical value.

The empirical formula for oxalic acid is CHO_2, but oxalic acid will form salts in which only *half* the hydrogen is replaced by a metal. Therefore the true formula *must* be *at least* $C_2H_2O_4$, and *may* be still more complex. Similarly the empirical formula of naphthalene is C_5H_4, but chlorine will replace *one-eighth* of the hydrogen in the naphthalene molecule. Hence the true formula for naphthalene must be at least $C_{10}H_8$ and *may* be still more complex.

In short, the percentage composition of a substance enables us to calculate its *empirical* formula ; to get its *true* formula we need additional evidence, which is often directly obtainable by molecular weight determinations, but is sometimes of an indirect nature.

Questions

1. What does a chemical equation tell you, and what does it not tell you, about the reaction which it represents ?

2. Explain the terms *gram-molecular-weight* and *gram-molecular-volume.*

3. What volume of acetylene, C_2H_2, measured dry at 15° C. 740 mm., could be obtained by the action of water on 20 grams of calcium carbide, CaC_2 ?

$$CaC_2 + 2H_2O = Ca(OH)_2 + C_2H_2.$$

4. What is the *empirical formula* of a substance ? How is it related to its *true* formula ?

5. Cobaltite has the following percentage composition :—

Cobalt, 35·53 per cent. Arsenic, 45·18 per cent. Sulphur, 19·29 per cent.

Find the empirical formula of the mineral.

(Co = 59. As = 75. S = 32.)

6. Olivine has the following percentage composition :—

Magnesium, 34·3 per cent. Silicon, 20·0 per cent. Oxygen, 45·7 per cent.

Find its empirical formula.

(M = 24. Si = 28. O = 16.)

7. A platinum compound has the following percentage composition :—

Platinum, 52·56 per cent. Nitrogen, 7·55 per cent. Hydrogen, 1·62 per cent. Chlorine, 38·27 per cent.

From these data find its empirical formula.

(Pt = 195. N = 14. H = 1. Cl = 35·5.)

8. An organic compound contains the following percentages :—

Carbon, 12·76 per cent. Hydrogen, 2·13 per cent. Bromine, 85·11 per cent.

Its vapour density is 94. Find its formula.

(C = 12. H = 1. Br = 80.)

9. Sodium glycocholate has the following composition :—

Carbon, 64·07 per cent. Hydrogen, 8·62 per cent. Nitrogen, 2·87 per cent. Oxygen, 19·71 per cent. Sodium, 4·73 per cent.

Find its empirical formula.

(C = 12. H = 1. N = 14. O = 16. Na = 23.)

CHAPTER VIII

THE KINETIC THEORY OF GASES

The behaviour of gases expressed by the gas laws, Avogadro's Hypothesis, the phenomena of evaporation and vapour-pressure, the fact that all gases are completely miscible with one another, and many other facts, are simply explained by the Kinetic Theory. This theory is largely due to CLAUSIUS (1857), BOLTZMANN (1868), and CLERK-MAXWELL (1860), and is shortly as follows :—

The molecules of a gas are in constant and rapid motion, and at ordinary pressures the spaces between the molecules are very large in comparison with the actual size of the molecules. If, for example, all the hydrogen molecules in a gas-jar "full" of the gas were to be packed so closely together that they were in actual contact, they would take up no more than a very minute fraction of the volume of the jar. How is it, then, that the jar *appears* to be full of hydrogen ? Suppose you were in a room in one corner of which was a small box of golf-balls. The volume of the golf-balls would be negligible in comparison with the total volume of the room. But suppose that by some means those golf-balls began to move about in the room at the rate of 60 miles or so a minute ! In what part of the room would you feel safe ? The *effective* volume of the golf-balls, that is, the volume throughout which their effect is felt, would now be the whole room. Now, hydrogen molecules *do* move with an average velocity of rather more than 60 miles a minute ; hence a number of them that might occupy only a fraction of a cubic millimetre in *actual* volume would *appear* to fill a large flask if placed in it.

It is easy now to see why gases will all mix with one another ; there are such comparatively wide spaces between their molecules and the latter move so quickly that mixing has nothing to prevent it and would in fact be expected.

The pressure which a gas exerts is considered to be due to the bombardment of the walls of the vessel by the gas molecules. Think of one of those machines that invite you to "test your punch." If you hit it, a momentary pressure is recorded, and if you are quick enough you can hit again before the pointer has gone back to zero. If you could administer several thousand punches a second, all of about the same strength, the pointer would indicate a *steady pressure*. In a volume of gas confined in a closed space, the walls of the containing vessel get hit many millions of times in a second, and *gas-pressure* is caused in this way. This gives us an explanation of Boyle's Law. If we halve the volume in which a gas is confined we shall clearly double the number of hits which the molecules make on the walls of the vessel, that is, we shall double the pressure. Similarly, if the volume be increased to 3 times its original value, there will be only $\frac{1}{3}$ of the number of molecular impacts in a given time, and therefore the pressure will be reduced to $\frac{1}{3}$ of its original value.

Suppose we have n molecules of mass m and velocity c enclosed in a cubical vessel with length of side l. If we can find the pressure on unit area of the walls of this vessel caused by a single molecule, and then multiply this pressure by the total number of molecules, we shall have the pressure per unit area caused by the gas as a whole.

By the laws of symmetry we may assume, for purposes of calculation, that $\frac{1}{3}$ of the total number of molecules are moving with uniform velocity c between one pair of parallel faces of the cube, another third between one of the remaining pairs of parallel faces, and the last third between the final pair of parallel faces. The time which any one molecule takes to travel from one face of the cube to the parallel face will be $\frac{l}{c}$, and therefore the number of hits per second that

it makes on these two faces will be $\frac{c}{l}$, or $\frac{c}{2l}$ on one of the faces.

The molecule is moving with a velocity c and its mass is m, therefore its momentum is mc, and if we suppose the molecules and the walls to be perfectly elastic, the molecule will rebound from the wall after impact with a momentum of $-mc$. Therefore the total *change* of momentum is $mc - (-mc) = 2mc$. This is balanced by the equal and outward reaction in the wall, that is, the momentum acquired by the wall from each impact is $2mc$. Now there are $\frac{c}{2l}$ impacts per second on one face from one molecule, therefore the total effect per second produced on one face by one molecule

$$= \frac{c}{2l} \times 2mc = \frac{mc^2}{l}.$$

Hence the total effect produced on one of the faces by all the molecules moving towards that face will be $\frac{n}{3} \times \frac{mc^2}{l}$. The total area of this face $= l^2$, therefore the effect or pressure per unit area of the face $= \frac{1}{3} \cdot \frac{nmc^2}{l \times l^2} = \frac{1}{3} \cdot \frac{nmc^2}{l^3}$, i.e., $p = \frac{1}{3} \cdot \frac{nmc^2}{v}$ where v is the volume of the cube, or $pv = \frac{1}{3} \cdot nmc^2$.

By a simple manipulation of this formula,

$$pv = \frac{2n}{3} \times \frac{mc^2}{2}.$$

Now $\frac{mc^2}{2}$ is the kinetic energy of one molecule of the gas, and $\frac{nmc^2}{2}$ is the kinetic energy of all the molecules of the gas.

It seems legitimate to assume that the kinetic energy of the molecules of a gas is a measure of the temperature of the gas, whence $\frac{2}{3} \cdot \frac{nmc^2}{2} \propto T$, or $\frac{2}{3} \cdot \frac{nmc^2}{2} = RT$, where R is a constant. And since the pressure of a gas is directly proportional to the kinetic energy of its molecules, that is,

to their speed since their mass is constant, we arrive at the conclusion that the pressure exerted by a gas is directly proportional to the absolute temperature if the volume is constant—a law with which we have met before (p. 30).

Again, at absolute zero, when $T = 0°$, $RT = 0$ and $\frac{2}{3} \cdot \frac{nmc^2}{2}$ also $= 0$, that is, the molecules will have no motion at all.

Boyle's Law also follows from the equation $pv = \frac{2}{3} \cdot \frac{nmc^2}{2}$, for $\frac{2}{3} \cdot \frac{nmc^2}{2}$ will be constant at constant temperature and therefore p must vary inversely as v.

Charles' Law, too, is shown to have a theoretical basis, for $pv = \frac{2}{3} \cdot \frac{nmc^2}{2} = RT$; now if p is constant, v must vary directly as $\frac{2}{3} \cdot \frac{nmc^2}{2}$ which varies as T since R is constant.

If we assume that equal volumes of gases at the same temperature and pressure have equal kinetic energies, which is more reasonable to assume than that they have different kinetic energies, then $\frac{2}{3} \cdot \frac{nmc^2}{2} = \frac{2}{3} \cdot \frac{n'm'c'^2}{2}$, where n and n' are the respective numbers of the molecules in the equal volumes of the two gases, and m and m' their respective masses. Then since average kinetic energies of the molecules of these gases are assumed to be the same,

$$\frac{mc^2}{2} = \frac{m'c'^2}{2}.$$

But $$\frac{2}{3} \cdot n \cdot \frac{mc^2}{2} = \frac{2}{3} \cdot n' \cdot \frac{m'c'^2}{2}$$

$$\therefore \quad \frac{2}{3} \cdot n = \frac{2}{3} \cdot n'$$

or $$n = n'.$$

In other words, equal volumes of gases at the same temperature and pressure contain equal numbers of molecules, which is Avogadro's Hypothesis.

By further assumptions and measurements, it has been

found possible to calculate the number of molecules in any given volume of gas at a stated temperature or pressure. Approximately, 1 c.c. of a gas at N.T.P. contains $2{\cdot}70 \times 10^{19}$ molecules. The G.M.V. of a gas at N.T.P. contains about $6{\cdot}06 \times 10^{23}$ molecules; this number is called *Avogadro's Constant.*

Velocity of Molecules.—In the equation $pv = \frac{2}{3} \cdot \frac{nmc^2}{2}$, suppose that the volume is the G.M.V. (22·4 litres) and the pressure 760 mm. and that the gas is at 0° C. Then the kinetic energy of this volume of gas will be the kinetic energy of a gram-molecule of the gas, since the G.M.V. is the volume of the gram-molecule of any gas at N.T.P.

∴ The kinetic energy at N.T.P. of the gram-molecule of a gas, i.e., $\frac{nmc^2}{2}$,

$$= \frac{3}{2} pv = \frac{3}{2} \times (760 \times 13{\cdot}6 \times 981) \times 22{,}400 \text{ ergs.}$$

$$= \text{about } 34 \times 10^9 \text{ ergs.}$$

This is called the molecular energy of translation of a gas at N.T.P., and from it we can calculate the speed of the molecules, c; thus, at N.T.P.—

$$34 \times 10^9 = \frac{nmc^2}{2} \text{ where } nm = \text{M, 1 gram molecule.}$$

In the case of hydrogen M = 2,

$$\therefore c^2 = \frac{2 \times 34 \times 10^9}{\text{M}}.$$

$$\therefore c^2 = 34 \times 10^9 \therefore c = \sqrt{34 \times 10^9}$$

$$= \text{about } 170{,}000 \text{ cm. per sec.}$$

For carbon dioxide, $c^2 = \frac{2 \times 34 \times 10^9}{44} \therefore c = \sqrt{\frac{34 \times 10^9}{22}}$

$$= \text{about } 36{,}200 \text{ cm. per sec.}^1$$

[1] These velocities are only approximate *average* velocities; the *actual* velocities of the molecules of a specimen of gas vary considerably from molecule to molecule.

Rate of Diffusion of a Gas (Graham's Law).—GRAHAM found that the rates at which two gases passed through a porous partition were inversely proportional to the square roots of the densities of the gases, or

$$\frac{R'}{R} \propto \frac{\sqrt{D}}{\sqrt{D'}}.$$

[This phenomenon of the passage of a gas through a porous partition is more properly called *effusion*, "diffusion" being reserved to describe the passage of one gas (or liquid) into another when they are not separated by a partition.]

Graham's Law may be deduced from the equations of the kinetic theory. For

$$\frac{mc^2}{2} = \frac{m'c'^2}{2} \quad \therefore \quad \frac{c^2}{c'^2} = \frac{m'}{m} \quad \therefore \quad \frac{c}{c'} = \sqrt{\frac{m'}{m}};$$

that is, the velocities of the molecules of two gases at the same temperature and pressure are inversely proportional to the square roots of their masses, and therefore to the square roots of their densities.

An apparatus, the Effusiometer, was devised in 1858 by BUNSEN to measure the rates of effusion of gases, and in this way to compare their molecular weights. The apparatus consists of a tube inverted in a trough of mercury and closed at the upper end by a platinum plate in which is a very fine hole. The gas under observation is placed in the tube, which is then sunk in the mercury to such a depth that the gas is under a suitable pressure, when it slowly escapes through the fine hole in the platinum. By measuring the volumes of two gases that escape through the hole in a constant time the ratio of the two molecular weights may be calculated.

Evaporation and Vapour Pressure.—The molecules of a liquid, like those of a gas, are in motion, but they do not move so fast as those of gases. However, if a surface of liquid be exposed, some of the molecules which come to the surface will have sufficiently high velocities to leave the liquid altogether. Continuation of this process will finally cause the entire conversion of the liquid into gas, if the

molecules which leave the liquid never return to it. If, however, the liquid be placed under a bell-jar, the escaping molecules have only a limited space in which to move, and after a time some of them will strike the liquid again and will be absorbed in it. When the number of molecules that leave the liquid in a given time is equal to the number that return to it in that time, no apparent change will take place, and the space in the bell-jar will be *saturated* with the vapour.

A current of air blown over the surface of a liquid will sweep away all the molecules that come off from it and will therefore aid evaporation.

The cause of vapour pressure will be apparent from the above considerations.

Deviations from the Gas-Laws.—No gas obeys the gas-laws exactly. The deviations that occur are considered to be due to two things, (i) the *actual* volume of the molecules of the gas, and (ii) to their mutual attraction. For a given mass of an "ideal" gas at constant temperature, PV should be absolutely constant; in practice it is found that PV is only approximately constant, the deviations becoming greater as the pressure increases. Let us see how (i) and (ii) above will affect the behaviour of a gas. Under ordinary pressures, the actual volume of the molecules will be negligible in comparison with their effective volume, and the molecules will be so far apart from one another that any attraction they have for one another will also be so small as to be negligible. Hence under these conditions PV will be very nearly constant; it may in fact be so nearly constant that deviations cannot be detected.

But suppose that the pressure is increased so much, and the volume proportionately diminished, that the actual volume of the molecules is an appreciable fraction of the volume in which they are confined. It is clear that the molecules will strike the walls more often than they would if they were mere points. Thus, if the diameter of a molecule is 1 unit and the distance between two parallel faces of the vessel in which it is confined 5 units, instead of having to travel 5 units from one wall before it strikes the other, it will

have to travel only 4 units, and the "pressure" it exerts will therefore be increased proportionately. If, on the other hand, the distance between the walls is 100,000 units, it will have to travel 99,999 units; now the difference between 100,000 and 99,999 is probably too small to be detected in ordinary experiments, whereas the difference between 5 and 4 is 20 per cent. of the former number and therefore easily detectable.

In short, the fact that molecules have a definite volume and are not mere points causes the pressure to increase too rapidly for PV to remain constant; or, what comes to the same thing, the volume V in the expression PV should represent the *volume in which the molecules move*. This will be the volume occupied by the gas *minus* an incompressible part which is proportional to the actual volume of the molecules. VAN DER WAALS allowed for this by writing $P(V - b) = a$ *constant*, where b is a constant *proportional to* the actual volume of the molecules.[1] This constant, b, is known as the *molecular co-volume*.

Turning now to the second factor in the deviation from the gas-laws, namely, the attraction of the molecules for one another, it is evident that this will tend to draw the molecules closer together, and therefore to make the volume decrease too rapidly. Van der Waals corrected for this by writing $\left(P + \frac{a}{V^2}\right)$ instead of P, where a is a constant and $\frac{a}{V^2}$ is a measure of the molecular attraction.

Van der Waals' Equation therefore is

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT$$

and gives results that correspond fairly well with the experimental figures. A more exact equation was suggested by DIETERICI in 1899, but for ordinary pressures van der Waals' equation is sufficiently accurate.

Critical Phenomena.—When gases are cooled to a sufficiently low temperature, they become liquids, even under

[1] b is not the *actual* volume of the molecules.

atmospheric pressure. If the pressure is increased, liquefaction may be brought about at higher temperatures, but for each gas there is a certain temperature above which it is impossible to liquefy that gas, whatever may be the pressure applied. This temperature is called the *critical temperature* of the gas, and the minimum pressure which is required to bring about liquefaction at the critical temperature is called the *critical pressure.* The first chemist to study critical phenomena seriously was ANDREWS, who in 1869 described some of his results in these words : " On partially liquefying carbon dioxide by pressure alone, and gradually raising at the same time the temperature to 31·1° C., the surface of demarcation between the liquid and gas became fainter, lost its curvature, and at last disappeared. The space was then occupied by a homogeneous fluid, which exhibited, when the pressure was suddenly diminished, or the temperature slightly lowered, a peculiar appearance of moving or flickering striæ throughout the entire mass. At temperatures above 31·1° C. no apparent liquefaction of carbonic acid, or separation into two distinct forms of matter, could be effected, even when a pressure of 300 or 400 atmospheres was applied." Other gases gave similar results.

The explanation of the phenomenon is that at the critical temperature and pressure the specific volumes, *i.e.*, $\frac{1}{\text{density}}$, of the gas and liquid become the same.

Liquefaction of Gases.—All known gases have been liquefied. Helium gave the most trouble, but in 1907 ONNES succeeded in preparing liquid and even solid helium. Many gases can be liquefied at 0° C. by application of pressure only ; in other words, their critical temperatures lie above 0° C. Such are sulphur dioxide, carbon dioxide, ammonia, chlorine and cyanogen (C_2N_2). Others, such as oxygen, hydrogen, methane (CH_4) and nitrogen have first to be strongly cooled. On account of the apparent impossibility of liquefying these gases, they were formerly called the " permanent " gases ; but when it was realized that a low temperature and not a high pressure was the important factor it was soon found

possible to liquefy them. The necessary low temperatures were at first obtained by allowing liquid carbon dioxide to boil rapidly, when the absorption of the latent heat of vaporization causes the temperature of the remaining liquid to fall lower and lower. This method has, however, been superseded by another process, based on a different principle called the *Joule-Thomson* effect, discovered by JOULE and SIR WILLIAM THOMSON (who later became LORD KELVIN). When a gas is compressed and then allowed to escape through a porous plug into a region of low pressure, it becomes cooler. This depends upon the fact that in the compressed gas the molecules are close together, while after passage through the plug they are much farther apart, and therefore the force of attraction that they have for one another must have been overcome. To overcome this attraction energy is required, and this is supplied by the heat of the gas itself, which therefore becomes cooler.

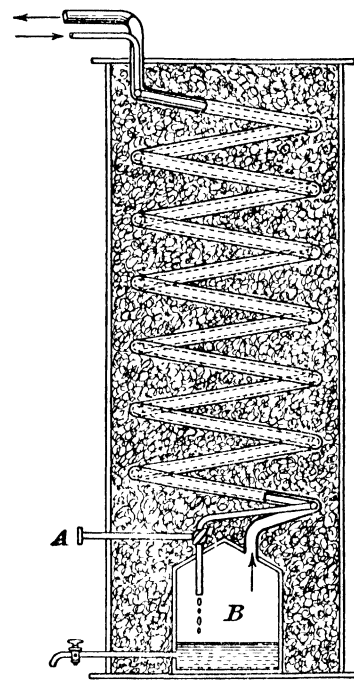


FIG. 14.—Liquefaction Apparatus.
A. Valve screw. *B*. Receiver.

If the cold gas thus produced is allowed to circulate around the tube that contains the compressed gas, the latter will be cooled before it reaches the plug, and will therefore be colder still after passage through the plug. By continuing this process, the gas will get colder and colder and will finally issue from the plug as a liquid (Fig. 14).

The liquefaction of gases is now a regular industry, and for

details of the various processes employed the technical books should be consulted.

Liquid air, etc., can be preserved for some days in DEWAR or vacuum vessels, which are double-walled vessels with a high vacuum between the walls. The inner surfaces of the walls are silvered in order to reduce absorption of heat, while the vacuum allows very little heat to pass through it.

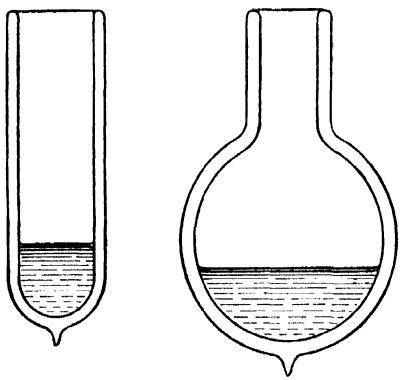


FIG. 15.—Dewar Flasks.

QUESTIONS

1. What is the kinetic theory of gases ?
2. How are evaporation and vapour pressure explained by the kinetic theory ?
3. Show how Boyle's Law may be deduced theoretically.
4. Explain the terms *critical pressure* and *critical temperature.*
5. What are the main principles involved in the various methods employed for the liquefaction of gases ?
6. Show that Avogadro's Hypothesis has a theoretical basis, if the kinetic theory of gases is " true."

CHAPTER IX

THERMAL DISSOCIATION

The formula for ammonium chloride is NH_4Cl; its molecular weight is therefore 53·5, and we should expect its vapour density to be 26·75. Experiments show, however, that its vapour density is 13·37. How are we to explain this, and what does it mean? Let us consider the possibilities.

(i) If our previous work is correct, then the molecular weight of ammonium chloride should be twice its vapour density, that is 26·75. But one molecule of ammonium chloride cannot contain less than one atom of chlorine, and the atomic weight of chlorine is 35·5! We could assume that the molecular weights of nitrogen and chlorine had been incorrectly established, and that instead of being 14 and 35·5 they were 7 and 17·75 respectively. This would give us a formula NH_2Cl for ammonium chloride, for N now = 7, Cl = 17·75, and H = 1 $\therefore$ NH_2Cl = 26·75, which corresponds with the vapour density of 13·37.

Unfortunately, however, this explanation at once lands us in far more serious difficulties concerning the other compounds in which nitrogen and chlorine are found. Thus, the molecular weight of hydrochloric acid calculated from its vapour density is 36·5. Now if the atomic weight of chlorine is 17·75, the formula for hydrochloric acid will be HCl_2, where the chlorine has a valency of 0·5—a fact that at once arouses our suspicions. Moreover, the ratio of the specific heats of hydrochloric acid gas agrees with that of a diatomic gas and differs from that of a triatomic. Hence we must abandon

the idea that the atomic weights of chlorine and nitrogen are half the generally accepted values.

(ii) Still assuming that the molecular weight of ammonium chloride vapour is twice its vapour density, we might argue that the formula for ammonium chloride is $N_{\frac{1}{2}}H_2Cl_{\frac{1}{2}}$. But this involves a splitting of atoms and therefore an abandonment of the atomic theory. We should, therefore, not accept this suggestion unless no alternative could be found.

(iii) We might suppose that Avogadro's Hypothesis was not universally true, and that ammonium chloride vapour was one of the cases in which the Hypothesis was inapplicable. But, as we have seen, the Hypothesis has a theoretical basis, and chemists would be reluctant to admit the possibility of exceptions to it. We should, indeed, be explaining a difficulty by creating a greater one.

(iv) The suggestion finally adopted by chemists was that the ammonium chloride vapour really does not consist of ammonium chloride molecules, but of a mixture of ammonia and hydrochloric acid molecules in equal numbers—

$$NH_4Cl = NH_3 + HCl.$$

A mixture of these two gases in equal volumes will obviously have a density half-way between that of ammonia, 8·5, and that of hydrochloric acid, 18·25, that is $\frac{8{\cdot}5 + 18{\cdot}25}{2} = 13{\cdot}37$, which is the observed value.

When the vapour is cooled, ammonium chloride is reformed. It is evident that this theory is much more satisfactory than any of the others, especially as it is quite easy to prove that *some* ammonia and hydrochloric acid are present in the vaporized ammonium chloride, although it is not easy to demonstrate the *complete* splitting-up.

Unexpected values for the vapour densities of many other substances have been obtained, and in every case it has been found possible to explain the observed values by assuming that a splitting-up of the original molecules has occurred. We can define the phenomenon as follows :—

When the molecules of a substance split up, on heating, into simpler molecules that recombine on cooling, the phenomenon

is called DISSOCIATION, and the substance is said to dissociate.[1]

Other substances that dissociate on heating are—
iodine ($I_2 \rightleftharpoons I + I$),
nitrogen peroxide ($N_2O_4 \rightleftharpoons NO_2 + NO_2$),
phosphorus pentachloride ($PCl_5 \rightleftharpoons PCl_3 + Cl_2$),
hydrogen iodide ($2HI \rightleftharpoons H_2 + I_2 \rightleftharpoons H_2 + I + I$),
calcium carbonate ($CaCO_3 \rightleftharpoons CaO + CO_2$),
and many more.

These actions are, then, *reversible*, the direction in which they proceed depending upon the external conditions of temperature, and, in most cases, pressure. To indicate this reversibility the sign $\rightleftharpoons$ is used instead of $=$.

Nitrogen Peroxide.—Nitrogen peroxide is a brown liquid that boils at 22° C. At temperatures just above the boiling-point its vapour density is 46, but as the temperature rises the vapour density decreases until it reaches a minimum value of 23 at 140° C., as shown in the following table :—

Temperature.	*Vapour Density.*	*Temperature.*	*Vapour Density.*
22·5°	45·8	100°	24·3
27°	38·3	135°	23·1
60°	30·2	140°	23·0

These figures may be explained by assuming that at 22·5° the vapour of nitrogen peroxide consists almost entirely of N_2O_4 molecules, having a molecular weight of 92 and therefore a vapour density of 46, which corresponds to the observed value. On heating, some of the N_2O_4 molecules split up each into two NO_2 molecules, until at 140° C. they have all split up and the gas now consists entirely of NO_2 molecules of molecular weight 46 and vapour density 23. At intermediate temperatures, then, the gas will consist of a mixture of N_2O_4 molecules with NO_2 molecules. The percentage of NO_2 by volume or by weight at any given temperature may be calculated as follows from the observed vapour density, n :—

[1] If the splitting-up of the substance is irreversible, it is called *decomposition* and not dissociation.

(*a*) *Per cent. NO_2 by volume.*

Let x = % NO_2 by volume, when the V.D. of the mixture is n.

$\therefore$ $100 - x$ = % N_2O_4 ,, ,, ,, ,,

The density of NO_2 is 23 ; that of N_2O_4 is 46.

$$\text{Now density} = \frac{\text{weight}}{\text{volume}}$$

$\therefore$ *weight* of the $NO_2 = x \times 23$

and *weight* of the $N_2O_4 = (100 - x)46$

$\therefore$ total *weight* of gas $= 23x + 46(100 - x)$.

But there are 100 parts by volume of the gas and its density is n,

$\therefore$ total weight of the gas $= 100 \times n$.

$\therefore$ $23x + 46(100 - x) = 100 \times n$.

Hence for any given value of n, x may be calculated.

(*b*) *Per cent. NO_2 by weight.*

Let x = % NO_2 by weight, when V.D. of the gas is n.

$\therefore$ $100 - x$ = % N_2O_4 ,, ,, ,, ,,

V.D. of $NO_2 = 23$; that of N_2O_4 is 46.

$$\text{Density} = \frac{\text{weight}}{\text{volume}}$$

$$\therefore \text{ } \textit{volume} \text{ of the } NO_2 = \frac{x}{23}$$

$$\text{and } \textit{volume} \text{ of the } N_2O_4 = \frac{100 - x}{46}$$

$$\therefore \text{ total } \textit{volume} \text{ of the gas} = \frac{x}{23} + \frac{100 - x}{46}.$$

But there are 100 parts by weight of the gas and its density $= n$

$$\therefore \text{ total volume of the gas} = \frac{100}{n}$$

$$\therefore \frac{x}{23} + \frac{100 - x}{46} = \frac{100}{n}.$$

Hence for any given value of n, x may be calculated.

Effect of Changes of Pressure upon Dissociation.—This will be discussed again later (pp. 123 *ff.*), but we can consider it shortly here. When nitrogen peroxide, N_2O_4, dissociates, according to the equation $N_2O_4 \rightleftharpoons 2NO_2$, it is seen that 2 molecules are formed from 1 original molecule. If therefore the pressure remains constant, the volume of the gas will be doubled, by Avogadro's Hypothesis. Suppose now we take this volume of NO_2 molecules and increase the pressure, keeping the temperature constant. What will happen ? The volume having decreased, the NO_2 molecules

will have less room in which to move about and will therefore meet one another more often, and the chances of two NO_2 molecules recombining to form an N_2O_4 molecule will be increased. In other words, in this case *increase of pressure will cause a decrease of dissociation.* This is true in every case in which the products of dissociation occupy a larger volume than the original gas under the same conditions of temperature and pressure.

We shall find that the dissociation of hydriodic acid gas, however, is not accompanied by an increase in volume, for

$$2\ HI \rightleftharpoons H_2 + I_2,$$

i.e. we have started with 2 molecules and get 2 molecules after dissociation,[1] therefore there is no change in volume. In this case we should expect change of pressure to have no effect upon the degree or extent of dissociation, and this is confirmed experimentally.

Le Chatelier's Principle.—We can consider the effect of pressure (and also of temperature) on dissociation in terms of a principle enunciated by the French chemist LE CHATELIER. This is expressed as follows :—

If to a system in equilibrium a constraint be applied, a change takes place within the system tending to nullify the effect of the constraint and to restore the equilibrium.

This is a general law of chemistry, and we can understand very well what it means by an analogy from everyday life. Suppose a man to have regulated his expenditure in such a way that his expenditure + income-tax = total income.

We have here a " system in equilibrium." Let us now suppose that the Government apply a " constraint " by increasing the rate of income-tax. A change will have to take place within the system tending to restore the equilibrium which has been upset. If the income is fixed, the expenditure will have to be lowered—and this is an example of Le Chatelier's principle working in everyday life !

Let us take now a chemical example. Suppose we have

[1] *Assuming that the temperature is sufficiently high for the iodine to remain as vapour.*

some water in a cylinder fitted with a piston (Fig. 16). The space above the water is saturated with water-vapour, and the temperature is constant.

If as many H_2O molecules leave the water for the vapour in a given time as return from the vapour to the water in that time, the system will be in equilibrium. If now the piston is pushed down a little way, the pressure on the vapour will have been increased, and therefore by Le Chatelier we should expect a change to take place within the system the result of which would be to nullify the effect of pushing down the piston. In point of fact, what happens is that some of the water-vapour is condensed to

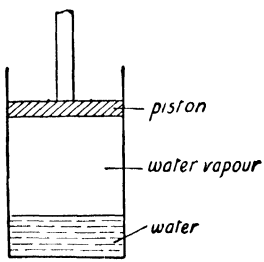


FIG. 16.

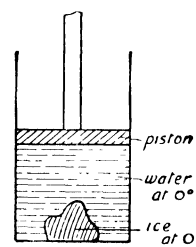


FIG. 17.

water; for since the volume is decreased, more molecules will pass from the vapour into the water in a given time than will leave the water in that time. When sufficient vapour has condensed in this way, the numbers of molecules leaving and entering the water per second will become equal again, and equilibrium will be restored.

For a second example, take ice at 0° and water at 0° in a similar cylinder (Fig. 17). If no heat enters or leaves the cylinder, the ice and water will remain unchanged, that is, the system will be in equilibrium. Now suppose we put weights on the piston—we shall be applying a " constraint " to the system, and according to Le Chatelier a change should take place within the system tending to nullify the constraint, i.e. to reduce the pressure. This can be done only by a

reduction of volume. Since 1 gram of ice at 0° occupies a greater volume than 1 gram of water at 0°, a reduction of volume could occur if the ice were to melt, and this in fact happens.

Applying now Le Chatelier's principle to cases of dissociation, it follows that if dissociation is accompanied by increase in volume, an increase in pressure on such a system in equilibrium will tend to *reduce* the dissociation, since in this way the volume and therefore the pressure will be lowered. If, however, dissociation is accompanied by no change of volume, change of pressure will have no effect on the degree of dissociation, since the latter will have no effect on the volume.

We have so far considered the effect of changes of pressure only, but by means of Le Chatelier's principle we can also predict the effect of temperature changes. Suppose the dissociation

$$A \rightleftharpoons B + C$$

is accompanied by an absorption of heat in the forward direction, $\rightarrow$. What effect upon the degree of dissociation will heating produce? Le Chatelier tells us that a change should take place tending to nullify the effect of heating, or, in other words, a change should take place which is accompanied by an absorption of heat. This means that the dissociation will be increased. Similarly, if dissociation is accompanied by evolution of heat, heating will decrease the dissociation.

Thermochemistry

Chemical change is usually accompanied by an evolution or an absorption of heat. A reaction in which heat is evolved is said to be *exothermic*, while one in which absorption of heat takes place is called *endothermic*. Exothermic reactions are more common than endothermic.

The heat evolved or absorbed in the formation of a compound from its elements is called the *heat of formation* of the compound. It is usually positive,[1] in which case the compound is exothermic, but is sometimes negative,[2] when the compound is said to be endothermic.

[1] That is, heat is evolved.

[2] That is, heat is absorbed.

The number of calories evolved or absorbed in a particular reaction may be measured by carrying out the reaction in a calorimeter surrounded by a known weight of water and measuring the change in temperature of the water. A simple type of calorimeter for this purpose is shown in Fig. 18. For measuring the *heats of combustion* of substances in oxygen special calorimeters capable of withstanding a high pressure

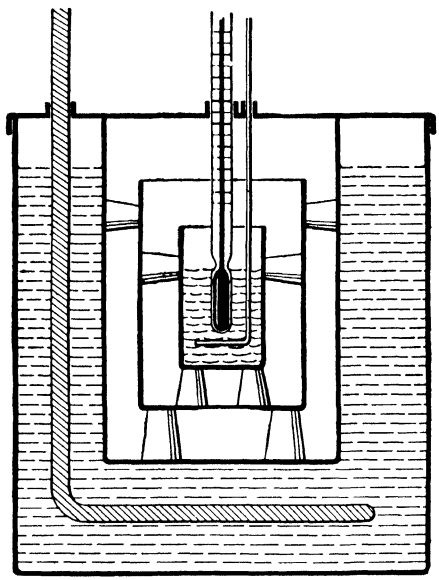


FIG. 18.

have been constructed; they are usually called "bomb-calorimeters."

The heat change of a reaction is expressed by adding the appropriate figures to the ordinary chemical equation representing the reaction; thus

$$C + O_2 = CO_2 + 97{,}000 \text{ calories}$$

means that when 12 grams of carbon combine with 32 grams

of oxygen, 44 grams of carbon dioxide are formed, with evolution of 97,000 calories. Carbon dioxide is therefore an exothermic substance.

Similarly,

$$C + S_2 = CS_2 - 28{,}700 \text{ calories}$$

shows us that when 76 grams of carbon disulphide are prepared by direct combination of carbon and sulphur, 28,700 calories are absorbed. Carbon disulphide is therefore an endothermic compound.

A little thought will show us that to make these thermochemical equations quite definite, we ought to specify the physical state of all the substances represented in them. Thus the equation

$$H_2 + \text{oxygen} = H_2O + 58{,}700 \text{ calories}$$

is true only if the hydrogen, oxygen and water are all in the gaseous state. If the water is allowed to condense, it is clear that the total heat evolved will be increased by the latent heat of vaporization given out by 18 grams of steam condensing to water, i.e. 9,700 calories; hence

$$H_2 + \text{oxygen} = H_2O + 58{,}700 \text{ calories} + 9{,}700 \text{ calories.}$$

Gas. Gas. Liquid.

Law of the Conservation of Energy.—In no case hitherto investigated has any creation or destruction of energy been observed; conversion of one form of energy, such as electricity, into another, such as heat, is a common phenomenon, but there is no loss or gain of energy in the process. This fact of experience is expressed in the law of the conservation of energy: *Energy can neither be created nor destroyed.* It is true that recent work has demonstrated that energy may be created by the annihilation of matter, and that the laws of the conservation of matter or energy ought really to be combined in a single law; but such considerations need not delay us at the moment.

From the principle of the conservation of energy we may deduce the **Law of Constant Heat Summation,** sometimes known as **Hess's Law,** after its discoverer: *The total amount*

of heat absorbed or evolved in a given reaction is independent of the number of stages in which the reaction is brought about. This law enables us to calculate the heats of formation of many compounds that cannot be made directly from their elements.

Thus (i) we may calculate the heat of formation of carbon monoxide from the following data :—

$$\underset{\text{Solid.}}{C} + \underset{\text{Gas.}}{O_2} = \underset{\text{Gas.}}{CO_2} + 97{,}000 \text{ calories.}$$

$$\underset{\text{Gas.}}{CO} + \underset{\text{Gas.}}{\text{oxygen}} = \underset{\text{Gas.}}{CO_2} + 68{,}000 \text{ calories.}$$

Therefore, by subtraction,

$$\underset{\text{Solid.}}{C} + \underset{\text{Gas.}}{\text{oxygen}} = CO + (97{,}000 - 68{,}000) \text{ calories.}$$

$$= CO + 29{,}000 \text{ calories.}$$

ii. Consider, again, the heat of formation of acetylene, C_2H_2. We know from experiment that

$$C + O_2 = CO_2 + 97{,}000 \text{ calories}$$

$$\text{and } H_2 + \text{oxygen} = \underset{\text{Liquid.}}{H_2O} + 68{,}400 \text{ calories.}$$

The heat of combustion of acetylene is found experimentally to be 310,200 calories—

$$C_2H_2 + 2\tfrac{1}{2}O_2 = 2CO_2 + \underset{\text{Liquid.}}{H_2O} + 310{,}200 \text{ calories.}$$

But the heat of formation of $2CO_2 + H_2O$ will be

$$2 \times 97{,}000 + 68{,}400 = 262{,}400 \text{ calories.}$$

Hence the decomposition of 1 gram molecule of acetylene must be accompanied by the *evolution* of 310,200 − 262,400 calories, or the *heat of formation* of acetylene is − 47,800 calories.

iii. The heat of combustion of 1 gram molecule of alcohol, C_2H_5OH, is 340,500 calories, i.e.,

$$\underset{\text{Liquid.}}{C_2H_6O} + 3O_2 = 2\underset{\text{Gas.}}{CO_2} + 3\underset{\text{Liquid.}}{H_2O} + 340{,}500 \text{ calories.}$$

But the heat of formation of $2CO_2$ and $3H_2O$ will be

$$2 \times 97{,}000 + 3 \times 68{,}400 = 399{,}200 \text{ calories.}$$

Hence the heat of formation of alcohol is 399,200 − 340,500 calories, = 58,700 calories.

Heat of Solution.—When a substance is dissolved in water, there is usually either an evolution or absorption of heat. The heat change that occurs when 1 gram molecule of a substance is dissolved in *a large quantity* of water is called the heat of solution of that substance. In the thermochemical

equation the water in which the substance is dissolved is written Aq. Thus

$$\underset{\text{Solid}}{\text{NaOH}} + \text{Aq} = \text{NaOH} \,.\, \text{Aq} + 9{,}800 \text{ calories}$$

means that when 40 grams of caustic soda are dissolved in a large quantity of water, to form caustic soda solution (NaOH . Aq), 9,800 calories are evolved.

Atomic Heats.—The law of DULONG and PETIT has been mentioned previously. It states that the atomic weight of solid element × its specific heat is approximately equal to 6·4, or *the atomic heat of all solid elements is the same.* At ordinary temperatures this is roughly true for metals, but

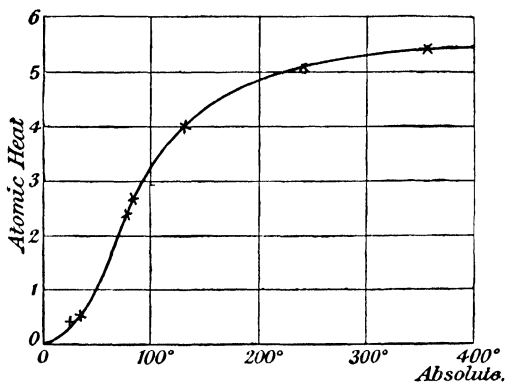


FIG. 19.—Curve showing Atomic Heats of Aluminium at various temperatures.

not for most non-metals. At higher temperatures the law is obeyed more exactly, while at the temperature of liquid hydrogen it does not hold at all. The atomic heats of all elements decrease as the temperature is lowered, a phenomenon which, with very many others, has been satisfactorily explained by **Planck's quantum theory.** This is too advanced a subject for discussion here, but may be stated in the following words: *Atoms emit or absorb energy in small definite amounts, directly proportional to the frequency of*

vibration of the atom; they do *not* emit or absorb energy *continuously*. The "small definite amounts" of energy are called *quanta*.

QUESTIONS

1. Write a general account of Thermal Dissociation.

2. The vapour density of nitrogen peroxide at 60° is 30·2. Calculate the percentage by weight of NO_2 molecules present.

3. State Le Chatelier's principle and explain its application.

4. What is Hess's Law? Show how it may be applied in the determination of heats of formation.

5. Calculate the heat of formation of methane, CH_4, from the following data—

$$C + O_2 = CO_2 + 97{,}000 \text{ calories.}$$
$$H_2 + \tfrac{1}{2}O_2 = H_2O + 68{,}400 \text{ calories.}$$
$$CH_4 + 2O_2 = CO_2 + 2H_2O + 211{,}800 \text{ calories.}$$

CHAPTER X

ELECTROLYSIS

NICHOLSON and CARLISLE showed in 1800 that if the wires from an electric battery are immersed in acidulated water the water is decomposed into hydrogen and oxygen. The hydrogen comes off from the wire attached to the negative pole of the battery, and the oxygen from that attached to the positive pole. This decomposition of a substance by the passage of electricity through it is called *electrolysis*. Pure water will not conduct electricity,[1] but if a little sulphuric acid be added conduction takes place and the water is electrolysed.

The two metallic plates or wires that are placed in the liquid to bring about electrolysis are called the *electrodes*. The electrode connected to the positive pole of the battery is called the *anode* or positive electrode, and that connected to the negative pole is called the *cathode* or negative electrode. BERZELIUS showed that aqueous solutions of acids, bases and most metallic salts will conduct electricity and are decomposed in the process. Thus, if a current of electricity is passed through a solution of copper chloride, chlorine is evolved at the anode (if this is made of a substance, like carbon, not attacked by chlorine) and copper is deposited on the cathode. Substances that are liberated at the anode are said to be *electro-negative*, since they are attracted to the *positive* pole, and it is a general rule of electricity that a positively-charged body repels another positively-charged

[1] This statement is not *strictly* accurate. Even the purest water will conduct the current to a slight extent. See p. 137.

body but attracts a negatively-charged one, and *vice versâ*. In the same way, substances that make their appearance at the cathode are called *electro-positive*.

The phenomena of electrolysis were first carefully studied by FARADAY in 1832. He called solutions that are decomposed when electricity passes through them *electrolytes*, but this name is now usually given to the substances dissolved and not to the solutions themselves. *Non-electrolytes*, then, are substances whose [aqueous] solutions do not conduct electricity.

The substances that appear at the electrodes during electrolysis Faraday called *ions* (from the Greek, because they *wander* to the electrodes). Those that go to the anode are called *anions*, and those that go to the cathode *cations*. (Note that the modern significance of these terms is rather different from that used by Faraday. See Chapter XIII.) Diagrammatically we can represent these ideas as follows :—

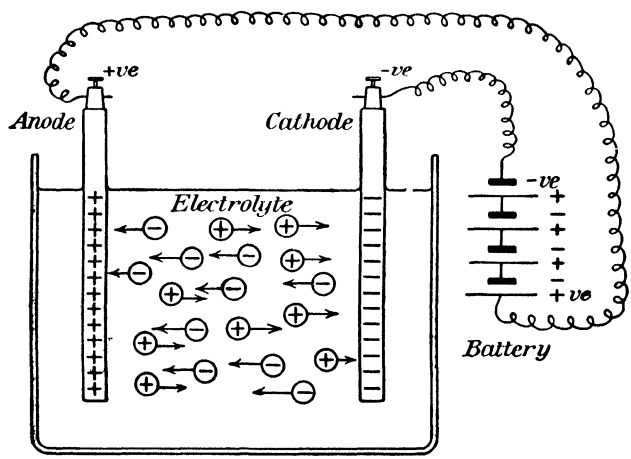
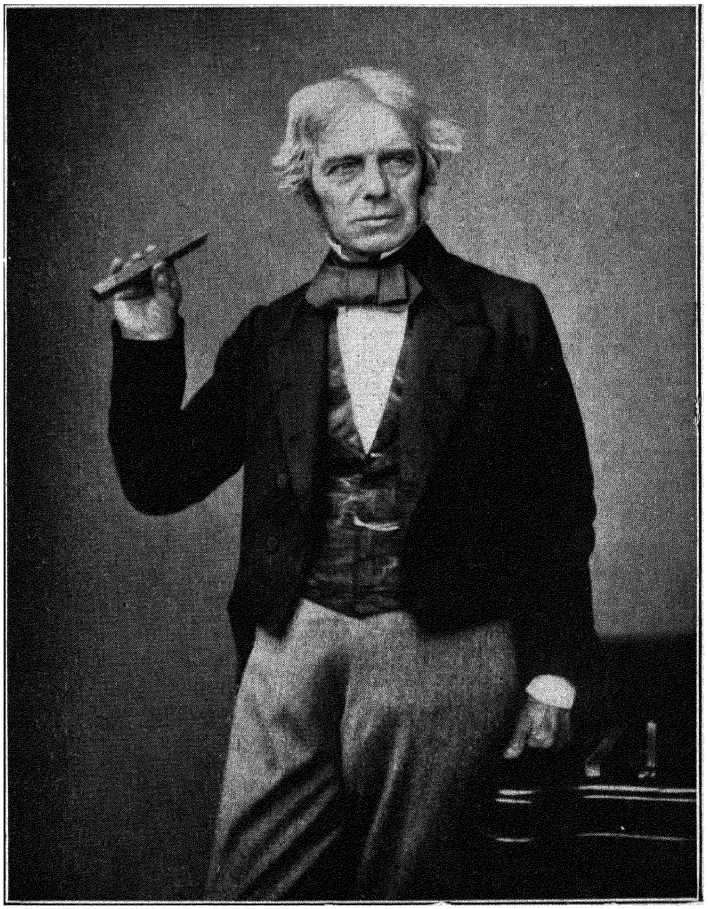


FIG. 20.

The conventional sign for a single cell of a battery is ⏐|, where the short, thick stroke represents the negative pole



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and the long, thin one the positive pole. A battery of 5 such cells connected in series is shown in Fig 21*a*, or more simply in Fig. 21*b*.

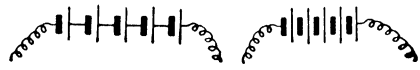


FIG. 21.

If the positive pole of one cell is connected to the negative of the next, and the positive of this to the negative of the third, and so on, as shown in the diagram, the battery is said to be composed of cells connected *in series*. The terminal poles of the *battery* are then the negative pole of the cell at one end of the series and the positive pole of the cell at the other end. Fig. 22 shows 3 electrolytic cells and a battery connected in series.

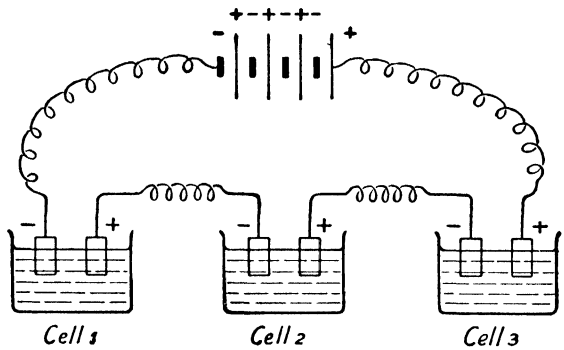


FIG. 22.

Note that the electrode in Cell 1 connected with the negative terminal pole of the battery is also negative—it is really an extension of the pole; similarly with the anode in Cell 3.

Faraday's Laws of Electrolysis.—Faraday showed that *the same quantity of electricity passed through solutions of electrolytes connected up in series will liberate in each cell weights of the products of electrolysis that are in the ratio of their chemical equivalents.* Thus the same quantity of elec-

tricity that liberates 1 gram of hydrogen will liberate 35·5 grams of chlorine or 108 grams of silver or 31·7 grams of copper or 8 grams of oxygen, etc.

The unit of quantity of electricity is the *coulomb*, which is the quantity of electricity conveyed by a current of 1 *ampère* flowing for 1 second. The number of coulombs required to liberate the equivalent in grams of any substance is found to be 96,000. A smaller or a greater number will liberate a proportionately smaller or greater weight. Faraday's Laws may therefore be expressed in the following terms :—

First Law. The weight of an ion liberated in electrolysis is proportional to the quantity of electricity which has passed through the electrolyte (i.e. to current × time).

Second Law. The quantity of electricity required to deposit the equivalent in grams of an ion is 96,000 *coulombs* (or 1 "*faraday*").

Theories of electrolysis will be dealt with later (Chapter XIII). For the apparatus used in various electrolytes, see under water, caustic soda, hydrochloric acid, etc. The quantity of electricity which flows through the circuit is measured by noting the time in seconds and multiplying this by the number of ampères of the current as shown by an ampère-meter or *ammeter* connected up in series in the circuit. An electrolytic cell is often called a *voltameter* ; this must not be confused with a voltmeter which is an instrument used for measuring the *voltage* or potential difference between two points of a conductor.

It is also necessary to note that the primary products of electrolysis will often act upon water or upon one another, so that the products actually obtained may be *secondary*. Thus, when a solution of caustic soda is electrolysed, the primary products are *sodium* at the cathode and "*hydroxyl*" *groups* (OH) at the anode. But the sodium formed immediately acts upon the water so that the *actual product* at the cathode is hydrogen [1]—

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

[1] It is possible that the hydrogen may be the primary product after all, but I have given the usual explanation.

while two hydroxyl groups react together at the anode, forming oxygen and water—

$$2OH = H_2O + \text{oxygen}.$$

Hence the final result of electrolysing a solution of caustic soda is that hydrogen is liberated at the cathode and oxygen at the anode, while the concentration of caustic soda round the cathode increases. In other words, it *appears* as though the *water* has been electrolysed, the weight of caustic soda remaining constant. The same sort of thing happens in the case of dilute sulphuric acid. Here the primary products of electrolysis are hydrogen and the " sulphate " group of atoms, SO_4. The latter groups, however, when liberated at the anode, act upon the water present to give sulphuric acid and oxygen—

$$2SO_4 + 2H_2O = 2H_2SO_4 + O_2,$$

hence the actual product at the anode is secondary, namely, oxygen.

To take a rather different case, suppose we electrolyse a solution of copper sulphate, using a platinum or copper cathode and a copper anode. Here the copper particles go to the cathode, where they are deposited, while the SO_4 groups at the anode dissolve the latter to form more copper sulphate—

$$Cu + SO_4 = CuSO_4.$$

The net result of electrolysis in this case is therefore *the transference of copper from the anode to the cathode.* This process is used in copper-plating, and similar ones in gold- and silver-plating, hence the term " electro-plate."

QUESTIONS

1. Explain the terms *electrolyte, anode, cathode, cation, anion.*
2. State Faraday's Laws of Electrolysis.
3. The same quantity of electricity that deposits 3·53 grams of a metal in an electrolytic cell will liberate 453 c.c. of hydrogen, collected over water at 18° C. 763 mm. What is the equivalent of the metal ?

CHAPTER XI

OSMOTIC PRESSURE

When a substance is dissolved in a liquid, the liquid is called the *solvent*, the substance dissolved the *solute*, and the product a *solution*. These terms are convenient, but it is easily seen that there may be cases in which they are rather difficult to apply systematically. For instance, if we dissolve 1 gram of alcohol in 100 c.c. of water, the alcohol is the solute and the water the solvent. Similarly, if we dissolve 1 gram of water in 100 c.c. of alcohol, here the alcohol is the solvent and the water the solute. But if we dissolve 50 c.c. of alcohol in 50 c.c. of water, both substances have an equal right to be called solvent, or solute. In practice, however, there is no difficulty over such matters ; it is necessary merely to remember that there is no essential property that marks off a solute from a solvent. It is just as correct to call brine a solution of water in salt as to call it a solution of salt in water —it is, in fact, a *homogeneous mixture* of two things. Perhaps, therefore, we may define a *solution* as a homogeneous mixture of two or more substances. By this definition we see that we may have solutions of gases in gases, gases in liquids, liquids in liquids, solids in liquids, solids in solids, and so on. It is with one of the properties of solutions of solids or liquids in liquids (generally in water) that we shall deal in this chapter.

If we examine the structure of a plant by means of the microscope, we shall find that the plant-tissues consist of a number of small chambers, each of which with its contents is called a cell (Fig. 23). Each cell is bounded by a cell-wall

of a substance called *cellulose* (*a*). Lining the wall is a layer of a semi-transparent gelatinous substance called *protoplasm*; this layer is sometimes called the *primordial utricle* (*b*). The central portion of the cell consists of a watery liquid containing dissolved substances and called *cell-sap* (*c*).

In 1854, PRINGSHEIM showed that if plant cells were placed

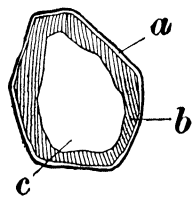


FIG. 23.—Single Plant Cell, seen *in Section.*

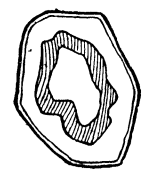


FIG. 24.—Diagrammatic Section of Plant Cell placed in Strong Salt Solution.

in concentrated solutions of salt the protoplasmic lining shrank away from the cell-wall, the volume of the cell-sap becoming less. If these cells were now placed in pure water, the volume of the cell-sap increased again, and the shrunken protoplasmic lining returned to its original size and place.

Thirty years later DE VRIES continued these experiments on a quantitative basis, taking as a standard the strength of a solution which was *just* sufficient to cause the protoplasmic lining to contract away from the cell-wall. By comparing the concentrations of solutions of different substances which were just able to produce this effect ("*isotonic*" solutions), he found that these concentrations were in the ratio of the chemical equivalents of the substances dissolved.

These phenomena were apparently connected with those observed by DUTROCHET (1726), the ABBÉ NOLLET (1748), PARROT (1803), and FISCHER (1822), on the passage of water through a parchment membrane into a solution of alcohol, cane-sugar or copper sulphate. If a solution of cane-sugar be placed in a thistle-funnel the mouth of which is closed by a piece of parchment or pig's bladder drawn tightly over it, and the funnel then immersed in a beaker of water, it will be

found that the level of the liquid in the stem of the funnel gradually rises (Fig. 25). When a solvent passes through a membrane as the water has clearly passed through in this case, the phenomenon is called *osmosis*, from the Greek ὠσμός, a push.

While water has passed through the membrane into the solution, no sugar can be detected in the water outside the funnel; hence the membrane is *semi-permeable*—that is, permeable to the solvent but impermeable to the solute.

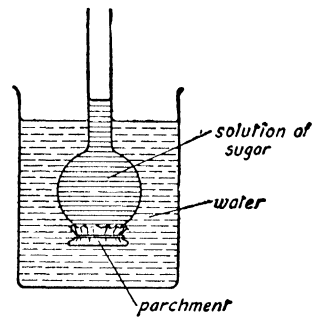


FIG. 25.

Up to the year 1867, the only semi-permeable membranes used were natural ones, such as pig's bladder in the above experiment and the protoplasmic lining of plant cells in the experiments carried out by Pringsheim. But in 1867 TRAUBE showed that artificial semi-permeable membranes could be prepared, the best of which was found to be copper ferrocyanide in the gelatinous state in which it is formed by precipitation from a solution of copper sulphate by addition of potassium ferrocyanide solution.

If a drop of a concentrated solution of copper sulphate is carefully introduced by means of a pipette into a dilute solution of potassium ferrocyanide, the drop becomes surrounded with a thin film of copper ferrocyanide. This acts as a semi-permeable membrane, and as the copper sulphate solution is concentrated and that of the potassium ferrocyanide dilute, it will be found that the drop gradually increases in size by the passage of water through the membrane into the copper sulphate solution inside.

PFEFFER made use of this artificial semi-permeable membrane to conduct quantitative experiments on osmosis. He published his results in 1877 in a work entitled *Osmotische Untersuchungen*. In Nollet's experiment with the thistle funnel, it will be remembered, a column of liquid was sup-

ported, against the action of gravity, in the stem of the funnel. This column of water is therefore exerting a hydrostatic pressure downwards, due to its weight. What is the force which balances this pressure, and keeps the column up ? The answer was given as "*the osmotic pressure of the solution.*" This, of course, is not an explanation of the phenomenon, it is only a means of defining "osmotic pressure." The osmotic pressure in the above case will be equal in magnitude to the hydrostatic pressure of the column of liquid in the stem of the funnel. It was found that the osmotic pressures of even moderately concentrated solutions were very high, while those of very concentrated solutions often reached surprising values. Thus the osmotic pressure of a solution of cane-sugar containing 171 grams of sugar in 1 litre of water was found to be over 11 atmospheres. Now these great pressures rendered the use of the very delicate artificial membranes impossible, and that of the natural membranes difficult. Traube therefore devised a plan for strengthening the copper ferrocyanide membrane. He soaked a porous pot in distilled water, then filled it with potassium ferrocyanide solution and placed it for some time in copper sulphate solution. The two solutions diffused into the wall of the pot and met in the middle, when a film of copper ferrocyanide was deposited in each pore. The pot was then washed in distilled water. The wall of the pot was now a sort of reinforced semi-permeable membrane of copper ferrocyanide, and the film deposited in this way was capable of withstanding high pressures. A further improvement was effected by MORSE in 1904, who used an electrolytic method for depositing the copper ferrocyanide in the pot. The membrane may also be strengthened by making it under pressure.

If a porous pot prepared in this way is filled with the solution whose osmotic pressure is to be determined, closed with a stopper carrying a tube connected to a manometer or pressure-gauge, and then surrounded by water, the latter will pass in and the mercury in the manometer will rise (Fig. 26). After the rise has stopped the osmotic pressure may be read off the scale attached to the manometer.

It is better in this experiment to add mercury to the open limb of the manometer until the pressure is just sufficient to prevent the water from entering the pot; the osmotic pressure may then be read off as before. The great pressures developed, however, often burst this apparatus, and therefore other forms have been invented. The EARL OF BERKELEY and E. G. J. HARTLEY (1904) placed the solution in a porous tube containing the copper ferrocyanide membrane in its walls, and enclosed the tube in a strong cylindrical vessel filled with water. Pressure was then applied to the solution by means of a narrow tube (Fig. 27) until the level of the liquid in the latter showed no tendency either to rise or to fall, but remained steady. The pressure necessary to produce this equilibrium is equal to the osmotic pressure of the

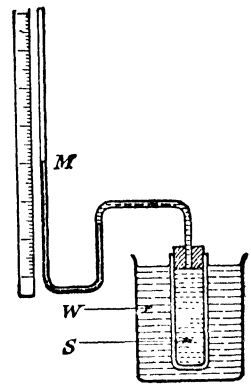


FIG. 26.—Diagram of Apparatus for Measuring Osmotic Pressure.
W = Water. S = Solution. M = Manometer.

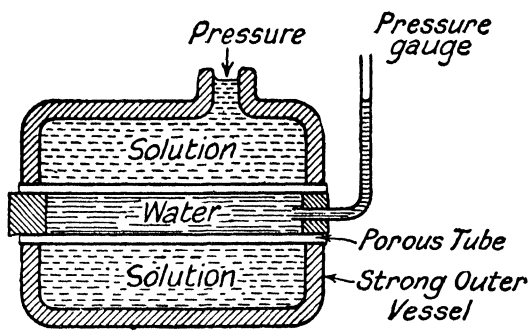


FIG. 27.

solution. This apparatus eliminates the danger of bursting the porous vessel.

Accurate measurements of osmotic pressure enabled VAN'T HOFF in 1887 to show that the *osmotic pressure of substances in solution*—

(i) *was directly proportional to the concentration of the solution*, for the same solvent and same solute, and at constant temperature ;

(ii) *was directly proportional to the absolute temperature* ; and

(iii) at constant temperature was *the same for all solutions of non-electrolytes that contain the molecular weight in grams of the solute in the same volume of solvent.*

From (i) it follows that the osmotic pressure is *inversely* proportional to the *volume* of the solution. Hence we see that there is a very close analogy between gas-pressure and osmotic pressure, as the following table shows :—

	GASES	SOLUTIONS
i	$P \propto \frac{1}{V}$ if T is constant [*Boyle*].	Osmotic $P \propto \frac{1}{V}$ if T is constant.
ii	$P \propto T$ if V is constant.	Osmotic $P \propto T$ if V is constant.
iii	Equal numbers of molecules confined in equal volumes exert equal pressures if T is constant. [Follows from Avogadro's Hypothesis.]	Equal numbers of molecules in the same volume of solvent exert equal *osmotic* pressures if T is constant.

Further investigation proved that *if the molecular weight in grams of a non-electrolyte is dissolved in* 22·4 *litres of solvent, the solution will exert an osmotic pressure of* 760 *mm. at* 0° *C.* Thus the analogy with gases is complete, for the G.M.V. of a gas at N.T.P. is 22·4 litres.

We may therefore write for solutions, as for gases,

$$PV = RT$$

where P in this case is the *osmotic* pressure. This obviously gives us another method of determining the molecular weights

of non-electrolytes, for *the M.W. of such a substance will be the number of grams of it which when dissolved in 22·4 litres of a solvent will produce a solution having an osmotic pressure of 760 mm. at 0° C.*

Example.—1·05 grams of a substance when dissolved in 112 c.c. of water gave an osmotic pressure of 940 mm. at 15° C. What is the Molecular Weight ?

If 1·05 grams in 112 c.c. give a pressure of 940 mm. at 15° C. (= 288° Abs.), they will give a pressure of $\frac{940 \times 273}{288}$ mm. at 0° C.

∴ 1·05 grams in 22,400 c.c. will give a pressure of

$$\frac{940 \times 273 \times 112}{288 \times 22{,}400} \text{ mm. at } 0° \text{ C.}$$

And since a pressure of $\frac{940 \times 273 \times 112}{288 \times 22{,}400}$ mm. at 0° C. is given by 1·05 grams.

∴ a pressure of 760 mm. is given by

$$\frac{1{\cdot}05 \times 760 \times 288 \times 22{,}400}{940 \times 273 \times 112} = 1791,$$

and this will be the molecular weight.

In practice, however, the difficulties of determining osmotic pressures accurately are so great that this method of finding molecular weights is seldom used, since simpler methods are available. The cause of osmotic pressure and the reason for the semi-permeability of the membranes are unknown, though various theories have been advanced.

It should be noted that, just as PV = RT is only approximately true for gases, the deviations becoming considerable at high pressures, so is it only roughly true for osmotic phenomena. At high concentrations abnormalities become very marked.

Phenomena related to Osmotic Pressure.

1. *Depression of the Freezing-Points of Solutions.*—Every pure liquid has a definite freezing-point. (It would be more correct to say *melting-point*, for on cooling a liquid it often happens that the temperature falls several degrees below the melting-point of the solid form before freezing begins. When freezing has once started, however, the temperature

at once jumps up to the "true" freezing-point; that is, the temperature at which the solid and liquid forms can exist in equilibrium. On the other hand, it is impossible to heat a solid above its melting-point without melting it. It should be understood, therefore, that in this connection, the "true" freezing-point, or melting-point, is meant.) If a substance is dissolved in a liquid, the freezing-point of the solution is lower than that of the pure solvent, and, for the same solvent and same solute, the extent of the lowering is directly proportional to the concentration. This is called *Blagden's Law*. Thus, if a 1 per cent. solution of a substance caused a depression or lowering of the freezing-point of 2·5°, a 2 per cent. solution of the same substance in the same solvent would depress the freezing-point by 5·0°, and so on. [The "depression" is the difference, in degrees, between the two freezing-points.] There is obviously an analogy, then, between depression of the freezing-point and osmotic pressure, since both are directly proportional to the concentration. Further investigation confirmed this, and showed that the depression of the freezing-point of a solution was indeed directly proportional to its osmotic pressure.

It will not surprise us, therefore, to learn that in 1883 RAOULT showed that, for non-electrolytes, the lowering of the freezing-points of solutions of these substances in the same solvent was directly proportional to the molecular concentrations, since, as we have seen, the osmotic pressure is also proportional to the molecular concentrations. To make Raoult's discovery quite clear, let us consider the following example :—

Suppose that in each of five beakers, i, ii, iii, iv and v, we place 1,000 c.c. of water. The freezing-point of this water will be 0° C. Let us now take the molecular weights in grams of the five following non-electrolytes—

Urea	(= 60 grams)	Alcohol	(= 46 grams)
Cane-sugar	(=342 grams)	Resorcinol	(=110 grams)
Grape-sugar	(=180 grams)		

and place the urea in i, the cane-sugar in ii, the grape-sugar

in iii, the alcohol in iv, and the resorcinol in v, and stir until they have completely dissolved. If we now determine the freezing-points of the five solutions, we find that in every case the freezing-point is — 1·86° C. Evidently we have here another method for determining the molecular weight of a non-electrolyte. All that we need do is to take another beaker with 1,000 c.c. of water in it, and find how many grams of the substance we have to dissolve in the water to get a solution that will freeze at — 1·86° C. This number of grams will be the molecular weight of the substance. A consideration of Blagden's Law, however, will show us that since the depression in solutions of the same substance is directly proportional to the concentration, we need in practice only to dissolve a known weight of the substance in a measured volume of solvent, and note the depression caused. We can then work out the result by proportion.

Thus, 0·346 grams of a substance dissolved in 10·3 c.c. of water gave a depression of the freezing-point of 0·21°. Find the molecular weight of the substance.

0·346 gms. dissolved in 10·3 c.c. produced depression 0·21°

∴ 0·346 gms. ,, ,, 1,000 ,, will give ,,

$$\text{of } \frac{0{\cdot}21 \times 10{\cdot}3^\circ}{1{,}000} \text{ (Blagden's Law).}$$

If a depression of $\frac{0{\cdot}21 \times 10{\cdot}3^\circ}{1{,}000}$ is caused by 0·346 gms. in 1,000 c.c.,

then a depression of 1·86° is caused by $\frac{0{\cdot}346 \times 1{\cdot}86 \times 1{,}000}{0{\cdot}21 \times 10{\cdot}3}$ gms.

$$= 298 \text{ gms.}$$

This is the molecular weight.

The freezing-point or *Cryoscopic* method of determining Molecular Weights is extremely useful. For substances that are not soluble in water other solvents may be used, such as benzene, acetic acid, and, for metals, mercury. In books of tables are given the " Constants " for 100 grams of these and other solvents, that is, the depression of the freezing-point produced by dissolving the molecular weight in grams of any non-electrolyte in 100 grams of the solvent. The numbers for water, benzene, acetic acid, and mercury, are as follows:

Solvent.	*Depression (K) for 100 grams of Solvent.*
Water	18·6°
Benzene	49°
Acetic acid	39°
Mercury	425°

The depression for 100 c.c. can be worked out if the specific gravity of the solvent is known. Thus, the S.G. of benzene is 0·8784, therefore 100 grams of benzene occupy 113·84 c.c., hence the constant for 100 c.c. of benzene

$$= \frac{49 \times 113{\cdot}84}{100} = 55{\cdot}8.$$

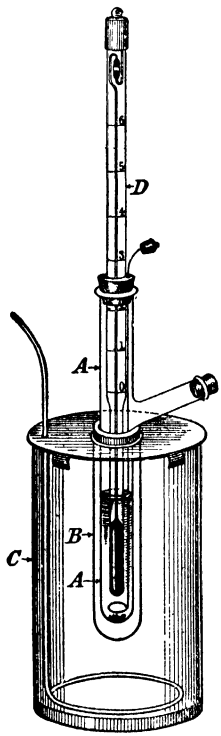


FIG. 28.—Freezing Point Apparatus.

A. Tube containing solvent. *B*. Jacket tube. *C*. Thick glass jar. *D*. Beckmann thermometer.

It is necessary to say that Raoult's Law of Depressions holds only for dilute solutions, hence the above values are *calculated* from the results of dilute solutions, according to Blagden's Law. It can also be shown theoretically that K for 100 grams of a solvent $= \frac{2T^2}{100L}$ where T = the freezing-point of the solvent on the absolute scale, and L is its latent heat of fusion in calories. Thus for water T = 273 and L = 79.

We can now work out a general formula for this method of molecular-weight determination—

Suppose w grams of a substance in S gms. of solvent give a depression $t°$

$\therefore$ 1 gram of a substance in S gms. of solvent gives a depression $\frac{t}{w}$

$\therefore$ M gms. (Molec. Wt.) of a substance in S gms. of solvent give a depression $\frac{t}{w} \times M$.

$\therefore$ M grams of a substance in 1 gm. of solvent

$$\text{give a depression of } \frac{t}{w} \times \text{M} \times \text{S}$$

$\therefore$ M grams of a substance in 100 gms. of solvent give

$$\text{a depression } \frac{t \,.\, \text{M} \,.\, \text{S}}{w \times 100} = \text{K}$$

$$\therefore \frac{t \,.\, \text{M} \,.\, \text{S}}{w \times 100} = \text{K}$$

$$\text{and } \text{M} = \frac{w \,.\, \text{K} \,.\, 100}{t \,.\, \text{S}}.$$

Example.—(*a*) Tammann showed in 1889 that 0·022 gms. of sodium dissolved in 100 gms. of mercury gave a depression of the freezing-point of mercury of 0·39°.

$$\therefore \text{M} = \frac{w \,.\, \text{K} \,.\, 100}{t \,.\, \text{S}} = \frac{0{\cdot}022 \times 425 \times 100}{0{\cdot}39 \times 100}$$

$$= 23{\cdot}8$$

Therefore the molecular weight of sodium *in mercury* is 23·8, i.e. here the molecular weight is the same as the atomic weight. Note that this gives us no information as to the molecular weight of *solid* sodium.

(*b*) 0·53 gms. of a solid dissolved in 51·5 gms. of benzene lowered the freezing-point of the latter by 0·61°.

$$\therefore \text{M} = \frac{w \,.\, \text{K} \,.\, 100}{t \,.\, \text{S}} = \frac{0{\cdot}53 \times 49 \times 100}{0{\cdot}61 \times 51{\cdot}5}$$

$$= 82{\cdot}7.$$

N.B.—As remarked before, it is much better to work out examples from *first principles* and not from a formula. Do not use the above formula, $\text{M} = \frac{w.\text{K}.100}{t \,.\, \text{S}}$, until you know exactly what it means, how to get it, and how to work out your results without it.

2. *Lowering of the Vapour Pressure of Solutions.*—At a constant temperature, the vapour pressure of a liquid is constant.[1] If a substance is dissolved in the liquid, the vapour pressure of the solution is lower than that of the pure liquid, and it has been shown by TAMMANN and RAOULT that, for non-electrolytes as solutes, the G.M.W. of a substance dis-

[1] Provided that the vapour is in contact with its liquid.

solved in a constant weight of the same solvent produces a constant relative depression of the vapour pressure. The "relative" depression is $\frac{f-f'}{f}$, where f is the vapour pressure of the pure solvent and f' that of the solution. Raoult found by experiment that the formula that agreed best with his observed results was $\frac{f-f'}{f} = \frac{n}{N+n}$, where n = number of gram-molecules of solute and N = number of gram-molecules of solvent. Hence by vapour-pressure measurements we can calculate molecular weights.

Example.—3·19 gms. of a substance dissolved in 115 gms. of benzene gave a solution of vapour pressure 731·5 mm. The vapour pressure of pure benzene at the same temperature was found to be 750 mm., and the molecular weight of benzene = 78. Find the molecular weight of the substance.

$$\frac{f-f'}{f} = \frac{750-731{\cdot}5}{750} = \frac{18{\cdot}5}{750}$$

$$N = \frac{115}{78} \quad \therefore \frac{n}{N+n} = \frac{n}{\frac{115}{78}+n} = \frac{18{\cdot}5}{750}$$

$$\frac{n}{1{\cdot}47+n} = \frac{18{\cdot}5}{750}$$

$$\therefore 750\,n = 27{\cdot}2 + 18{\cdot}5\,n$$

$$\therefore 731{\cdot}5\,n = 27{\cdot}2$$

$$\therefore n = 0{\cdot}037$$

$$\text{But } n = \frac{3{\cdot}19}{\text{Molecr. Wt. of Substance}}$$

$$\therefore \text{M. Wt.} = \frac{3{\cdot}19}{0{\cdot}037}$$

$$= 86.$$

Vapour pressures are difficult to determine accurately in practice, hence this method is seldom employed, but since lowering of vapour pressure is, over short ranges, roughly proportional to the elevation of the boiling-point thereby

produced, an *ebullioscopic* method of finding molecular weights has been elaborated.

Liquids boil when their vapour pressures become equal to the external pressure, the normal value of which is 760 mm. In Fig. 29 AB represents the vapour pressure curve of the pure solvent, CD and EF the V.P. curves of two solutions, EF being that of the more concentrated.

When the vapour pressures of the liquids reach 760 mm. they will boil, but the solvent will reach this pressure at a

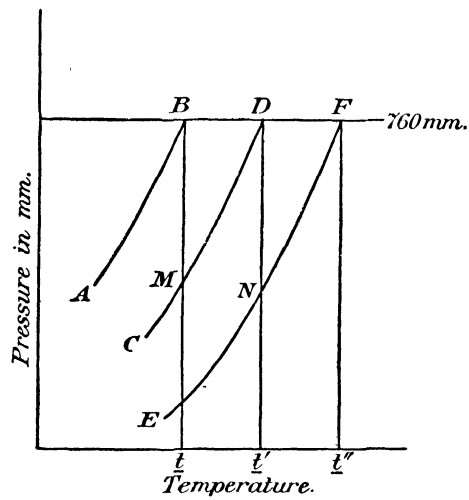


FIG. 29.

lower temperature (t) than the first solution (t') and this again at a lower temperature than the more concentrated (t''), t, t', and t'' represent the boiling-points of the solvent, first solution, and second solution respectively. Now it is found experimentally that *over short ranges* of temperature, the curves AB, CD, and EF are practically parallel. The vapour pressures at t are tB for the solvent, tM for the first solution, and tE for the second. Therefore the relative lowering of the vapour pressures are, for the first solution,

$\frac{tB - tM}{tB}\left(= \frac{BM}{tB}\right)$, and for the second $\frac{tB - tE}{tB}\left(= \frac{BE}{tB}\right)$. Therefore the ratio of the relative lowerings for the two solutions is $\frac{BM}{tB} / \frac{BE}{tB} = \frac{BM}{BE}$. But since AB, CD, and EF are practically parallel, $\frac{BM}{BE}$ is practically equal to $\frac{BD}{BF}$. In other words, since BD and BF are equal to $t' - t$ and $t'' - t$ respectively, the relative depressions of the vapour pressures of these two solutions are in the same ratio as the elevations of their boiling-points ($t' - t$ and $t'' - t$).

We can, therefore, use the elevation of the boiling-point of a solution exactly as we use the depression of the freezing-point, for purposes of molecular weight determination. The formula, worked out in exactly the same way, is $M = \frac{w.K.100}{t.S}$, where w is the weight of substance taken, K the constant elevation of the boiling-point for 100 grams of the solvent, t the observed elevation, and S the weight of solvent used. The constants for 100 grams of different solvents are here given—

Solvent.	*K, Constant for 100 Grams.*
Water	5·2
Alcohol	11·5
Ether	21·0
Benzene	25·7

Here also $K = \frac{2T^2}{100L}$, where T is the boiling-point of the pure solvent in degrees absolute, and L is the latent heat of *vaporization* of the solvent, in calories.

An apparatus used for the determination of molecular weights by boiling-point elevation is shown in Fig. 30.

General Remarks.—The osmotic pressure laws, and the relationships between the molecular concentrations of solutions and the depressions of the freezing-point and vapour pressure and elevation of the boiling-point, hold good only

for non-electrolytes and dilute solutions. We shall see later on (Chap. XIII) that the exceptions and irregularities that were discovered in the case of electrolytes gave rise to a great

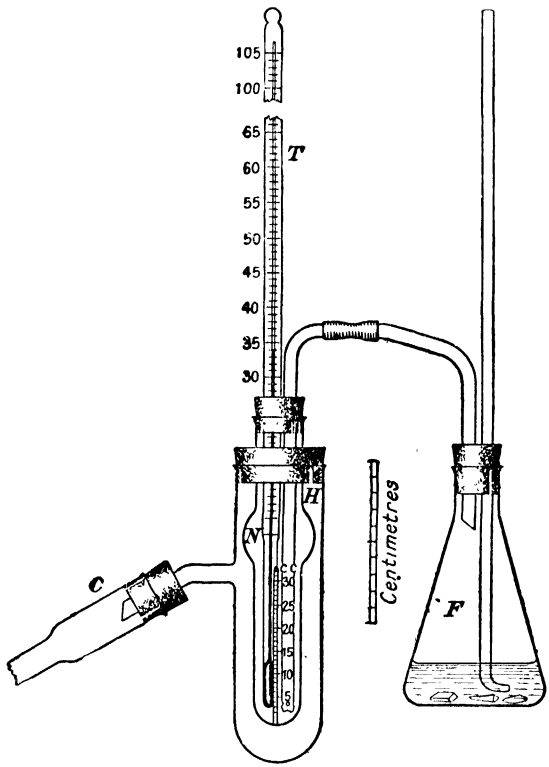


FIG. 30.—Boiling-Point Apparatus.

F. Flask for boiling liquid. *N*. Graduated Boiling Tube. *H*, *C*. Exit for vapours. *T*. Thermometer.

deal of theoretical speculation, much of which has been supported by experimental results.

QUESTIONS

1. What do you understand by the *osmotic pressure of a solution*?
2. Describe a method of measuring osmotic pressure.

3. Compare and contrast osmotic pressure with gas pressure.

4. What is the principle of Raoult's cryoscopic method of determining molecular weights ?

5. What physical properties of a solution are related to the osmotic pressure of the solution ? Of what practical value is the relationship ?

6. 0·6418 gm. cane sugar is dissolved in water and made up to 56·8 c.c. at a temperature of 15° C. Find, to the nearest mm. of mercury, the osmotic pressure produced. [Mol. wt. of cane sugar is 342.]

7. Find the osmotic pressure, in atmospheres, produced by a 13 per cent. solution of ammonia at 16° C. [Mol. wt. ammonia = 17.]

8. Find the percentage strength of a solution of cane sugar which at 7° C. is isotonic with a 2 per cent. solution of dextrose at 27° C. [Mol. wts.—Cane sugar, 342. Dextrose, 180.]

9. 0·4277 gm. of an organic compound is dissolved in water and made up to 100 c.c. at 12° C. The osmotic pressure produced is equal to 380 mm. of mercury. Find the molecular weight of the compound to the nearest whole number.

10. At what temperature is a 2 per cent. solution of glycerol isotonic with a 4·5 per cent. solution of glucose at 15° C., and what is the osmotic pressure in atmospheres of the isotonic solutions ? [Molecular wts.—Glycerol, 92. Glucose 180.]

11. Find, to the nearest atmosphere, the osmotic pressure of an aqueous solution of an organic compound, at its freezing-point, which is — 0·33° C. The molecular depression of the freezing-point of water is 18·6°.

12. 0·3132 gm. fructose was dissolved in 14·5 gms. water. The freezing-point of the solution was found to be — 0·223° C. The molecular depression for water is 18·6°. Find the molecular weight of fructose to the nearest whole number.

13. The freezing-point of a solution of 0·4813 gm. acetone in 42·8 gms. acetic acid is found to be 15·84° C. The freezing-point of pure acetic acid is 16·60° C., and its molecular depression 39°. Find the molecular weight of acetone.

14. A benzene solution containing 2 gms. of an organic compound to 100 gms. of the solvent is found to freeze at 4·07° C. Given that the molecular weight of the compound is 120 and the freezing-point of pure benzene 4·90° C., find the molecular depression of benzene.

15. A solution of 3 gms. of an organic compound in 100 gms. of phenol freezes at 38·94° C. Given that the molecular weight of the compound is 220 and the molecular depression of phenol 73·8°, find the freezing-point of pure phenol.

16. It is found that an aqueous solution of hydrogen peroxide freezes at — 0·35° C. Find the weight of hydrogen peroxide present per 100 gms. of water, given that the molecular depression of water is 18·6°. [Molecular weight of hydrogen peroxide = 34.]

17. Given that the fall in freezing-point of a solution containing 0·9152 gm. of an organic compound of molecular weight 59, in 25·0 gms. benzene is 2·42°, find the molecular weight of another compound, 1·5480 gms. of which when dissolved in 48·0 gms. benzene lower the freezing-point by 0·91°.

CHAPTER XII

CHEMICAL EQUILIBRIUM

Chemical Affinity.—It is characteristic of human nature to ask *why* a thing happens before investigating *how* it happens. Yet it is by finding out the exact way in which a thing happens that we are most often enabled to find out the reason for its occurrence. Chemists, however, being men of like passions with ourselves, began to make theories about the cause of chemical change long before they were in a position even to investigate thoroughly the progress of chemical change. EMPEDOCLES (*ca.* 500 B.C.) assumed that chemical changes were brought about by the love or hate which various substances had for one another; two substances that "loved" one another would unite to form a third substance, while decompositions represented the separation of substances that hated one another. As a matter of fact, we know very little more about the *cause* of chemical reaction at the present day than Empedocles did, but we conceal our ignorance in a much more imposing way.

In the Middle Ages, it was considered that substances which would combine together were more or less similar or related to one another—mercury, for example, readily dissolves metals—and in order to express this relationship the word *affinity* (from the Latin *affinitas*, relationship) was used. Substances therefore combine with one another on account of their chemical affinity. It was observed, however, by later chemists that in general it is substances which are most opposed in qualities that most readily react together, e.g., sulphur and iron, but the term *affinity* by then had become well estab-

lished, and has remained to the present day as the name for that chemical force which brings about reaction. The exact nature of this force still remains a mystery. NEWTON supposed that it might be gravitational; others have considered it to be electrical—a view which is now generally accepted. The electrical theory was warmly supported by BERZELIUS at the beginning of the nineteenth century, who pointed out that in a large number of cases it was elements of dissimilar electrochemical character which most readily combined together.

The "affinity" of acids for alkalis had of course been observed very early, and MAYOW (1674) explained the liberation of ammonia from sal-ammoniac, by the action of potash, by the greater affinity that the acid possessed for potash than for ammonia. Further elaboration of the theory led to the production, by GEOFFROY (1718) and BERGMANN (1775) of *Tables of Affinity*, in which substances were arranged in their supposed "order of affinity," or the order in which they would turn one another out of combination in a particular reaction. Thus copper will be precipitated if iron is placed in a solution of copper sulphate, therefore the affinity of iron is greater than that of copper, in this reaction. In general, it was supposed that if the element A has a greater affinity for C than B has, then A will decompose the compound BC *completely*, forming AC with liberation of B.

In the light of this theory, let us consider the reaction between steam and iron. If steam be passed over heated iron, iron oxide and hydrogen are formed, therefore the affinity of iron for oxygen must be greater than that of hydrogen for oxygen, for the iron has turned the hydrogen out—

$$3Fe + 4H_2O = \underset{\text{Magnetic oxide of iron.}}{Fe_3O_4} + 4H_2.$$

But if we pass hydrogen over heated iron oxide we shall find that steam is formed and iron left. Therefore the affinity of hydrogen for oxygen is greater than that of iron, which is the opposite conclusion to that at which we arrived before!

Similar phenomena were noticed by BERTHOLLET in 1801, who deduced from his results that there must be another important factor in chemical reaction, and suggested that this factor was the *concentrations* of the substances taking part. Thus in the above experiment, in the first case the concentration of the steam is great and that of the hydrogen negligible, since the latter is carried off as soon as formed, by the current of steam. In the second case, the hydrogen is in great concentration and the steam formed gets swept away. **Berthollet's Law**, then, may be stated in these words: *In a chemical reaction, each substance will react according to* (*a*) *its affinity*, (*b*) *its concentration.*

Chemical Equilibrium.—We have seen that the paradox of the reactions between iron, iron oxide, steam and hydrogen can be explained by the fact that in one case the hydrogen and in the other the steam are swept away from the sphere of action. What will happen if some iron and steam are heated together in a closed vessel? Experiments made to test this showed that at first iron oxide and hydrogen were formed, but that after a time no further change could be detected, although some of the iron and some of the steam were still left. However long the vessel was kept, at the same temperature, the composition of the mixture inside remained unaltered; in other words, a *state of equilibrium* has been reached. As, however, steam and iron, and iron oxide and hydrogen, are present, chemical reactions must still be going on, and the equilibrium is therefore explained by assuming that as much steam is formed in a given time as is decomposed in that time; that is, the speed of the one reaction is equal to the speed of the other, and the equilibrium is a *kinetic* equilibrium.

The speed of a chemical change may thus be defined as equal to $\frac{\text{weight of substance changed}}{\text{time taken}}$.

Reactions which, like that represented by the equation

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

can proceed either way, are called *reversible reactions*, and it

is usual in such cases to replace the sign of equality by the "reversed arrows" sign, $\rightleftharpoons$, e.g.,

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

When the conditions are so arranged that both the forward and the backward reactions are proceeding at the same speed, and equilibrium is thus established, the action is called a *balanced action.*

Many reactions are reversible, and it is possible that if we could produce the right conditions, all would be so; but since in the present state of our knowledge, "all the king's horses and all the king's men could never put" the products of the explosion of trinitrotoluene "together again," it is convenient to distinguish between reversible and irreversible reactions.

Examples of reversible reactions.

(i) If concentrated hydrochloric acid is poured on antimony sulphide, sulphuretted hydrogen and antimony chloride are formed—

$$Sb_2S_3 + 6HCl = 2SbCl_3 + 3H_2S.$$

If, however, sulphuretted hydrogen is passed through a solution of antimony chloride, the reverse reaction takes place, and antimony sulphide is precipitated.

(ii) If a mixture of 2 volumes of hydrogen and 1 volume oxygen is ignited, an explosion occurs and steam is formed—

$$2H_2 + O_2 = 2H_2O.$$

But if a stream of steam is passed over a white-hot platinum wire, some of the steam is split up again into hydrogen and oxygen.

(iii) "Dissociation" is a reversible reaction (Chap. IX).

(iv) The action of an organic acid upon an alcohol to form an ester, e.g., acetic acid upon ethyl alcohol—

$$CH_3.COOH + C_2H_5OH \rightleftharpoons \underset{\text{Ethyl acetate.}}{CH_3.COOC_2H_5} + H_2O.$$

If ethyl acetate is heated with water, the reverse change slowly occurs until equilibrium is set up.

(v) The decomposition of calcium carbonate by heat—

$$CaCO_3 \rightleftharpoons CaO + CO_2.$$

Guldberg and Waage's Law or The Law of Mass Action.

In 1850 WILHELMY showed that the rate of a chemical change at a given moment is directly proportional to the concentration of the reacting substances (Wilhelmy's Law). The work of Berthollet and Wilhelmy was generalized and put into a more definite form by GULDBERG AND WAAGE, as the *Law of Mass Action.*

This states that the rate of a chemical change at a given moment is directly proportional to the concentrations at that moment of the substances taking part in the change. The "concentration" for this purpose is usually expressed in gram-molecules per litre and is then called the *active mass* of the substance.

In its general form, then, the Law of Mass Action may be expressed as follows. If n molecules of A, of active mass M, n' molecules of B, of active mass M′, n'' molecules of C, of, active mass M″, etc., take part in a chemical change, then the rate of the reaction at the moment when the active masses have the above values is proportional to

$$M^n \times M'^{n'} \times M''^{n''} \times \text{etc.}$$

Consider the action $M + N = P$.

Let the active mass of M be a and that of N be b. Then the rate of change of M and N into P will be proportional to $a.b$, or equal to $a.b \times$ a constant, that is,

$$\text{rate of above reaction} = k.ab.$$

Similarly the rate of the reaction $2M + N = R$ will be $k.a^2b$ at the moment when the active mass of M is a and that of N is b.

If we have a reversible reaction, such as $A + B \rightleftharpoons C + D$, it is clear that equilibrium will be set up when the rates of the two opposing reactions are equal. Let the active masses of A, B, C, and D at equilibrium be respectively a, b, c and d. Then the rate of the forward reaction will be $k.ab$ and that of the reverse reaction $k'.cd$. These, however, are equal. Hence $k.ab = k'.cd$, or $\frac{ab}{cd} = K$.

It follows that if we now increase the concentration of

A or B the equilibrium should be shifted in such a way that more C and D are formed, a deduction which is very neatly proved by GLADSTONE'S experiment. When ammonium thiocyanate solution is added to ferric chloride solution, a blood-red colour is produced owing (it is said) to the formation of ferric thiocyanate—

$$FeCl_3 + 3NH_4CNS \rightleftharpoons Fe(CNS)_3 + 3NH_4Cl.$$

This action is reversible, as shown in the equation. Now if the Law of Mass Action and the deduction we have made from it are true, when we add ferric chloride to the liquid, the result should be an increase in the amount of ferric thiocyanate present, and therefore the liquid should become of a deeper tint. This is found to be the case ; addition of ammonium thiocyanate produces the same result ; addition of ammonium chloride makes the colour *paler*, because, the active masses on the right-hand side having been thus increased, the equilibrium is shifted in the direction of ferric chloride and ammonium thiocyanate.

To return to the action of iron on steam. Here we have an action,

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

that takes place between two substances which are in different physical states, one a solid and the other a gas. If at any moment the active mass of the iron is f and that of the steam s, then the velocity of the forward reaction will be $k.f^3s^4$, where k is a constant. But the iron can react with only that part of the steam which reaches its surface, while, owing to the movement of its molecules, any part of the steam is potentially capable of getting into contact with the iron. Now if we have a large surface of iron exposed, it is obvious that more steam may be in contact with it at a given moment ; but at the same time, this large surface of iron will also give a proportionately larger surface of iron oxide to be decomposed by the hydrogen present. What is the conclusion to be drawn from this ? It is surely this, that since any variation in the amount of solid present in a gaseous reversible reaction will affect the rates of *both* reactions equally,

the active mass of the solid may be taken as constant, whatever amount of it is present.

Thus, in the reaction $3Fe + 4H_2O \rightleftharpoons Fe_3O_4 + 4H_2$, let f be the active mass of the iron, s that of the steam, c that of the iron oxide, and d that of the hydrogen, at equilibrium.

$$\text{Then } k.f^3.s^4 = k'.c.d^4.$$

f and c, however, represent the active masses of solids and are therefore constant.

$$\therefore \frac{s^4}{d^4} \text{ is constant, whence } \frac{s}{d} \text{ is constant} = K.$$

This means that the percentage composition by volume of the gaseous mixture of steam and hydrogen which is in equilibrium with iron and iron oxide at a constant temperature is itself constant. Experiment shows that this is so.

K is called the *equilibrium constant* of the reaction.

Ester-formation.—Suppose we mix 1 gram-molecule of acetic acid with 1 gram-molecule of alcohol. A reaction occurs according to the equation

$$CH_3.COOH + C_2H_5OH \rightleftharpoons CH_3.COOC_2H_5 + H_2O.$$

Suppose that at a time t equilibrium has been set up, and that a gram-molecules of the acid have been transformed into ester. Let the volume of the liquid be V. Then the active mass of the acid at equilibrium $= \frac{1-a}{V}$, and it follows from the equation and from the fact that we started with 1 gram-molecule each of alcohol and acid, that the active mass of the alcohol is also $\frac{1-a}{V}$. Similarly, the active masses of the ester and water will be $\frac{a}{V}$ and $\frac{a}{V}$. But we have assumed that equilibrium has been set up

$$\therefore k \cdot \frac{1-a}{V} \cdot \frac{1-a}{V} = k' \frac{a}{V} \cdot \frac{a}{V}$$

$$\therefore \frac{k'}{k} = \frac{(1-a)^2}{a^2} \text{ or } \frac{(1-a)^2}{a^2} = K.$$

Hence by finding the weight of acid left at equilibrium we can calculate K.

By mixing acetic acid and alcohol in other proportions we can arrive at a general formula. In this example, only one molecule of each substance is concerned, so if we let C_1, C_2, C_3, and C_4 represent the active masses of acid, alcohol, ester, and water respectively at equilibrium, we get

$$k.C_1.C_2 = k'.C_3.C_4$$

$$\text{or } K = \frac{k'}{k} = \frac{\text{active mass of acid} \times \text{active mass of alcohol}}{\text{active mass of ester} \times \text{active mass of water}}$$

Analysis of various equilibrium mixtures of these four substances will enable us to test the theory by observing whether the values for K actually obtained are really constant. Experiments have shown that this is so. The value of K here is about 0·25.

Dissociation of Hydrogen Iodide.—It will be remembered that hydrogen iodide dissociates on heating.

$$2HI \rightleftharpoons H_2 + I_2,$$

and that since no change in volume occurs we concluded that, according to Le Chatelier's principle, pressure changes should have no effect on the degree of dissociation at a constant temperature. This can be shown also by the Law of Mass Action.

Suppose that at a certain temperature equilibrium has been attained in the above action. Let the active mass of hydrogen iodide be $\frac{a}{V}$, and that of hydrogen $\frac{b}{V}$, whence that of iodine must clearly also be $\frac{b}{V}$. Then

$$k \cdot \left(\frac{a}{V}\right)^2 = k' \cdot \left(\frac{b}{V}\right)^2 \quad \therefore \frac{k'}{k} = \frac{a^2}{b^2}$$

the V's cancelling out. Hence the proportion of hydrogen iodide dissociated is independent of the volume, and therefore of the pressure, if the temperature is constant. In cases where the V's do not cancel, we should expect to find that

changes of pressure would affect the degree of dissociation e.g.,

Nitrogen Peroxide.—$N_2O_4 \rightleftharpoons 2NO_2$. Suppose that equilibrium has been set up, and that the volume of the gas is V. Let there be a gm. molecules of N_2O_4 and b gm. molecules of NO_2. Then the active mass of N_2O_4 is $\frac{a}{V}$, and that of the NO_2 $\frac{b}{V}$.

$$\therefore k \cdot \frac{a}{V} = k' \cdot \left(\frac{b}{V}\right)^2$$

(since there are TWO NO_2 molecules concerned).

$$\therefore \frac{k'}{k} = \frac{a}{V} \times \frac{V}{b} \times \frac{V}{b}$$

$$= \frac{Va}{b^2}$$

Here, then, the degree of dissociation will depend upon the volume and therefore on the pressure.

Phosphorus Pentachloride.—$PCl_5 \rightleftharpoons PCl_3 + Cl_2$. At equilibrium let the volume of the gas be V, the number of gram-molecules of phosphorus pentachloride a, and that of phosphorus trichloride and chlorine b of each. Then the respective active masses are $\frac{a}{V}$, $\frac{b}{V}$, and $\frac{b}{V}$, and, as in the case of nitrogen peroxide, $\frac{k'}{k} = \frac{a \cdot V}{b^2}$, or the degree of dissociation will depend upon the pressure. Now Wurtz showed that if phosphorus pentachloride is heated in an atmosphere of chlorine, the dissociation of the former was reduced. Does the law of mass action enable us to understand this? Take the above equation

$$k \cdot \frac{a}{V} = k' \cdot \frac{b}{V} \cdot \frac{b}{V}.$$

Suppose we add more chlorine, *keeping the volume constant.* Then

$$k \cdot \frac{a}{V} = k' \cdot \frac{b}{V} \cdot \frac{(b+c)}{V}$$

where c = number of additional gram-molecules of chlorine introduced. It is clear that $b(b + c)$ is greater than $b.b$, therefore to maintain equilibrium a must have increased, that is, more undissociated phosphorus pentachloride will have been formed and the degree of dissociation thereby diminished.

But suppose we add more chlorine at the same concentration, say nV volumes. Then

$$k \cdot \frac{a}{V + nV} = k' \cdot \frac{b}{V + nV} \cdot \frac{b(n + 1)}{V + nV}$$

whence

$$k \cdot \frac{a}{V} = k' \cdot \frac{b}{V} \cdot \frac{b}{V},$$

which is the same equation as before the addition of the chlorine ; hence, adding chlorine at the same partial pressure has no effect on the degree of dissociation. To obtain his results, therefore, Wurtz must have added the chlorine without allowing the volume to increase.

Questions

1. Write an account of *chemical affinity.*
2. What do you understand by a *reversible reaction* ? Give examples.
3. State the Law of Mass Action. Discuss the equilibrium between iron, iron oxide, steam, and hydrogen in terms of this law.
4. What would be the composition of the equilibrium mixture finally formed if 1 gram-molecule of ethyl alcohol were added to 4 gram-molecules of acetic acid ? K = 0·25.
5. Discuss the equilibria

(i) $2HI \rightleftharpoons H_2 + I_2$.
(ii) $PCl_5 \rightleftharpoons PCl_3 + Cl_2$.
(iii) $CaO + CO_2 \rightleftharpoons CaCO_3$.

CHAPTER XIII

THE IONIC THEORY

It will be remembered that the laws of osmotic pressure and the related effects (such as depression of the freezing-point, elevation of the boiling-point, etc.) were found to be true as far as *non-electrolytes* were concerned. When, however, electrolytes are used, discrepancies and anomalies occur, of such a nature that they at once recall the "abnormal" vapour densities of ammonium chloride and other substances. Thus, if we determine the molecular weight of common salt by the depression of the freezing-point, we shall find that in dilute solution the value obtained is not 58·5, as would be expected from the formula NaCl, but 29·25. Potassium nitrate treated in the same way gives a molecular weight of 50·5, whereas $KNO_3 = (39 + 14 + 48) = 101$; sulphuric acid, again, by the cryoscopic method gives a molecular weight not of 98 but of approximately 33. If more concentrated solutions of these substances are taken, the molecular weights determined by the cryoscopic or osmotic pressure methods gradually rise, finally in very concentrated solutions approaching more or less closely the values calculated from the formulæ.

We are at once reminded of the phenomena shown by nitrogen peroxide. Here at a temperature of 22° the vapour density is 46 and the molecular weight therefore 92, corresponding to the formula N_2O_4. As the temperature rises, the vapour density falls till a constant value of 23 is reached, corresponding to the formula NO_2. This phenomenon we explained by assuming that *dissociation* had taken place:

can we explain the abnormal results obtained above in this way? Apparently not, for it is difficult to see how sodium chloride could dissociate! VAN'T HOFF therefore proposed to shelve the difficulty for the time being by frank admission that electrolytes were exceptions to the osmotic-pressure laws, and introduced the use of a coefficient, i, to represent the ratio of the *observed* value of the depression of the freezing-point, elevation of the boiling-point, osmotic pressure, or lowering of the vapour pressure, to the corresponding value *calculated* from the generally-accepted formula of the electrolyte used. Thus, we should expect 58·5 gms. (the G.M.W.) of sodium chloride, when dissolved in 10,000 c.c. of water, to give a solution freezing at $-0{\cdot}186°$ C. The actually observed freezing-point of the solution is, however, $-0{\cdot}37°$ C. In this case

$$i = \frac{0{\cdot}37}{0{\cdot}186} = \text{about } 2.$$

i is therefore the number by which one has to multiply the value for the osmotic pressure, etc., calculated from the formula, in order to get the observed value, or

$$\frac{P \text{ observed}}{P \text{ calculated}} = i.$$

The osmotic pressure equation will now become

$$PV = i\,RT$$

Another point that had puzzled chemists for some time was that when the gram-equivalents of many inorganic, and some organic, acids were neutralized by addition of the gram-equivalent of either potash or soda, the number of calories evolved was roughly the same in every case. This was expressed by saying that the *heat of neutralization* of acids is approximately constant (about 13,800 calories). The actual figures for a few acids are given below—

Acid.	*Heat of Neutralization.*	*Acid.*	*Heat of Neutralization.*
Nitric	13,700	Hydriodic	13,700
Hydrochloric	13,700	Oxalic	14,100
Sulphuric	15,600	Citric	13,100
Hydrobromic	13,800		

This seemed a very significant fact, but no satisfactory explanation of it was forthcoming.

Meanwhile, the study of electrolysis had not been neglected. We may recapitulate here the main features of electrolysis as formulated by Faraday.

(i) The substances that appear at the electrodes are called ions.

(ii) The passage of the same quantity of electricity through solutions of electrolytes will liberate weights of different ions in the ratio of the chemical equivalents of those ions ; in other words, the electrochemical equivalent of a substance is equal to its chemical equivalent.

(iii) The gram-equivalent of any ion carries 96,000 coulombs. From this it follows that each atom or group of atoms forming the particles of an ion must carry a number of unit charges equal in number to its valency, if the charge carried by a hydrogen atom is taken as unit. For 1 gram of hydrogen must contain the same number of atoms as 63·5 grams of copper, since 63·5 is the atomic weight of copper. But the electrochemical and chemical equivalent of copper is 31·8, therefore 31·8 grams of copper and 1 gram of hydrogen carry 96,000 coulombs each, or $\frac{n}{2}$ atoms of copper carry as much electricity as n atoms of hydrogen, $\therefore$ 1 atom of hydrogen carries half as much electricity as 1 atom of copper. If therefore we take the charge carried by a hydrogen atom as unit, the copper atom will carry 2 charges ; now the valency of copper is 2. Similarly, the valency of the SO_4 group is 2, therefore the SO_4 group carries 2 unit charges.

Another well-known fact was that the products of electrolysis appear *simultaneously* at the two electrodes, however far apart these may be. Hence, in the electrolysis of dilute sulphuric acid, for example, a hydrogen atom liberated at a particular moment at the cathode may not belong to the same molecule of sulphuric acid as the SO_4 group which is discharged at the anode at the same moment.

To explain these phenomena, various theories had been suggested, but they all assumed that the actual disruption

of the molecules of the solute was caused by the current. If this were so, then a current would have to do work during electrolysis, to overcome the chemical forces holding the parts of the solute molecules together; now experiment showed that no more work is expended by the current in passing through a solution of an electrolyte than it would expend in passing through a wire of the same resistance, when, of course, no electrolysis takes place.

All these apparently unrelated phenomena of "abnormal" osmotic pressure, heats of neutralization, and electrolysis, were shown to be explicable by a general hypothesis, due to the Scandinavian chemist ARRHENIUS and called the *Ionic Theory* or *Theory of Electrolytic Dissociation* (1887). Arrhenius supposed that when an electrolyte is dissolved in water it splits up completely in very dilute solution and to a less extent in more concentrated solution, into charged atoms or groups of atoms which, by a transference of Faraday's word, were called *ions*. Each ion is assumed to exert an osmotic pressure equal to that exerted by an un-ionized molecule; that is, as far as osmotic pressure and the related phenomena are concerned, ions and molecules produce the same effect.

This theory met with a great deal of opposition at first, partly owing to a misunderstanding. Critics objected that it seemed ridiculous to suppose that free sodium atoms and free chlorine atoms were present in a solution of common salt! Arrhenius, however, never made such a supposition. He suggested that not *ordinary* sodium and chlorine atoms were present in the free state in a solution of common salt, but *very highly charged* sodium and chlorine atoms. Now there is no difficulty in assuming that these highly charged atoms, or *ions*, might be very different in behaviour from the same atoms uncharged, and when this point was made clear opposition became less. Even now, however, the ionic theory is not wholly without objection, though with the advance of our knowledge of the electrical structure of matter it has immeasurably strengthened its position and undoubtedly represents a triumph of man's insight into the phenomena of Nature.

The most serious difficulty which the ionic theory has to face, and which up to the present has received no entirely satisfactory explanation, is the *source of the energy required for ionization.* When 23 grams of sodium combine with 35·5 grams of chlorine to form 58·5 grams of sodium chloride, 97,800 calories are evolved. To ionize 58·5 grams of sodium chloride it would seem that in addition to the energy represented by the heat of formation one must supply the extra energy required to overcome the electrostatic attraction of the charged sodium and chlorine ions for one another.

A solution of an electrolyte is electrically neutral because it contains equal numbers of positive and negative ions. To represent an ion carrying one positive charge, a dot is placed after the symbol for the uncharged atom or group of the ion, thus $Na^{\cdot}$ represents an ion of sodium and $NH_4^{\cdot}$ an ion of ammonium. $Fe^{\cdot\cdot}$ and $Fe^{\cdot\cdot\cdot}$ represent a *ferrous* ion with 2 positive charges and a *ferric* ion with 3 positive charges respectively. In the same way dashes are used to indicate negative charges; thus Cl' is a chlorine ion carrying one negative charge and SO_4'' a "sulphate" group carrying 2 negative charges.

In a fairly concentrated solution of an electrolyte, some of the solute molecules are ionized and others remain un-ionized, and the fraction of the whole that exists as ions is called the *degree of ionization* of the electrolyte at the particular concentration (or "dilution") used. We may imagine that in the solution molecules of the electrolyte are continually being ionized and that ions are continually recombining to form un-ionized molecules. In other words, there is a state of kinetic equilibrium between ions and un-ionized molecules, e.g., in a solution of salt—

$$NaCl \rightleftharpoons Na^{\cdot} + Cl'.$$

The degree of ionization will be increased by further dilution and becomes practically equal to 1, with most electrolytes, at a dilution of about a thousandth normal, N/1,000. A degree of ionization of 1 means that the *whole* of the solute is ionized; this clearly could theoretically occur only at

infinite dilution. However, the degree of ionization at a dilution of N/1,000 so closely approaches to 1 that the difference is usually negligible.

Calculation of Degree of Ionization.—Two independent methods of determining the degree of ionization of a solute in solution will be described. As they give more or less concordant results, the probability of the "truth" of the ionic theory is thus rendered greater.

(i) Suppose that we take 1 gram-molecule of an electrolyte which would give 2 ions per molecule, i.e., a "binary" electrolyte, such as salt, potassium nitrate, or hydrochloric acid.

Let the degree of ionization be x.

Then we should have in solution $1 - x$ undissociated molecules and $2x$ ions. But molecules *and ions* behave in the same way as far as osmotic pressure and related effects are concerned; therefore the ratio of the observed osmotic pressure (etc.) of such a solution to the osmotic pressure (etc.) calculated on the assumption that 1 gram-molecule of the electrolyte has been dissolved without ionization would be $\frac{1 - x + 2x}{1}$. This ratio, however, is van't Hoff's coefficient i (p. 127). We may therefore write

$$i = \frac{1 - x + 2x}{1}$$

$$\text{or} \qquad x = i - 1.$$

Thus in the case of a binary electrolyte we may find the degree of ionization as follows:

(i) Calculate the *theoretical* depression of the freezing-point for the solution (d), from the formula of the electrolyte.

(ii) Find the *actual* depression (d') of the freezing-point for the solution, experimentally.

Then the degree of dissociation of the electrolyte at this concentration will be $i - 1$ or $\frac{d'}{d} - 1$

For an electrolyte that forms n ions per molecule the expression will become

$$i = \frac{1 - x + nx}{1}$$

$$\therefore \quad x = \frac{i - 1}{n - 1}.$$

(iii) The conducting power or "*conductivity*" of a solution will be directly proportional to (*a*) the number of ions present per c.c. and to (*b*) the speed with which they move. For different solutions of the same solute in the same solvent we may legitimately assume that (*b*) is constant at constant temperature. Hence the conductivity will be proportional to the number of ions per c.c. This will be increased by dilution in so far as the degree of ionization is raised, but will be decreased by dilution in so far as the solution becomes weaker. We can allow for the second of these factors in the following way. The *specific conductivity* of a solution is the conductivity between two parallel faces of a centimetre cube of it. Suppose that for a solution containing 1 gram-molecule of an electrolyte in g litres the specific conductivity is s. If we dilute the solution with an equal volume of water, and suppose for the moment that the degree of ionization remains the same, there will be only half as many ions per c.c. in the diluted solution as in the origina solution. Hence the specific conductivity will now be $\frac{sl}{2}$. But if we take the *molecular conductivity* as the specific conductivity of the solution multiplied by the number of litres of the solution containing 1 gram-molecule of the electrolyte, then the molecular conductivity of the first solution will be $s \times g$, say m, while that of the second will be $\frac{s}{2} \times 2g$, or $s \times g$, i.e., again m. In other words, by taking the *molecular* conductivity instead of the *specific* conductivity, we cut out any change due *merely* to dilution. Any change in molecular conductivity on dilution must therefore be due to a change in the *degree of ionization.*

If λ = molecular conductivity of a solution and α its degree of ionization,

then λ varies as α or $\lambda = \alpha \times$ a constant.

The value of the constant can be calculated from the conductivity at "infinite" dilution (practically, at a dilution of N/1,000), for here $\alpha = 1$ and λ then = the constant.

Hence, if x = the degree of ionization of a solute in a solvent at a given dilution, λ_d = the molecular conductivity of this solution, and λ_∞ = the molecular conductivity of an "infinitely" dilute solution of the solute in the same solvent, then

$$x = \frac{\lambda_d}{\lambda_\infty}.$$

We have therefore two entirely independent methods of determining the degree of ionization of an electrolyte in solution, and in many cases the results obtained by the two methods agree very closely.

Ostwald's Dilution Law.—Suppose we have 1 gram-molecule of a binary electrolyte dissolved in V litres. Let the degree of ionization be x. Then the active masses of the un-ionized portion and of the two sorts of ions will be

$$\frac{1-x}{V}, \frac{x}{V} \text{ and } \frac{x}{V} \text{ respectively.}$$

Hence, by the law of mass action

$$k \cdot \frac{1-x}{V} = k' \cdot \frac{x}{V} \cdot \frac{x}{V}$$

or

$$K = \frac{k}{k'} = \frac{x^2}{(1-x)V}$$

In other words, if x is small (as in "weak" electrolytes) the degree of ionization is proportional to the square root of the dilution, since $1 - x$ is practically equal to 1 in these cases.

K is called the "dissociation constant" of the electrolyte. Strong electrolytes, i.e. those that have a high degree of ionization, do not obey Ostwald's Law.[1]

[1] There is reason to believe that strong electrolytes are completely dissociated even at comparatively high concentrations.

Uses of the Ionic Theory.

(i) *Heat of Neutralization of Acids.*—Suppose we neutralize caustic soda with hydrochloric acid. Then

$$NaOH + HCl = NaCl + H_2O.$$

Of the four substances represented in the equation, all are highly ionized with the exception of the water; water, as we know from the fact that it is almost a non-conductor, is practically non-ionized. Writing the equation in the ionic way, therefore, we should have

$$Na^{\cdot} + OH' + H^{\cdot} + Cl' = Na^{\cdot} + Cl' + H_2O.$$

The only change that has taken place, in fact, is the combination of hydrogen ions and hydroxyl ions to form unionized water.

Since most acids, bases and salts are highly ionized in aqueous solution, it follows that the process of neutralization of an acid by a base in all these cases is nothing more than the *formation of water from hydrogen ions and hydroxyl ions,*

$$H^{\cdot} + OH' = H_2O.$$

If, therefore, we take *gram-equivalents* of acids and neutralize them with *gram-equivalents* of bases the essential change is the formation of 18 grams of water from 1 gram of hydrogen ions and 17 grams of hydroxyl ions. Hence the *heat of neutralization of an acid is merely the heat of formation of* 18 *grams of water from hydrogen ions and hydroxyl ions*; we should therefore expect all acids to have the same heat of neutralization, which is roughly true.

(ii) *Solubility Product.*—If a solid electrolyte is in contact with its saturated aqueous solution, the following equilibria exist—

solid $\rightleftharpoons$ undissociated molecules in solution $\rightleftharpoons$ ions.

Suppose we have a binary electrolyte in equilibrium with its saturated solution. Let the active mass of the undissociated part in solution be c, that of the one sort of ion a, and that of the other sort of ion b. Then by the law of mass action,

$$a.b = K.c.$$

Now the solution is, by hypothesis, saturated and in contact with the solid, hence the value of c must be constant. What will happen if we increase a or b? Obviously more undissociated molecules of the electrolyte will be formed; that is, c will be increased. It was, however, already at its maximum value, therefore the excess of undissociated molecules cannot remain in solution and must be precipitated.

This deduction can easily be tested by experiment. If we take a saturated solution of common salt and pass hydrochloric acid gas into it, we shall increase the active mass, b, of the chlorine ions. Hence the product ab will be greater than it was before, more un-ionized molecules of salt will be formed, and, the maximum value for c now being exceeded, salt should be precipitated. This is what actually does happen. Addition of caustic soda ought theoretically to produce the same effect, and does so in practice.

The maximum value of ab for a given compound (at a particular temperature) is called the *solubility-product* of the compound (at that temperature).

(iii) *Addition of Salts to Acids and Bases.*—If to a solution of an acid or a base we add a salt giving one of the ions of the acid or of the base, the degree of ionization of the latter compounds will be reduced, and if the original ionization was small it may be suppressed almost completely.

Thus, in a solution of ammonium hydroxide we have the equilibrium—

$$NH_4OH \rightleftharpoons NH_4^{\cdot} + OH',$$

in which the equilibrium lies chiefly to the left, since ammonium hydroxide is a "weak" base (i.e. little ionized in solution). Addition of ammonium chloride, which is, like practically all salts, highly ionized, will greatly increase the active mass of the ammonium ions, with the result that the active mass of the hydroxyl ions will be correspondingly reduced and the equilibrium $NH_4OH \rightleftharpoons NH_4^{\cdot} + OH'$ shifted still more to the left. This is extremely important in analytical chemistry. At the stage of Group III in the Analytical Tables there may still be in the solution (among other metals) iron, chromium, aluminium, zinc, cobalt,

nickel and manganese, all of which form "insoluble" hydroxides, that is, hydroxides with a low solubility product. If ammonium hydroxide is added to a solution in which the ions of these metals are present, the concentration of the hydroxyl ions will be sufficient to cause the solubility products of all the hydroxides to be exceeded, and precipitation will occur.

If, however, ammonium chloride is added first, followed by ammonium hydroxide, the ionization of the latter is suppressed so far that the concentration of hydroxyl ions in the solution is no longer high enough to cause precipitation of the hydroxides of zinc, cobalt, nickel and manganese, while still sufficient to precipitate the hydroxides of iron, chromium and aluminium.

(iv) *Solubility of Salts of "Weak" Acids in Solutions of Stronger Acids.*—A "weak" acid is an acid that ionizes only little in solution. Many organic acids are weak acids; so are carbonic and sulphurous acids. It is often found that an "insoluble" salt of a weak acid will readily dissolve in a solution of a stronger acid. This is satisfactorily explained by the ionic theory, as will be made clear by an example.

Calcium oxalate, CaC_2O_4, is "insoluble" in water, but soluble in dilute hydrochloric acid. Oxalic acid is a weak acid. Now, no "insoluble" salt is *absolutely* insoluble, so that we may assume that when calcium oxalate is in contact with water a little of it dissolves and forms a saturated solution. Part of the dissolved salt will ionize, so that we shall have the following equilibria—

$$CaC_2O_4 \text{ solid} \rightleftharpoons CaC_2O_4 \text{ dissolved} \rightleftharpoons Ca^{\cdot\cdot} + C_2O_4''.$$

The solubility product is, however, very low. If we now add hydrochloric acid we shall have present in solution hydrogen ions, chlorine ions, calcium ions and "oxalate" ions. Oxalic acid, however, is a weak acid, and as soon as hydrogen ions meet with oxalate ions they combine to form un-ionized oxalic acid (the ionization of which is suppressed still further by the excess of hydrogen ions present. See Section iii). Hence, oxalate ions are removed from the solution and thus the equilibrium $Ca^{\cdot\cdot} + C_2O_4'' \rightleftharpoons CaC_2O_4$ is upset, and more

calcium oxalate will ionize to try to restore it. This attempt in turn upsets the equilibrium—

$$\underset{\text{Dissolved.}}{CaC_2O_4} \rightleftharpoons \underset{\text{Solid.}}{CaC_2O_4},$$

and therefore more calcium oxalate will dissolve. If sufficient hydrochloric acid is present the process will continue until all the calcium oxalate has passed into solution.

(v) *Hydrolysis.*—the salts of weak acids with strong bases show an alkaline reaction in solution and those of weak bases with strong acids show an acid reaction. This phenomenon is easily understood in the light of the ionic theory. Although water is a very poor conductor, it nevertheless is *slightly* ionized into $H^{\cdot}$ and OH' and there is therefore an equilibrium

$$H_2O \rightleftharpoons H^{\cdot} + OH',$$

lying very largely to the left. Now the concentration of hydrogen ions formed from a weak acid, and of hydroxyl ions formed from a weak base, may be less than the concentration of those ions in pure water. If so, certain changes occur, which will be most readily understood by considering a definite example. Let us take the case of sodium carbonate, the salt of a strong base (NaOH) with a weak acid (H_2CO_3, carbonic acid). In solution this salt will ionize into $Na^{\cdot}$, $Na^{\cdot}$ and CO_3''. CO_3'' ions, however, immediately combine with the hydrogen ions of the water to form un-ionized carbonic acid, H_2CO_3; this disturbs the equilibrium $H^{\cdot} + OH' \rightleftharpoons H_2O$, and more water ionizes. The hydrogen ions formed, however, are immediately seized upon by CO_3'' ions and so the process goes on until practically all the CO_3'' ions have become converted into un-ionized H_2CO_3. But for every hydrogen ion removed in this way, there remains in solution a hydroxyl ion, and the accumulation of these hydroxyl ions in the solution gives the liquid an alkaline reaction.

(vi) *Indicators.*—Substances like litmus, phenolphthalein and methyl orange, which change colour with acids and alkalis, are themselves either weak acids or weak bases, which on ionization produce ions differing in colour from the undissociated molecules. Thus methyl orange acts as a weak base, and in solution gives colourless hydroxyl ions and red

cations. The undissociated substance is yellow, hence when dissolved in water methyl orange gives an orange-red solution. Addition of alkalis suppresses the ionization of the indicator and the solution therefore turns yellow—the colour of the undissociated molecules. Addition of acids, on the other hand, turns the solution red, since the hydrogen ions of the acid combine with hydroxyl ions of the indicator and further ionization of the latter occurs. The colour of the cations thus becomes apparent.

Phenolphthalein behaves as a weak acid ; the undissociated molecule is colourless while the anion is pink. Addition of an acid produces no obvious effect, but addition of an alkali increases ionization and the pink colour of the anions appears.

The sensitiveness of an acid indicator depends upon the concentration of hydrogen ions necessary to suppress its ionization and upon that of hydroxyl ions necessary to make its ionization great enough for the characteristic colour of the anions to appear.

The active mass of hydrogen ions in pure water is 10^{-7}; that of hydroxyl ions is of course the same. It is clear that in a *neutral* solution the concentration of hydrogen ions must be equal to that of hydroxyl ions, and this concentration must be the same as that of the ions of water, namely, 10^{-7}. An excess of hydrogen ions in solution renders the liquid *acid*, while an excess of hydroxyl ions makes it *alkaline*.

A good indicator is therefore one that changes colour with a *small* excess of hydrogen ions or of hydroxyl ions ; judged by this criterion, the best indicator is undoubtedly litmus, which is blue when the concentration of hydrogen ions is 10^{-7} and red when the concentration is 10^{-6}. Methyl orange changes colour at a concentration of hydrogen ions of 10^{-4}, and phenolphthalein at 10^{-9}. Methyl orange is therefore obviously useless for titrating weak acids, but may be useful for weak bases ; with phenolphthalein the contrary is true.

Hydrogen ion concentration has now become so extensively used in examination of the properties of liquids, not merely in pure chemistry but in medicine, agriculture, physiology and industry, that a special symbol has been introduced to

represent it. This symbol is p_H, which stands for the logarithm to the base 10 of the true concentration, with the minus sign omitted. Thus $p_H = 6{\cdot}8$ indicates a hydrogen ion concentration of $10^{-6{\cdot}8}$.

(vii) *Strengths of Acids (and Bases).*—The strengths of acids (and bases) are compared by measuring their degree of ionization at equivalent concentrations. Thus, the degree of ionization in normal solutions of sulphuric, nitric and hydrochloric acids is shown in the table—

N-Sulphuric acid	0·51
N-Hydrochloric acid	0·78
N-Nitric acid	0·82

In normal solution, therefore, sulphuric acid is less than two-thirds as "strong" as hydrochloric acid or nitric acid.

QUESTIONS

1. Write an account of the *ionic theory.*
2. What is van't Hoff's coefficient ?
3. Define *degree of ionization.* Show how the degree of ionization of an electrolyte in solution may be calculated.
4. State, deduce and interpret Ostwald's Dilution Law.
5. Show that the ionic theory affords a satisfactory explanation of the fact that the heat of neutralization of strong acids is fairly constant.
6. Calcium phosphate is insoluble in water, but dissolves in dilute hydrochloric acid. Explain this.
7. Explain, in terms of the ionic theory, the precipitation of salt from its saturated solution on addition of hydrochloric acid gas.
8. Discuss the use of (*a*) ammonium hydroxide, (*b*) sulphuretted hydrogen, in qualitative analysis.
9. Write a short account of the theory of indicators.
10. Calculate the degree of ionization of a solution of common salt given that the solution contains 0·724 gm. of salt in 100 gms. water and freezes at − 0·44° C. The molecular depression of the freezing point of water is 18·6° and the molecular weight of sodium chloride is 58·5.
11. The equivalent conductivity of a 5 per cent. solution of hydrochloric acid is 281, while the conductivity at infinite dilution is 349. Find the degree of ionization of the acid.
12. Find the freezing point of a solution of acetic acid containing 1 gram-molecular weight in 120 litres, given that the conductivity of the solution is 16·75, and that the conductivity at infinite dilution is 364. The molecular depression of the freezing point for water is 18·6 and the molecular weight of acetic acid is 60.
13. Explain what is meant by the symbol p_H.

CHAPTER XIV

CATALYSIS, COLLOIDS, PHASE RULE

Catalysis

Many chemical reactions can be hastened, and many can be retarded, by the addition of small quantities of substances that are left unchanged in mass and in chemical composition at the end of the reaction. This phenomenon is called *catalysis* and the substances that bring it about are called *catalysts* or *catalytic agents*. Catalysts that increase the speed of a reaction are called positive catalysts; those that retard an action are called negative catalysts. Positive catalysts are much more common than negative catalysts, hence "catalyst" generally means *positive* catalyst, just as we write a for $+a$.

The first example of catalysis usually met with is the use of manganese dioxide in the preparation of oxygen from potassium chlorate by the action of heat. If potassium chlorate be heated alone, oxygen is given off at a comparatively high temperature, but if a little manganese dioxide be mixed with the chlorate the latter yields its oxygen much more quickly at the same temperature, or at the same rate at a lower temperature. Since the rate of a chemical change is roughly doubled for a rise in temperature of 10°, it is clear that the reaction has been hastened in both of the above cases. The manganese dioxide, however, is unchanged in weight and in chemical composition at the end of the reaction; a fact which may easily be proved by adding a known weight of manganese dioxide to some potassium chlorate, heating until

all the oxygen is driven off and then adding sufficient water to the residue to dissolve all the potassium chloride left. If the residual manganese dioxide is then filtered off, washed, dried, and weighed, its weight will be found equal to the original weight.

Many other substances will also act as catalysts in the decomposition of potassium chlorate by heat, e.g. ferric oxide, Fe_2O_3, and cupric oxide, CuO.

Ostwald compared the action of a catalyst upon a chemical reaction to that of oil upon a machine. The similarity is, in fact, very great as we can see from the following points—

(i) The catalyst is left unchanged in weight and in chemical composition after the reaction: lubricating oil is not *consumed* by lubrication although it may be scattered and lost in this and other ways.

(ii) The addition of a catalyst affects the *speed* of the reaction only, not the products; similarly, if oil be added to a machine making paper bags, the machine will continue to make paper bags and not packets of cigarettes.

(iii) Within certain limits, the more catalyst is added, the greater its effect: the same is true of oil.

(iv) A catalyst will not start a reaction as a rule, and in no case unless the action is potentially possible: it is of no use adding oil to a machine if the necessary driving force is absent.

(v) A catalyst may be either positive or negative: axle-grease will increase the speed of a railway-truck but would probably retard the action of a watch.

(vi) A substance which is a catalyst in one reaction may not be a catalyst in another reaction in which it is used (e.g. manganese dioxide in (*a*) decomposition of potassium chlorate and (*b*) oxidation of hydrochloric acid to chlorine); similarly, the same oil which is a "catalyst" when used for lubrication may be converted into margarine and used for food.

In the case of a reversible reaction the final *state* of equilibrium is not affected by use of a catalyst, although the *time* taken for the establishment of that equilibrium may be altered considerably. If the catalyst *did* affect the final equilibrium we could obtain a continuous supply of energy, *out of nothing*,

by allowing the reaction to take place alternately in the presence and absence of the catalyst. As the creation of energy is entirely opposed to all our ideas and observations on nature, we must assume that the catalyst cannot affect the final state of equilibrium in a reversible reaction; it therefore affects the velocities of the forward and reverse reactions *to the same extent.* This seems a very significant fact for the theory of catalysis, but it must be admitted that the above argument has been severely criticized, and that certain cases are known in which a catalyst at least *appears* to alter the final state of equilibrium in a reversible reaction.

Many examples of catalysis are known, and the idea is of very respectable antiquity, for, describing the properties of the Elixir which (supposedly) changes the baser metals into gold, MARY THE COPT (the inventor of the water-bath), who flourished in Egypt long before the Muslim Conquest, says, "*One dirham* [1] *thereof is sufficient for all which lies between the East and the West.*" The catalytic effect of yeast upon dough is probably the earliest recorded example of the phenomenon.

Up to the present, no completely satisfactory theory of catalysis has been suggested. It is probable that the mechanism of the process may differ in different cases. The formation of *unstable intermediate compounds* of the catalyst and one or more of the reacting substances has been suggested, and in many cases of catalysis this may be the correct explanation. However, the whole subject is still shrouded in mystery and we must content ourselves at this stage with recording examples of catalytic actions, leaving their detailed study for a more advanced course.

(i) The use of copper chloride in DEACON'S process for the manufacture of chlorine, p. 499.

(ii) The use of oxides of nitrogen in the lead-chamber process for the manufacture of sulphuric acid, p. 469.

(iii) Catalytic combination of sulphur dioxide and oxygen by means of platinized asbestos, p. 473.

(iv) Catalytic decomposition of hydrogen peroxide by means of finely-divided metals, p. 433.

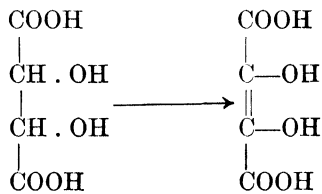
[1] About the weight of a sixpence.

(v) The *hydrogen ions* of acids will accelerate catalytically the *hydrolysis of esters* by water, e.g.—

$$\underset{\text{Ethyl acetate.}}{CH_3.COOC_2H_5} + \underset{\text{Water.}}{H_2O} \longrightarrow \underset{\text{Acetic Acid.}}{CH_3.COOH} + \underset{\text{Ethyl alcohol.}}{C_2H_5OH}.$$

(vi) Synthetic formation (p. 340) and oxidation (p. 356) of ammonia.

(vii) The catalytic action of ferrous sulphate on the oxidation of certain organic compounds by hydrogen peroxide; thus *tartaric acid* is oxidized to *dihydroxymaleic acid*—



[See FENTON, *Outlines of Chemistry*, p. 180.]

(viii) Many reactions between gases occur in the presence of platinum black, reduced nickel, and other finely-divided metals.

(ix) Many substances when *absolutely dry* will not react together; they will do so, however, in the presence of even a trace of water. Thus dry ammonia has no action upon dry hydrochloric acid gas.

(x) *Enzymes.*—Enzymes are certain complicated compounds of carbon which are very important catalysts in many organic reactions. They are present in, and can be extracted from, living animals and plants and play an essential part in the life-processes. The *fermentation of sugar* by means of the yeast plant is a catalytic action. Yeast contains two enzymes called *invertase* and *zymase*; the first of these acts as a catalyst upon the hydrolysis of the cane-sugar—

$$\underset{\text{Cane-sugar.}}{H_2O + C_{12}H_{22}O_{11}} = \underset{\text{Grape-sugar.}}{C_6H_{12}O_6} + \underset{\text{Fruit-sugar.}}{C_6H_{12}O_6},$$

which results in the formation of a mixture of grape-sugar and fruit-sugar. (It will be noticed that both grape-sugar and fruit-sugar have the formula $C_6H_{12}O_6$; the atoms are,

however, arranged in different ways in the molecules of the two substances, and grape-sugar and fruit-sugar are said to be *isomeric* with one another.)

The mixture of grape-sugar and fruit-sugar is then catalytically split up by the zymase into alcohol and carbon dioxide,

$$C_6H_{12}O_6 = \underset{\text{Alcohol.}}{2C_2H_5.OH} + 2CO_2$$

Colloids

In the middle of the nineteenth century Graham showed that if a solution of salt was placed in a parchment drum floating in a vessel of water, the salt gradually passed through the membrane into the surrounding water; glue, however, if made up into a solution and treated in the same way, would not pass through the membrane. Further investigation showed that most crystalline substances behaved in the same way as salt, while silicic acid, gum, starch, albumen, caramel and certain other substances, behaved like glue. The latter bodies Graham therefore called *colloids*, because they were "like glue" (Greek, *kolla*, glue); those which readily passed through a membrane he called *crystalloids*. It follows that if we have a mixture of a colloid and a crystalloid in solution, the two may be separated by floating the solution in a parchment drum in a vessel of pure water, when the crystalloid will slowly pass through while the colloid remains. This process Graham called *dialysis*.

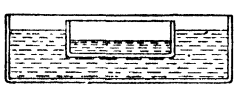


Fig. 31.—Graham's Dialyzer.

More recent work has shown that this classification of substances into colloids and crystalloids is unsound; *any* substance may be obtained as a colloid under suitable conditions, and it is therefore preferable to talk of a *colloidal state* of matter, into which some substances pass more readily than others.

In a *colloidal solution* of a solid in a liquid, the particles of the solid are so fine that they will not settle to the bottom, and yet are not so fine that the substance can be regarded as in a "true" solution. In practically all colloidal solutions

the particles of the colloidal substance can be observed either directly or indirectly by means of the microscope or ultra-microscope.

A colloidal solution is usually easily *coagulated*, that is, the colloid is precipitated from the solution. Often mere rise of temperature is sufficient to cause coagulation ; in other cases addition of an electrolyte will bring it about, the tervalent cations of iron, chromium and aluminium being especially active in this respect—hence the use of alum to stop bleeding. Blood is a colloidal solution of an albuminoid substance and is coagulated to a clot by the tervalent aluminium ion ; the clot closes the ends of the capillary blood-vessels and thus the flow of blood is arrested.

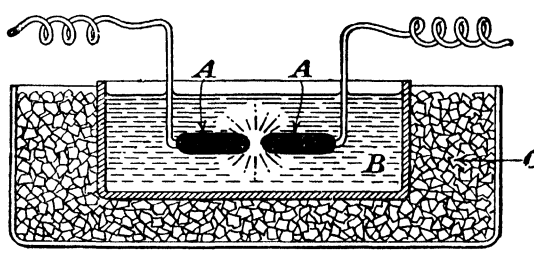


FIG. 32.—Bredig's Method for obtaining Colloidal Metals.
A, *A*. Electrodes of the metal. *B*. Water. *C*. Ice.

On the other hand, addition of a more stable colloid to a colloidal solution may often make the latter much more resistant to coagulating agents ; this phenomenon is called *protection*. Thus a colloidal solution of graphite is rendered very stable by the addition of colloidal tannin (see p. 286).

Finally, it should be noted that the particles of colloids are usually *negatively* charged, although in a few cases they are positively charged. The liquid in which the particles are suspended has an opposite charge to that on the particles themselves.

Colloidal metals are conveniently obtained by BREDIG'S method, which consists in striking the electric arc between

two poles of the metal beneath the surface of extremely pure water.

In the form of a *solid* colloidal solution, colloidal gold (*Purple of Cassius*, p. 237) has been known since 1685, while a rudimentary variety was employed by the ancient Assyrians in the manufacture of artificial red coral. A colloidal solution of gold in water has recently been used in medicine; it will be interesting to know whether the extravagant claims of the alchemists for the healing qualities of "potable gold" were justified!

The study of colloids finds many applications in industry and various arts and crafts. Thus dyeing, photography, the rubber industry, the purification of drinking-water and the manufacture of artificial silk all present problems in colloid chemistry, investigation of which has led to important and beneficial advances. In biology and biochemistry research into the nature of such colloidal substances as protoplasm and albumen has already thrown much light upon the mechanism of vital processes—while even ice-cream manufacturers add protective colloids such as gelatin to improve the "feel" of their product in the mouth!

The Phase Rule

The Phase Rule deals with the equilibria between the various parts of a *heterogeneous system*, such as the system ice, water and water-vapour, or calcium carbonate, calcium oxide and carbon dioxide, in which each part is homogeneous in itself but in a different physical state from other parts. The homogeneous parts of the system are called *phases*, and the *least* number of substances from which all the phases of the system can be made is called the number of *components* of the system. Thus, in the system ice, water and vapour, there are *three phases* and *one component*; in the system calcium carbonate, calcium oxide and carbon dioxide there are *three phases* and *two components*, since all three phases may be made from carbon dioxide and calcium oxide.

The equilibria between the phases of a heterogeneous system may be affected by temperature, pressure and con-

centration, and the number of these factors that must be arbitrarily fixed in order that the system under consideration shall be in a definite state of equilibrium is called the number of *degrees of freedom* of the system.

The Phase Rule may then be stated as follows—

The number of phases + the number of degrees of freedom = the number of components + 2,

or $P + F = C + 2$.

Consideration of the following examples will render the simple application of the Phase Rule easily intelligible; for more advanced work the standard textbooks on the subject must be consulted—the student is recommended to read the excellent and fascinating book by Professor FINDLAY (*The Phase Rule*, Longmans & Co.).

(i) **Water and Water-vapour.**—Here we have 2 phases and 1 component, hence by the phase rule the number of degrees of freedom is 1, i.e. the system is *univariant*. This means that if we fix the *temperature* at which the water and water-vapour are to exist together in equilibrium, then the *pressure* will adjust itself to a definite value; or if we wish to have water and water-vapour in equilibrium with one another, at a certain *pressure* of the vapour, then the *temperature* will have to be adjusted to a definite value.

(ii) **Ice, Water and Water-vapour.**—In this system we have *three* phases and 1 component; hence the number of degrees of freedom = 0, or the system is non-variant. This means that we *cannot* fix arbitrarily *any* of the factors governing the equilibrium; ice, water and water-vapour can exist together in equilibrium only at one particular temperature and pressure, dependent entirely on the system and not subject to any arbitrary decision on our part.

(iii) **Calcium Carbonate, Calcium Oxide and Carbon Dioxide.**—There are here 3 phases and 2 components; the system is therefore *univariant*. We can fix arbitrarily the *temperature* at which we wish the system to exist in equilibrium, but if we do, the *pressure* will automatically adjust itself. In other words, at a given temperature,

calcium carbonate will give a definite *pressure* of carbon dioxide.

(iv) **Iron, Iron Oxide, Steam and Hydrogen.**—The steam and hydrogen form a homogeneous mixture and thus constitute *one* phase; the total number of phases is therefore 3. The number of components is 3, since we could make all the phases from iron, hydrogen and oxygen, hence the system is *bivariant.* Now the factors concerned are the *temperature*, the *total pressure* of the gaseous system, and its *concentration* or volumetric composition. If two of these factors are arbitrarily fixed the third will adjust itself. At a constant pressure, therefore, the ratio by volume of hydrogen to steam will be constant at a constant temperature. Of course, if liquid water is present in the system as well, the system will then be *univariant.*

QUESTIONS

1. Give a general account of *catalysis*, with examples.
2. Write a short essay on *colloids.*
3. State and explain the Phase Rule, and in terms of this law discuss the following equilibria—

(i) $CuSO_4.5H_2O \rightleftharpoons CuSO_4 + 5H_2O$.
Solid. Solid. Gas.

(ii) Ice $\rightleftharpoons$ water.

(iii) Rhombic sulphur $\rightleftharpoons$ monoclinic sulphur.

CHAPTER XV

THE PERIODIC SYSTEM

One of the strongest instincts of mankind is to classify, and the chemical elements form a fascinating object for the exercise of this instinct. As soon as a sufficiently large number of elements had been isolated and described, attempts at a classification of them began to appear and have continued ever since. The distinction between *metals* and *non-metals* was obvious and was made in remote antiquity; it is convenient still, although there is no sharp line of demarcation between the two groups, and several elements are known that possess both metallic and non-metallic properties. These may be called the *metalloids*. The chief properties characteristic of **metals** are as follow—

(i) High density and melting-point.
(ii) High conductivity for heat, and for electricity *without decomposition*.
(iii) Metallic lustre and capability of taking a high polish.
(iv) Malleability, ductility, and great tensile strength.
(v) Metallic oxides are usually *basic*.
(vi) Metallic chlorides are generally not hydrolysed by water.
(vii) Metallic hydrides are rarely formed and in any case are unstable.

The main characteristics of **non-metals** are :—

(i) Low density.
(ii) Poor conductivity for heat and electricity.
(iii) Lack of metallic lustre; will not take a polish.

(iv) They are not malleable or ductile and their tensile strength is small.

(v) Non-metallic oxides are usually acidic.

(vi) Non-metallic chlorides are often hydrolysed by water.

(vii) Non-metallic hydrides are common and are usually very stable.

To each of these characteristics, however, both of metals and of non-metals, exceptions are numerous, and in deciding whether a particular element is a metal or a non-metal its general properties have to be considered as a whole. There is no one unfailing criterion for distinguishing between a metal and a non-metal, and even the general consideration of all the properties of an element may still leave us undecided as to its metallic or non-metallic nature. Arsenic, for example, possesses certain well-marked metallic properties and other, equally well-marked, non-metallic properties. It is therefore said to be a metalloid.

These facts serve to show us that while the distinction between metals and non-metals may be convenient in practice it cannot be applied too rigidly. The student will find it a useful exercise to make a list of " non-metallic " properties shown by certain metals and of " metallic " properties shown by certain non-metals ; he may also act as judge, jury and advocate in deciding the claims of arsenic, antimony and bismuth to be considered metals and of boron to be considered a non-metal.

More systematic groupings of the elements were made by DÖBEREINER (1829) and by PETTENKOFER (1850). Döbereiner showed that many chemically related elements formed well-marked groups of three (" *Döbereiner's Triads* "), the atomic weight of the middle member of each group being approximately the mean of the atomic weights of the other two. Thus the atomic weight of bromine (80) is roughly the mean of 35·5 and 127, the atomic weights of chlorine and iodine respectively. Calcium (40), strontium (87) and barium (137) form another such group.

Greater progress was scarcely to be expected at the time owing to the uncertainty as to the atomic weights of many

elements. However, when CANNIZZARO, in the middle of the nineteenth century, drew the attention of chemists to the great value of Avogadro's Hypothesis for deciding between rival values for atomic weights, and the latter were therefore first definitely fixed, interesting relationships became obvious almost at once.

A great advance was made in 1863 by NEWLANDS, who pointed out that when the elements were arranged in order of their atomic weights, the eighth element resembled the first, fifteenth, etc., the ninth resembled the second, sixteenth, etc., and so on. Each element, in fact, more or less closely resembled the elements which were seven, or some multiple of seven, places before it or after it, thus recalling the arrangement of *octaves* in music. Newlands therefore called his discovery the **Law of Octaves.** Here again, however, there were many discrepancies, and the reception accorded to Newlands' work by the chemical world was the reverse of enthusiastic.

Shortly afterwards, the Russian chemist MENDELÉEFF (1869) published an important paper on the classification of the elements, in which he described an arrangement of the elements that has since become famous as the **Periodic System.** Like Newlands, Mendeléeff arranged the elements in the order of their atomic weights, starting from the lowest, and called attention to the fact that a kind of periodicity in their properties was thus manifested, that is, chemically similar elements recurred at approximately equal intervals. This, of course, had been shown by Newlands previously (although it seems that Mendeléeff was not acquainted with Newlands' work), but Mendeléeff carried the classification much further, and was able to overcome many of the difficulties that had told against the Law of Octaves.

In his Faraday Lecture to the Chemical Society in 1889, Mendeléeff gave the following summary of the conclusions at which he had arrived :—

1. The elements, if arranged according to their atomic weights, exhibit an evident *periodicity* of properties.

2. Elements which are similar as regards their chemical properties have atomic weights which are either of nearly the

same value (e.g., platinum, iridium, osmium), or which increase regularly (e.g., potassium, rubidium, cæsium).

3. The arrangement of the elements, or of groups of elements, in the order of their atomic weights corresponds to their so-called *valencies*, as well as, to some extent, to their distinctive chemical properties, as is apparent, among other series, in that of lithium, beryllium, barium, carbon, nitrogen, oxygen and iron.

4. The elements which are the most widely diffused have *small* atomic weights.

5. The *magnitude* of the atomic weight determines the character of the element, just as the magnitude of the molecule determines the character of a compound body.

6. We must expect the discovery of many yet unknown elements, for example, elements analogous to aluminium and silicon, whose atomic weights would be between 65 and 75.

7. The atomic weight of an element may sometimes be amended by a knowledge of those of the contiguous elements. Thus, the atomic weight of tellurium must lie between 123 and 126, and cannot be 128.[1]

8. Certain characteristic properties of the elements can be foretold from their atomic weights.

The Periodic Table in its present form is given on page 153. The general arrangement is due to Mendeléeff, but many new elements have been discovered since his time, and these are included. The numbers in thick black type are the Atomic Numbers (see Chapter XVI).

It will be observed that the elements fall into 7 *periods* and 9 *groups*. The first period contains one element only, hydrogen. The second and third periods contain 8 elements each, the fourth and fifth periods 18 elements each, the sixth period 32, and the seventh period at present contains 6 elements. The first three periods are called *short* periods and the rest *long* periods. In each period the elements show a gradation in properties from the chemically neutral helium elements through the strongly electropositive alkali metals to the strongly electro-negative halogens.

[1] Here Mendeléeff was wrong. See p. 157.

PERIODIC TABLE.

Period.	Group 0.	Group I.	Group II.	Group III.	Group IV.	Group V.	Group VI.	Group VII.	Group VIII.
1		H 1 1·008							
2	He 3·99 2	Li 6·94 3	Be 9·1 4	B 11·0 5	C 12·00 6	N 14·01 7	O 16·00 8	F 19·0 9	
3	Ne 20·2 10	Na 23·00 11	Mg 24·32 12	Al 27·1 13	Si 28·3 14	P 31·04 15	S 32·07 16	Cl 35·46 17	
4	A 39·88 18	K 39·1 19 29 Cu 63·57	Ca 40·07 20 30 Zn 65·37	Sc 44·1 21 31 Ga 69·9	Ti 48·1 22 32 Ge 72·5	V 51·0 23 33 As 74·96	Cr 52·0 24 34 Se 79·2	Mn 54·93 25 35 Br 79·92	Fe 55·84 26 Co 58·97 27 Ni 58·68 28
5	Kr 82·92 36	Rb 85·45 37 47 Ag 107·88	Sr 87·63 38 48 Cd 112·40	Yt 89·0 39 49 In 114·8	Zr 90·6 40 50 Sn 119·0	Cb 93·5 41 51 Sb 120·0	Mo 96 42 52 Te 127·5	Ma 99 43 53 I 126·92	Ru 101·7 44 Rh 102·9 45 Pd 106·7 46
6	Xe 130·2 54	Cs 132·81 55 79 Au 197·2	Ba 137·37 56 80 Hg 200·6	La 139·0 57 81 Tl 204·0	Ce 140·25 58 and *rare earths* (59–72) 82 Pb 207·10	Ta 181·0 73 83 Bi 208·0	W 184·0 74 84 Po	Re 188·7 75 85 —	Os 190·9 76 Ir 193·1 77 Pt 195·2 78
7	Rn 222·5 86	87 —	Ra 226·4 88	Ac 89	Th 232·4 90	Pa 91	U 238·5 92		

In each *group*, however, the elements show a *similarity* in properties. The elements of each group which fall in the periods after the first three can be divided into two *sub-*

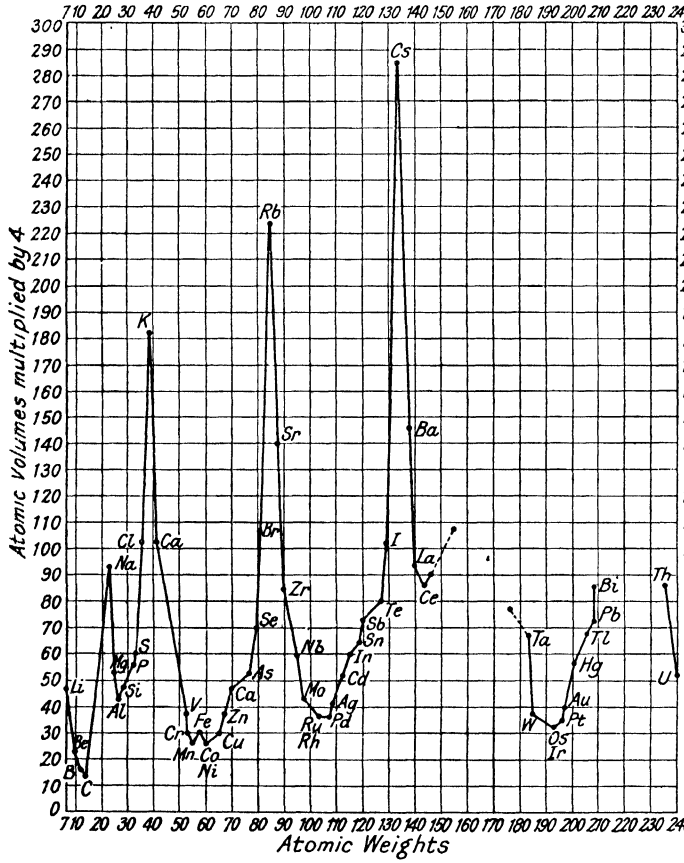


FIG. 33.—Lothar Meyer's Atomic Volume Curve.

groups; the elements of one sub-group more closely resemble those elements of the group which fall in the second and third periods than do those of the other sub-group. Thus, in Group I, potassium, rubidium (Rb) and cæsium (Cs) have

a greater resemblance to lithium and sodium than have copper, silver and gold; while in Group VII bromine and iodine are much more similar to fluorine and chlorine than is manganese.

The elements in Group VIII are called the *transition elements*; thus iron, cobalt and nickel show a gradual transition in properties, iron being similar to manganese and cobalt, cobalt to iron and nickel, and nickel to cobalt and copper.

LOTHAR MEYER (1869) pointed out that many of the physical properties of the elements are also "periodic functions of the atomic weight." Thus if a curve is made by plotting atomic weights against *atomic volumes* (i.e., atomic weight divided by specific gravity), it is found that the curve shows a periodic nature (see Fig. 33), similar elements occupying similar positions on the curve. Specific gravity, hardness, melting-point, thermal and electric conductivity, latent heat of fusion, and ductility of elements are all periodic functions of their atomic weights, and will give similar curves to the Atomic Volume curve if plotted in the same way.

The *specific heats* of the elements, however, are non-periodic (cf. Dulong and Petit's Law, p. 54).

The *valencies* of the elements very often rise from 0 in Group 0 to 4 in Group IV and fall again to 1 in Group VII, e.g.,

	Group.							
	0	**I**	**II**	**III**	**IV**	**V**	**VI**	**VII**
Valency	0	1	2	3	4	3	2	1
Element	He	Li	Be	B	C	N	O	F
	Ne	Na	Mg	Al	Si	P	S	Cl

Or, since the elements towards the right of the table often show *two* valencies, we may get a constant *rise in valency* from Group 0 to Group VII, e.g.,

	Group.							
	0	**I**	**II**	**III**	**IV**	**V**	**VI**	**VII**
Valency (shown by compound)	—	Li_2O	BeO	B_2O_3	CO_2	N_2O_5	SO_3	Cl_2O_7
Element	He	Li	Be	B	C	N	S	Cl

Gaps in the Table.—When Mendeléeff first arranged his Periodic Table he had to leave 2 gaps between zinc and arsenic in period 4 and another between calcium and titanium, as no elements were then known that could fill them. Mendeléeff prophesied, however, that these three elements, which he called "*eka*-aluminium," "*eka*-silicon," and "*eka*-boron," would be discovered if search were made for them, and foretold their chief properties by a consideration of the properties of the neighbouring elements already known. A few years afterwards three elements were discovered which were found to have almost exactly the properties foretold by Mendeléeff. These elements were *gallium* (eka-aluminium), *germanium* (eka-silicon), and *scandium* (eka-boron). Thus what had at first appeared a weakness in Mendeléeff's system was later shown to be a brilliant vindication of it.

The Periodic System proved useful in another direction, namely, the *correction of the atomic weights* of certain elements. WINKLER had shown that the equivalent weight of indium (In) is 38, and the atomic weight was considered to be twice this, i.e., 76. There was, however, no place in the system for an element of atomic weight 76 having the properties of indium, and Mendeléeff therefore suggested that the valency of the element was probably 3 and the atomic weight 38×3, or 114. This would make indium fall into the (at that time) vacant space in Group III between cadmium and tin. Further research on indium compounds showed that Mendeléeff was right. The atomic weights of beryllium, uranium and gold were similarly corrected.

Defects of the System.—Argon has a higher atomic weight than potassium, cobalt than nickel, and tellurium than iodine. If these elements are placed in the order of their atomic weights they are obviously in their wrong positions; argon, for example, would be with the alkali metals and potassium with the inactive gases! These difficulties puzzled chemists for a great many years until it was discovered that, after all, atomic weights are not really *fundamental* characteristics of the elements, and that many elements exist in two or more forms of different atomic weights (see *isotopes*,

Chapter XVI). A more fundamental property of an element is its *atomic number* or the number of resultant positive charges on the nucleus of the atom. If the elements are arranged in order of their atomic numbers the above discrepancies disappear, as shown in the following table :—

Element.	Atomic Number.	Atomic Weight.
Argon	18	39·88
Potassium . . .	19	39·10
Cobalt	27	58·97
Nickel	28	58·68
Tellurium . . .	52	127·5
Iodine	53	126·92

For the *position of hydrogen* in the Periodic System see page 185. The chief defect of the system is undoubtedly the fact that it often separates elements of a similar chemical nature and groups dissimilar elements together.

QUESTIONS

1. Write an essay on the Periodic System.
2. What are the main characteristics of (*a*) metals, (*b*) non-metals ?
3. In what ways has the Periodic System proved useful ?
4. What are the chief defects of the Periodic System ? Illustrate your answer fully, by examples. Do you think any other system of classification of the elements would be an improvement on the Periodic System ?

CHAPTER XVI

STRUCTURE OF THE ATOM

In the last decade of the nineteenth century two discoveries were made that were destined to lead to a revolution in scientific thought. These were the discovery of radioactivity (1896) by BECQUEREL and the CURIES, and that of the X-rays (1895) by RÖNTGEN.

In 1896 Becquerel showed that uranium salts have the power of acting upon a photographic plate even when the latter is wrapped in black paper. This can easily be shown by wrapping a plate in a piece of black paper and putting a few crystals of uranium nitrate on the paper. If the crystals are left in position for a day or two, on developing the plate it will be found that the crystals have photographed themselves. Compounds of thorium behave in the same way. Such substances were termed "radioactive," as the action was supposed to be caused by rays emitted by them.

Uranium compounds occur in the mineral *pitchblende*, and when investigating this substance Madame Curie found indications of a much more powerfully "radioactive" body in it. She successfully devised methods of extracting this body, and showed that it was a new element, which she isolated in the form of a mixture of its bromide with barium bromide. This new element was called *radium*. By fractional crystallization from alcohol it was found possible to separate the radium bromide from the barium bromide, and in 1910 metallic radium was prepared by the electrolysis of a solution of radium chloride, using a mercury cathode. The radium liberated at the cathode dissolves in the mercury to form an

amalgam, from which the mercury may be distilled off, leaving the radium as a white metal which quickly rusts in the air, and which, like calcium and barium, acts upon water in the cold with evolution of hydrogen. It melts at about 700° C.

Radium salts will discharge an electroscope, and investigation of this property led to the discovery that radium gives off three different kinds of rays, called respectively the α-, β-, and γ-rays. The nature of these radiations will be discussed later.

Metals, and solutions of acids, bases and salts in water and certain other solvents, conduct electricity, but gases under ordinary pressures are non-conductors unless high potentials are employed. If, however, the pressure is lowered, it is found that gases begin to conduct more easily, but at still lower pressures exceedingly high potentials must be employed to drive the discharge through. The phenomena of conduction are very characteristic. At a pressure of 0·01 mm. a phosphorescence is produced on the walls of the glass tube opposite the cathode. The cause of this phenomenon was investigated by SIR WILLIAM CROOKES, who showed that the phosphorescence was caused by a stream of exceedingly minute negatively-electrified particles which he called the **Cathode Rays.**

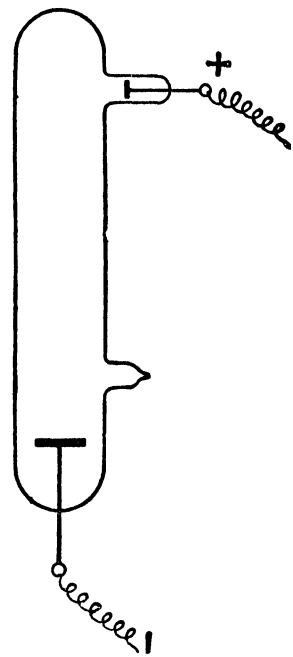


FIG. 34.—Crookes' Tube.

These cathode rays are deflected by electric or magnetic fields in exactly the way that would be expected of a stream of negatively-charged particles, and are capable of passing through thin plates of various metals. In 1895 Röntgen showed that from the phosphorescent spot produced by

allowing cathode rays to strike upon the end of the vacuum tube in which they were formed, another beam of rays was projected, of great penetrating power. These rays Röntgen called X-rays.

The particles of which the cathode rays consist are called *negative electrons* or simply "electrons." Each negative electron has a mass of about $\frac{1}{1850}$ of that of a hydrogen atom, and carries a charge equal (but opposite in sign) to that carried by a hydrogen ion.

It has been shown that X-rays are similar to light vibrations except that their wave-lengths are very much smaller; they can be diffracted and polarized by suitable means. The beam of X-rays produced from an ordinary X-ray tube consists of a mixture of rays of different wave-length, in the same way that white light consists of a mixture of light rays of different wave-lengths. For the general properties of X-rays, textbooks of Physics should be consulted; it is sufficient for our purpose to note here a very important feature, namely, that *every element is capable of emitting X-rays of wave-lengths peculiar to itself*, if stimulated in an appropriate way. Such a way is to allow X-rays of a shorter wave-length to strike the substance, when the latter at once gives off its characteristic radiation. Now, just as the ordinary spectrum of an element is mapped and measured by means of a spectrometer, so it is possible to map and measure the X-ray spectrum of a substance by means of an instrument called the X-ray spectrometer.

To understand how this works it is necessary to know the principle of an instrument called the *diffraction grating*. If ordinary white light is passed through a prism it is split up into light of various wave-lengths, and a spectrum may be produced. This analysis of light may also be brought about by another arrangement called the diffraction grating, which consists of a large number of very fine parallel lines accurately drawn upon a plane sheet of glass in such a way that the spaces separating the lines are all equal. Light which falls on this grating is "diffracted" or bent out of its normal path through an angle that is constant for a given wave-

length of light but that differs for different wave-lengths, so that the grating "sorts out" the light into a spectrum. If the width of the space between two lines of the grating is known, it is possible to calculate the wave-length of any line in the spectrum, and it is in this way that the wave-lengths of rays of light are measured.

Now X-rays are of the same nature as light-rays, but the wave-lengths of light-rays are several thousand times greater than those of the X-rays, and therefore the ordinary diffraction gratings are much too coarse to be of any use for the purpose of forming an X-ray spectrum and measuring the wave-lengths of the various lines. However, in 1912 LAUE suggested that the atoms in a crystal might serve as the lines of a diffraction grating, and the spaces between two consecutive parallel planes of them as the spaces of the grating. If this is so, then a crystal forms a natural diffraction grating which should apparently be of suitable dimensions for giving an X-ray spectrum. Upon investigation this was found to be the case. When X-rays fall on a crystal they are diffracted in exactly the same way as light is by an ordinary diffraction grating. Hence, to measure the wave-length of X-rays all we need to know is the distance between the planes of atoms of a particular crystal. Fortunately it has been found possible to calculate this distance, and therefore to find the actual wave-length of any X-ray.

The X-ray spectrometer makes use of the fact that a crystal will act as a diffraction grating for X-rays. The X-rays to be examined are passed through a slit in a sheet of lead and then through a second slit which serves to cut off any scattered radiations. The pencil of rays then impinges on and is diffracted from a crystal fixed by means of a piece of wax on a horizontal arm that can revolve on a vertical axis over a graduated circle. After diffraction from the crystal the X-rays are made to pass through a third slit into a tube containing a gas which is easily "ionized" (or made to conduct) by the rays; sulphur dioxide is commonly used for the purpose. In this "ionization chamber" is an electrode (placed in such a position that the X-rays entering the chamber

do not strike it) connected to an electroscope. The ionization chamber is mounted on a horizontal arm which can revolve around the same axis as that on which the crystal is mounted.

To conduct the experiment, the X-rays are diffracted from the crystal and the ionization chamber turned until an X-ray

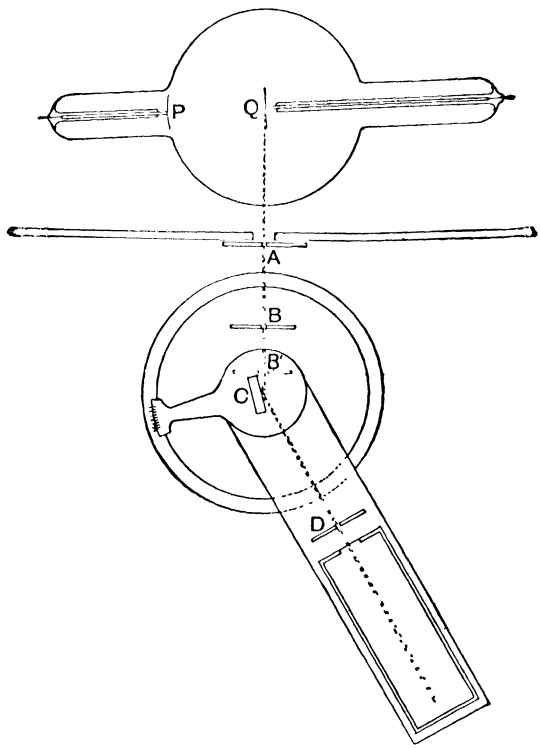


FIG. 35.—Plan of X-ray Spectrometer.
Q B D. Path of rays. C. Crystal.

passes into it, causing the gas inside the chamber to become ionized; this is indicated by the electroscope. The angle through which the ionization chamber has been turned is noted, and the latter is then moved still further until the next X-ray passes into it, as shown by the electroscope.

In this way the X-ray spectrum of the substance under observation can be measured, and the intensity of any given line in the spectrum is indicated by the degree to which the electroscope is affected.

The wave-length of the ray is calculated from the formula $\lambda = 2d \sin \theta$, when θ is the angle at which the X-ray has been refracted from the crystal, and d is the distance between the planes of atoms in the crystal.

If a pencil of X-rays is passed through a crystal and then on to a photographic plate, spots are produced on the plate, arranged in a symmetrical way. These spots are caused by the scattering of the X-rays by the atoms in the crystal, and by constructing space-models from the photographs it has been found possible to determine the spatial arrangement of the atoms within the crystal. Thus Sir William and W. L. Bragg have shown that the atoms in a crystal of potassium chloride are arranged in the way shown in the following diagram, the potassium atoms being represented by black circles ● and the chlorine by white ○.

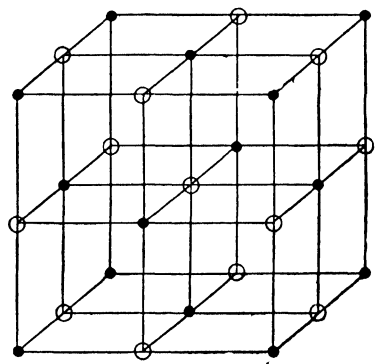


Fig. 36.—Space Lattice of Potassium Chloride.

The atoms of carbon in the diamond are arranged in groups of six in such a way that each carbon atom is at the centre of the regular tetrahedron formed by the 4 atoms nearest it. See fig. 37.

The method has been extended to liquids, and the shape and even the size of the benzene molecule have been determined. The shape is that of a regular hexagon, of side 0·0000000602 cm. and thickness 0·0000000119 cm.

Radiations from Radium.—Let us return now to the

α-, β-, and γ-rays emitted by radium. It has been shown that the α-rays consist of positively-charged particles of atomic dimensions and of atomic weight 4. Each carries 2 unit positive charges. The β-rays consist of negative electrons moving with a very high velocity while the γ-rays are X-rays of very short wave-lengths. These rays are produced by the disintegration of the radium atoms. The atomic weight of radium is 226; when 1 atom of radium gives off an α-particle of atomic weight 4, an atom of atomic weight 222 should be left. This is actually the case. It has been shown that the α-particle is an atom of helium carrying 2 unit positive charges, while the "element" of atomic weight 222 has been isolated and is called "radium emanation" or *radon*. *Radon* itself is radioactive and splits up into helium and a solid substance called the "active deposit," which is still radioactive.

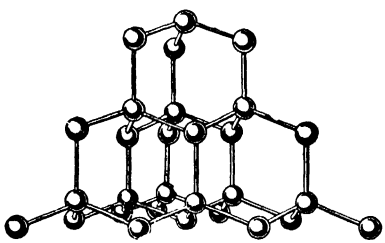


FIG. 37.

This spontaneous disintegration of atoms led scientists to formulate hypotheses on the *structure of the atom*, since atoms were clearly no longer to be considered as indivisible. Many suggestions were made, but that which agreed best with observed facts considered the atom to consist of an exceedingly minute positively-charged nucleus surrounded by a number of negative electrons which revolve in more or less spherical orbits around the nucleus. Bragg showed that the α-particles emitted from radium could pass through thin sheets of solid substances, and proved that in doing so they pass not only through *the spaces between the atoms* of these substances, but also actually *through the atoms themselves* if these happen to be on their path. When the α-particles pass through atoms, most of the particles are not deflected from their rectilinear path, but a small number of them suffer large deflections. This phenomenon is explained by assuming that when an

α-particle passes through an atom and is not deflected thereby, it has not gone near the nucleus but only through the outer regions of the atom—those in which the negative electrons revolve in their orbits. If we compare the atom to our solar system we could regard the sun as the positive nucleus and the planets as the negative electrons ; now it is conceivable that a foreign sun might rush through our solar system yet never come anywhere near the Sun. It seems that the chances of an α-particle coming within close range of the nucleus of an atom are about equally likely. When, however, an α-particle does happen to pass close to the nucleus of an atom it is violently deflected. In LORD RUTHERFORD'S words,[1] "to account for these results, it was found necessary to assume that the atom consists of a charged massive nucleus of dimensions very small compared with the ordinarily accepted magnitude of the diameter of the atom. This positively charged nucleus contains most of the mass of the atom, and is surrounded at a distance by a distribution of negative electrons equal in number to the resultant positive charge on the nucleus. Under these conditions, a very intense electric field exists close to the nucleus, and the large deflection of the α-particle in an encounter with a single atom happens when the particle passes close to the nucleus. Assuming that the electric forces between the α-particle and the nucleus varied according to an inverse square law in the region close to the nucleus, [Rutherford] worked out the relations connecting the number of α-particles scattered through any angle with the charge in the nucleus and the energy of the α-particle. Under the central field of force, the α-particle describes a hyperbolic orbit round the nucleus, and the magnitude of the deflection depends on the closeness of approach to the nucleus. From the data of scattering of α-particles then available, it was deduced that the resultant charge on the nucleus was about $\frac{1}{2}$ Ae, where A is the atomic weight and e the fundamental unit of charge [i.e., is equal in magnitude to the charge carried by a single negative electron]. . . .

[1] *Proc. Roy. Soc.*, xcvii, p. 374 (1920).

"Since the atom is electrically neutral, the number of external [negative] electrons surrounding the nucleus must be equal to the number of units of resultant charge on the nucleus. It should be noted that, from consideration of the scattering of X-rays by light elements, Barkla had shown, in 1911, that the number of electrons was equal to about half the atomic weight. . . .

"Two entirely different methods had thus given similar results with regard to the number of external electrons in the atom, but the scattering of α-rays had shown in addition that the positive charge must be concentrated on a massive nucleus of small dimensions. It was suggested by van den Broek that the scattering of α-particles was not inconsistent with the possibility that the charge on the nucleus was equal to the *atomic number* [1] of the atom, i.e. to the number of the atom when arranged in order of increasing atomic weight," taking Hydrogen as 1, Helium as 2, Lithium as 3, and so on.

It will be convenient here to consider the results of an independent line of research carried out by MOSELEY, who investigated the X-ray spectra of various elements by means of the X-ray spectrometer. He found that the X-ray spectra obtained in this way show two strong lines for each element, accompanied by a number of weaker lines (see Fig. 38). Of the two strong lines, one is stronger than the other and is called the α-line, while the weaker is called the β-line. It has been shown that if v is the frequency (i.e. number of vibrations per second) of the α-line, and N the atomic number of the element, then

$$v = \tfrac{3}{4} (N - 1)^2 \times \text{a constant.}$$

This constant is called Rydberg's constant and has the value 109 677. If, therefore, we know the frequency of the α-line of the X-ray spectrum of an element, we can calculate the position that it ought to occupy in the Periodic Table, that is, its Atomic Number.

[1] Italics mine.—E. J. H.

This important discovery made it possible for the first time to call the roll of the chemical elements and to determine how many there were and how many remained to be discovered. There are between hydrogen and uranium 92

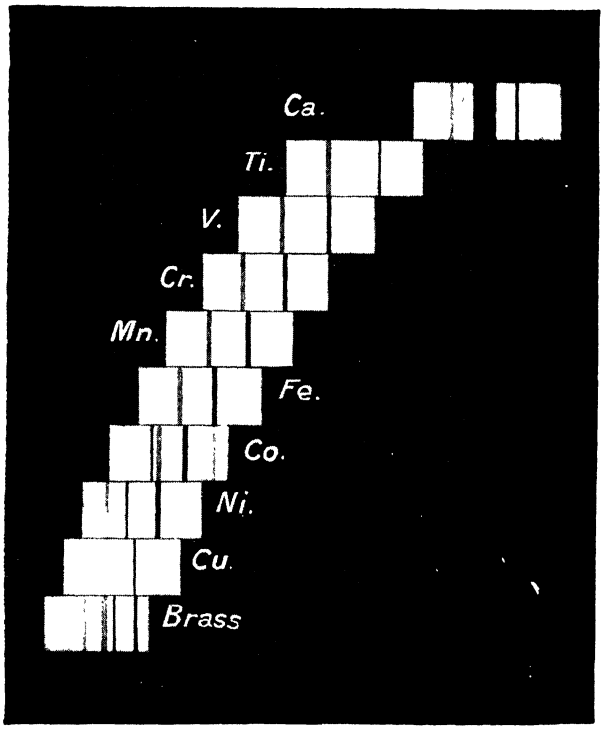


FIG. 38.—X-ray Spectra.

possible elements, of which only two (1931) remain to be found—namely, the two heaviest analogues of iodine and cæsium respectively.

Moseley's work, in fact, showed that the "properties of an atom were defined by a number which varied by unity

in successive atoms. This gives a new method of regarding the periodic classification of the elements, for the atomic number, or its equivalent the nuclear charge, is of more fundamental importance than its atomic weight." [1] Most of the physical and chemical properties of an atom depend upon the number and arrangement of the negative electrons in the atom, and these will clearly depend upon the charge on the nucleus. In other words, the actual *mass* of the atom is of secondary importance.

Hence we are led to the conclusion that "it is quite possible to imagine the existence of elements of almost identical physical and chemical properties, but which differ from one another in mass, for, provided the resultant nuclear charge is the same, a number of possible stable modes of combination of the different units which make up a complex nucleus may be possible." [2] In other words, we may get atoms which are chemically indistinguishable and yet of *different atomic weights*! Are we to regard such atoms as atoms of different elements, or as atoms of the same element? According to Dalton, all the atoms of the same element have the same atomic weight; therefore from this point of view atoms which are chemically identical but which have different atomic weights belong to different elements. On the other hand, chemical considerations would lead us to regard atoms that are chemically identical as atoms of the same element. SODDY gave the name *isotopes* or *isotopic elements* to those elements which fall into the same place in the periodic system, and are chemically identical, but have different atomic weights.

We have already seen that when an α-particle (or helium atom carrying two positive charges) is expelled from a radium atom, the product (radon) is an element which falls into

[1] Rutherford, *loc. cit.*

[2] Rutherford, *loc cit.* N.B. The idea of isotopes was by this time (1920) well understood, having been elaborated by chemical work on the disintegration of radium and its congeners. In order to make the subject clearer the historical sequence has not been strictly adhered to.

Group O of the periodic system, or *two columns to the left* of that in which the parent radium atom is placed. Study of other radioactive products has shown that this is a general phenomenon—expulsion of an α-particle from the atom of an element in Group N results in the formation of an atom of an element which falls into Group N–2 and which has an atomic weight differing by 4 units from that of the parent atom. Further investigation has produced evidence to show that when one β-particle is expelled from the atom (probably from the nucleus), an atom is formed which is that of an element which falls into a column *one to the right* of that in which the parent element is placed, but of the *same atomic weight.* "Each of the successive places in the periodic table thus corresponds with unit difference of charge in the constitution of the atom"—which is the conclusion previously arrived at by van den Broek. We see, too, that there is, in addition to the existence of isotopes, a possibility of the existence of *different elements with the same atomic weight*: these are called *isobaric heterotopes.* Elements that differ in chemical properties and also in atomic weight are called *heterobaric heterotopes.* All heterotopes are separable by chemical means.

The existence of isotopes suggested above is rendered still more probable by the following considerations. Suppose an atom loses an α-particle by radioactive change. We have seen that an atom will be formed of atomic weight 4 units less, and belonging to an element 2 columns to the left in the periodic table. Suppose now this daughter-atom loses 2 β-particles. It will have moved two places to the right in the table and will therefore have reached the position from which it set out, with no further change in atomic weight. We should now have two atoms differing by 4 units in atomic weight, but *absolutely identical in chemical properties,* that is, they are isotopic elements, or isotopic forms of the same element with different atomic weights. Fig. 39 will make this clear.

It will be seen that atoms A and B occupy the same position in the table, and are chemically identical; but they differ

in atomic weight by 4 units: they are isotopes. C and D are isobaric heterotopes.

The first case in which these views were tested experimentally was that of lead. It had been proved that the end-products of the radioactive disintegrations of thorium and of uranium both fell into the place in the periodic table occupied by lead, but a consideration of the intermediate stages led to the conclusion that the lead derived from uranium should have an atomic weight of 206, while that from thorium

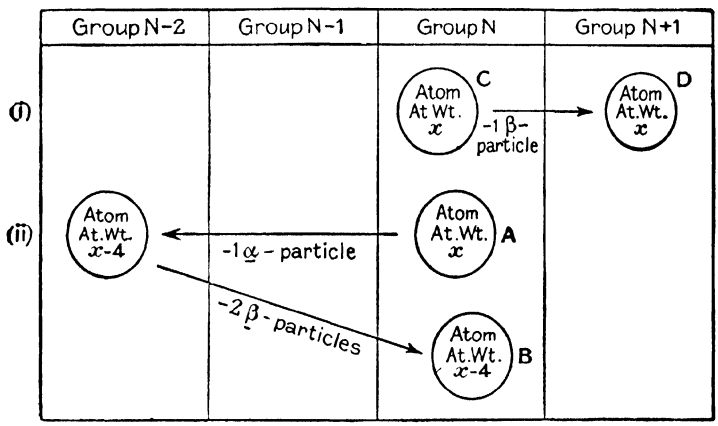


FIG. 39.

should have an atomic weight of 208. Now uranium minerals often contain small quantities of lead and it is reasonable to suppose that this lead has been derived from uranium by radioactive changes; similarly, the lead found in thorium minerals has probably been derived from thorium. Lead was extracted from both these sources and the atomic weights of the specimens carefully determined by chemists skilled in atomic weight determinations. It was found that the lead from uranium minerals had an atomic weight of 206·05 and that from thorium minerals 207·9! Thus the theory was triumphantly justified. Ordinary lead, of atomic weight

207·2, is a mixture of these isotopes with a third isotope, A.W. 207, in the appropriate proportion. The 206·05 lead and the 207·9 lead were proved to be chemically identical as predicted by the theory.

Since this date (1914), much more work has been done on isotopes of common elements, largely by means of SIR J. J. THOMSON'S *positive-ray method* of gas-analysis. Some account of this will first be given.

If holes are cut in the cathode of a Crookes' tube, such as that used for obtaining the cathode rays, it is found that a stream of rays travels from the cathode in the opposite direction to that of the cathode rays. By observation of the effect produced on these rays by electric and magnetic fields, they were found to consist of positively charged atoms or molecules of the gas which is present in the tube under very low pressure. Sir J. J. Thomson showed that the magnitude of the deviation of these particles caused by the application of a magnetic or an electric field was proportional to the ratio of the mass of the particle and its charge, or $\frac{e}{m}$. By using as cathode a fine aluminium rod with a capillary copper tube running through it from end to end, it was possible to get a fine pencil of the rays passing through the cathode and striking a photographic plate at a point directly opposite (A) (Fig. 40). If now a magnetic field be applied, the particle will be deflected and will strike the plate say at a point B. If the magnetic field be replaced by a suitable electric field the particle will be again deflected in a direction at right angles to that produced by the magnetic field, and will strike the plate say at C. Under the combined influence of both fields directly the particle will move in a resultant deflection and may strike the plate say at point D. Now in a stream of identical particles, not all will be travelling with the same speed, and therefore they will

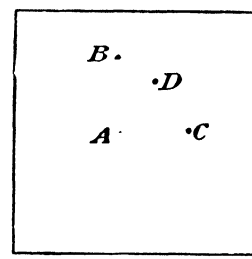


FIG. 40.

not all strike the plate at the same spot. It can, however, be proved by a simple calculation that if the deflection caused by the electric field is x and that by the magnetic field y, then $\frac{y^2}{x}$ is constant and equal to $\frac{e}{m}$ for all identical particles, whatever their speed. $\frac{y^2}{x} = a$ *constant* is of course the equation of a parabola, and therefore the photographic plate will on development show a parabolic streak caused by a stream of particles all of one kind. These parabolas will, however, be different for particles of different substances. Thus, if one particle is a hydrogen atom and another an atom of argon, the values of the expression $\frac{y^2}{x}$ will be different in the two cases, and if we have a stream of hydrogen atoms mixed with argon atoms we shall get two parabolas, one caused by the hydrogen and one by the argon. If the mass of the one kind of particle is m and that of another m', suitable measurement of the parabolas will enable us to get the ratio $\frac{m}{m'}$, and hence if we know m we can calculate m' (assuming the charge carried by each particle to be the same). The advantages of this method of analysis were well summed up by STEWART,[1] who said (1920) :—

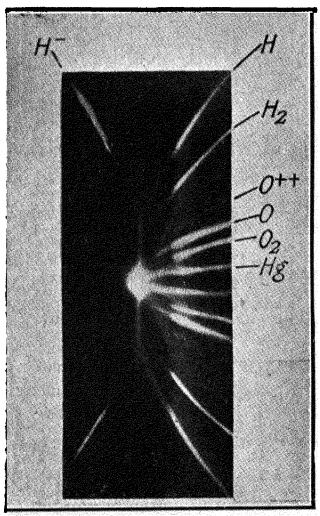


FIG. 41.—Typical Positive Ray Parabola.

"In the first place, it permits the analysis of extremely small quantities of a gas-mixture. Thus a quantity of helium which does not exceed 4×10^{-6} c.c. can be detected in a c.c. of air.

[1] *Recent Advances in Physical and Inorganic Chemistry.*

"Secondly, it carries our knowledge further than spectrum analysis can do. If we have only a trace of an element mixed with large quantities of other gases, the spectrum of the mixture may fail to reveal the presence of the trace owing to its characteristic lines being swamped by the spectra of its companions; whereas in the case of the positive ray method, each constituent is sifted out from the others.

"Thirdly, in the case of a new element, an examination of the spectrum tells us only that new lines are present; but with positive ray analysis it may be possible to go much further. For example, if we find two parabolas characteristic

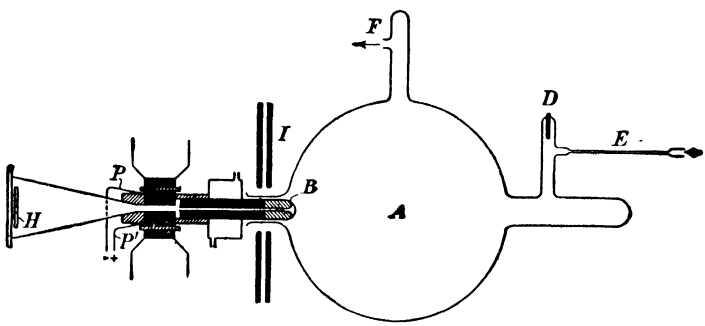


FIG. 42.—Positive Ray Apparatus.

A. Discharge flask. *B*. Cathode. *D*. Anode. *E*. Gas entry. *F*. Gas exit. *P*, *P'*. Analyser. *H*. Photographic plate.

of the new element, one must arise from the atom and the other from the diatomic molecule. If the substance is monatomic there will be only one parabola, or, if there be more than one produced (owing to the atom taking up more than a single charge), we can detect the nature of the charged body.

"These facts prove that in the positive ray method we have gained a new and formidable weapon for the chemical armoury."

Improvements of the positive-ray method of the analysis of gases, in the hands of ASTON and others, have shown that

many elements are heterogeneous, that is, the "element" as ordinarily met with is a mixture of isotopes. The following table, given by Aston, shows the results of the investigations of 20 elements :—

TABLE OF ELEMENTS AND ISOTOPES

Element.	Atomic Number.	Atomic Weight.	Minimum Number of Isotopes.	Masses of Isotopes, in order of their Intensity.
Hydrogen	1	1·008	1	1·008
Helium .	2	4·00	1	4
Boron .	5	10·82	2	11, 10
Carbon .	6	12·00	1	12
Nitrogen .	7	14·01	1	14
Oxygen .	8	16·00	1	16
Fluorine .	9	19·00	1	19
Neon . .	10	20·20	2	20, 22
Silicon .	14	28·06	2	28, 29, 30
Phosphorus	15	31·02	1	31
Sulphur .	16	32·06	3	32, 33, 34
Chlorine .	17	35·46	2	35, 37
Argon .	18	39·88	2	40, 36
Potassium	19	39·10	2	39, 41
Arsenic .	33	74·96	1	75
Bromine .	35	79·92	2	79, 81
Krypton .	36	82·92	6	84, 86, 82, 83, 80, 78
Iodine .	53	126·92	1	127
Xenon .	54	130·2	9	129, 132, 131, 134, 136, 128, 130, 126, 124
Mercury .	80	200·60	6	202, 200, 199, 198, 201, 204

It will be noticed that in every case the atomic mass of each isotope is a whole number (O = 16·00).[1]

To give an explanation of this, it has been suggested that the nuclei of other atoms are composed of hydrogen nuclei and helium nuclei. This theory has received support from work of Lord Rutherford, who has shown that by bombarding nitrogen atoms with α-particles it is possible to obtain

[1] Except in that of hydrogen, H = 1·008.

disintegration of a few of the nitrogen atoms, one of the products of the disintegration being swiftly-moving positively charged hydrogen atoms.

Within the last few years, the electronic structure of the atoms of many elements has been worked out to a high degree of probability. Thus the *hydrogen* atom is considered to be composed of one unit positive charge, or *proton*, acting as nucleus, round which revolves one electron describing a circular orbit. The *helium* atom consists of a nucleus of 4 protons and 2 electrons, round which revolve 2 electrons, i.e. the nucleus of helium—as of all other elements except hydrogen—consists of both protons and electrons—the number of " orbital " or revolving electrons being equal to the net or *resultant* charge on the nucleus.

The orbital electrons are believed to be arranged in concentric groups or " shells " in all cases where there are more than 2 in the atom, i.e. in all atoms except those of hydrogen or helium. Putting the matter another way, we may say that the orbital electrons fall into groups, the orbits of those in the same group being of the same radius, but of greater or smaller radius than those of inner or outer groups. The shells become " complete " when they contain $2n^2$ electrons, where $n = 1, 2, 3$ or 4.

The numbers of electrons in the shells are shown for several elements in the table following, where it will be observed that the total number of orbital electrons is, as previously stated, equal to the resultant charge on the nucleus, i.e. to the atomic number.

It will be noticed that the number of electrons in the outermost group is equal to the normal valency of the atom, except in the case of the rare gases. It is, in fact, believed that elements show a tendency to complete an outermost group or sub-group consisting of 8 electrons, or they do so in combination with other elements by parting with electrons of their own or acquiring those of the atoms with which they combine. An element that normally has a complete outer group of 8 electrons therefore shows no tendency to combine with other elements, i.e. its valency is 0.

ELECTRONIC STRUCTURE OF ATOMS

Element.	Atomic Number.	Electronic Groups						
		I.	II.	III.	IV.	V.	VI.	VII.
Hydrogen .	1	1						
Helium . .	2	2						
Lithium . .	3	2	1					
Beryllium .	4	2	2					
Boron . . .	5	2	3					
Fluorine . .	9	2	7					
Neon . . .	10	2	8					
Sodium . .	11	2	8	1				
Magnesium .	12	2	8	2				
Aluminium .	13	2	8	3				
Argon . . .	18	2	8	8				
Potassium .	19	2	8	8	1			
Calcium . .	20	2	8	8	2			
Copper . .	29	2	8	18	1			
Zinc . . .	30	2	8	18	2			
Gallium . .	31	2	8	18	3			
Krypton . .	36	2	8	18	8			
Rubidium .	37	2	8	18	8	1		
Strontium .	38	2	8	18	8	2		
Silver . . .	47	2	8	18	18	1		
Cadmium . .	48	2	8	18	18	2		
Xenon . .	54	2	8	18	18	8		
Cæsium . .	55	2	8	18	18	8	1	
Barium . .	56	2	8	18	18	8	2	
Gold . . .	79	2	8	18	32	18	1	
Mercury . .	80	2	8	18	32	18	2	
Radium . .	88	2	8	18	32	18	8	2

The electronic groups in the figure, except Group I, may be still further subdivided.

When sodium, with one valency electron, combines with fluorine, with 7 valency electrons, we assume that the sodium atom parts with its valency electron and is thus left with a complete outer ring of 8 electrons. The fluorine atom takes up the valency electron of the sodium, and thus completes its outer ring of 8. But the sodium atom thereby becomes *positively* charged (as it was electrically neutral before) and

the fluorine atom similarly becomes *negatively* charged. The two atoms are therefore bound together by electrostatic attraction.

All the orbital electrons in an atom—and possibly the nucleus as well—are believed to be in constant and rapid motion, hence any conception of the atom that shows them at rest (e.g. that suggested by LEWIS and LANGMUIR) is necessarily inadequate. The theories of BOHR, SCHROEDINGER, DIRAC and others are, however, too complicated for us to consider here; they deal with the movement, spin and magnetic moment of the electrons and the nucleus.

In this chapter we have seen the opening stages of what will surely be progress more wonderful than was witnessed even by the nineteenth century. Dalton's Atomic Theory is shown to be a rough generalization only—amply sufficient for everyday use and likely to be so for a very long time—but inaccurate in every particular. If we wonder at the genius of men like Dalton and Avogadro who could make measurements, by the eye of faith, of atoms and molecules, what are we to think of the chemists and physicists of to-day, who deal with particles so small that in comparison with them an atom is like our solar system compared with the earth?

What more striking example could we desire of that great truth of Science, so ably expressed by one of her most brilliant followers, JABIR IBN HAYYAN:—

"*Scientists delight not in abundance of material; they rejoice only in the excellence of their experimental methods*"?

QUESTIONS

1. What do you know of (*a*) positive-ray analysis, (*b*) X-ray spectra, (*c*) atomic numbers?
2. Give an account of modern views on the structure of the atom.
3. Explain fully the term *isotopes*.
4. Write an essay on a Clifton boy's dictum: "***Chemistry is a soul-destroying subject.***"

PART II

THE ELEMENTS AND THEIR COMPOUNDS

CHAPTER XVII

HYDROGEN

Group in Periodic System : unique ; *Symbol :* H ; *Valency :* 1 ; *Atomicity :* 2 ; *Atomic Weight :* 1·008.

History.—Although hydrogen must have been obtained by the alchemists, it was first recognized as a definite substance by CAVENDISH (1766), who prepared it by the action of dilute sulphuric acid upon iron or zinc. He called it *inflammable air*, and considered it to be practically pure *phlogiston* (p. 399). It was called hydrogen (" water-producer ") by LAVOISIER, on account of the fact (discovered by Cavendish) that a mixture of it with half its volume of oxygen on explosion yields water.

Occurrence.—Hydrogen is one of the most widely-distributed of the elements, not only on the earth but throughout the universe—the atmosphere of the sun, for example, consists largely of incandescent hydrogen. Free hydrogen occurs to some extent on the earth, in volcanic and natural gas and hence—but in the most minute traces—in the atmosphere. Combined hydrogen is found in abundance. Thus $\frac{1}{9}$ by weight of water consists of hydrogen, petroleum is a mixture of compounds of carbon and hydrogen, and hydrogen

is an essential constituent of all living matter. The percentage of hydrogen in the earth's crust is about 0·95.

Formation.—Pure hydrogen is obtained by the electrolysis of a dilute solution of barium hydroxide; the hydrogen is evolved at the cathode and pure oxygen at the anode. The gases are, however, moist and must be dried by standing over phosphorus pentoxide (P_2O_5). Electrolysis of dilute sulphuric acid yields a rather less pure hydrogen, and some of the oxygen is lost owing to the formation of persulphuric acid ($H_2S_2O_8$) and hydrogen peroxide (H_2O_2).

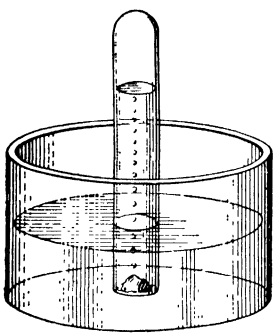


FIG. 43.

Hydrogen may also be obtained from water by the action of certain metals, which are oxidized by the oxygen present and the hydrogen thus set free. Sodium and potassium decompose water in the cold, forming the hydroxide of the metal, and hydrogen—

$$2Na + 2H_2O + 2NaOH + H_2.$$

The heat evolved is sufficient to melt the metals, which float on the water as molten globules, and in the case of potassium the temperature becomes high enough to cause the hydrogen to burn, the flame having a lilac colour owing to some of the potassium burning as well. The action of sodium and potassium upon water is not suitable as a means of preparing hydrogen in the laboratory, as the action is too violent. If, however, sodium is dissolved in mercury, the *sodium amalgam* so formed will decompose water more slowly, and as the amalgam sinks in water the hydrogen evolved may be easily collected by inverting a gas-jar full of water over the lump of amalgam in a pneumatic trough (Fig. 43).

Calcium is heavier than water and therefore sinks in it. It decomposes water in the cold—

$$Ca + 2H_2O = Ca(OH)_2 + H_2,$$

forming calcium hydroxide and hydrogen.

Magnesium will not attack cold water but acts upon hot water and readily burns in steam (Fig. 44), yielding magnesium oxide and hydrogen—

$$Mg + H_2O = MgO + H_2.$$

Magnesium amalgam and aluminium amalgam both liberate hydrogen from water, the former in the cold and the latter on heating. The action of aluminium amalgam on boiling water has been used for the manufacture of hydrogen.

LAVOISIER showed that hydrogen could be obtained by passing steam over heated iron.

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

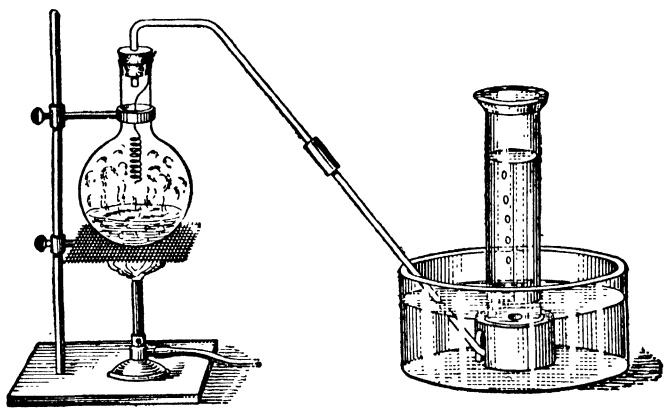


FIG. 44.

This action is reversible (p. 119). It is used commercially for the manufacture of hydrogen, the iron oxide formed being reduced to the metal again by treatment with water-gas (a mixture of carbon monoxide and hydrogen made by passing steam over red-hot coke, $C + H_2O = CO + H_2$). If a catalyst be employed (ferrous chloride and copper), liquid water under pressure readily reacts with iron at a temperature of 300°–340° C., with liberation of hydrogen, which, as it is produced under pressure, may be passed directly into the steel cylinders in which it is sold, without further compression.

Hydrogen is generally prepared in the laboratory by the action of dilute sulphuric acid upon zinc—

$$Zn + H_2SO_4 = ZnSO_4 + H_2.$$

For this reaction to take place at an appreciable rate, it is necessary that impurities should be present. If pure zinc and pure dilute sulphuric acid are used the evolution of gas is extremely slow, but addition of a little copper sulphate or platinum chloride will hasten the reaction.

Other metals, such as iron and magnesium, may be used, and hydrochloric acid may be substituted for sulphuric acid. Nitric acid, however, is not suitable, as it is readily reduced by hydrogen, and the product of the action of nitric acid on metals is therefore not hydrogen but a reduction product, or a mixture of reduction products, of the acid (see p. 357).

Hydrogen is evolved when zinc, tin or aluminium is heated with caustic soda or caustic potash solution—

i. $Zn + 2NaOH = Na_2ZnO_2 + H_2.$
Sodium zincate.

ii. $2H_2O + 2Al + 2NaOH = 2NaAlO_2 + 3H_2.$
Sodium meta-aluminate.

iii. $Sn + 4NaOH = Na_4SnO_4 + 2H_2.$
Sodium stannate.

"*Silicol*" *process.* An alloy of silicon and iron (*ferrosilicon*) is added to a concentrated solution of caustic soda, when sodium silicate and hydrogen are formed, roughly according to the equation

$$Si + 2NaOH + H_2O = 2H_2 + Na_2SiO_3.$$

In reality the reaction is rather more complicated. A mixture of slaked lime and caustic soda gives better results than caustic soda alone. From a commercial point of view the chief disadvantage of this method lies in the fact that the materials are expensive.

"*Hydrolith*" *process.* Hydrolith is the trade name for impure (90 per cent.) calcium hydride, CaH_2. This substance is prepared by heating calcium in hydrogen, and on treatment

with cold water it yields calcium hydroxide and hydrogen—

$$CaH_2 + 2H_2O = Ca(OH)_2 + 2H_2.$$

Most of the hydrogen of commerce is obtained as a by-product in the manufacture of sodium and caustic soda by electrolytic methods. A good deal, however, is prepared from water-gas (p. 301) by the removal of the carbon monoxide, e.g. by passing the gas over heated calcium carbide, when a mixture of calcium carbonate and calcium oxide is left, the hydrogen being unaffected.

Properties.—Hydrogen is a colourless gas, with no taste or smell. It is the lightest substance known (1 litre weighs 0·0896 grams at N.T.P.), and is therefore used for filling airships, although its inflammable nature makes it a constant source of danger. Owing to the serious disasters that have occurred from this cause, the modern practice is to substitute helium for hydrogen where this can be done. Helium has about 92 per cent. of the lifting-power of hydrogen and is absolutely non-inflammable. It is, however, considerably more expensive than hydrogen.

Liquid hydrogen was first obtained by Sir James Dewar in 1895. It is a colourless liquid, of density 0·07, which boils at — 253° C. By rapidly evaporating liquid hydrogen under reduced pressure, solid hydrogen can be obtained, in the form of white crystals melting at — 259° C. It was at one time supposed that hydrogen was the vapour of a metal, but this idea was disposed of by the production of solid hydrogen, which has no metallic properties.

Occlusion of Hydrogen.—Many metals have the power of absorbing hydrogen in the cold and giving it up again when heated. Palladium possesses this power in a high degree—1 volume of palladium wire will absorb 930 volumes of hydrogen at N.T.P. Cobalt powder will absorb about 100 volumes. Graham called this phenomenon the *occlusion* of hydrogen by metals. It was at one time supposed that in the case of palladium a *palladium hydride*, Pd_2H[1], was formed (Troost and Hautefeuille), but Roozeboom showed that

[1] Or Pd_3H_2.

the hydrogen probably dissolves in the palladium forming a solid solution. The question is, however, still unsettled. In any case, there seems to be a condensed layer of hydrogen on the surface of the occluding metal, and this probably accounts for the fact that a mixture of oxygen and hydrogen is ignited by the introduction of finely-divided platinum: the oxygen and hydrogen are brought into close contact at the surface of the metal, when reaction between them occurs, and the heat evolved is sufficient to ignite the rest of the mixture.

Charcoal will absorb hydrogen and many other gases, especially when it is cooled in liquid air. McBain (1909) has shown that this absorption takes place in two stages: (i) rapidly on the surface of the charcoal, and (ii) slowly by diffusion into the interior of the charcoal. The former process he calls *adsorption*, the latter *absorption*, and the two together *sorption*.

Reduction.—When hydrogen is passed over a heated metallic oxide, the latter often loses its oxygen, and the metal is liberated—

$$\text{metallic oxide} + \text{hydrogen} = \text{metal} + \text{water}.$$

This process is called *reduction*, and hydrogen is said to be a *reducing agent*. The phenomena of reduction and oxidation are considered in more detail on page 428.

"*Nascent*" *Hydrogen.*—Hydrogen is much more chemically active at the moment of its liberation in an exothermic chemical reaction. It is then said to be in the *nascent* state. Thus, if hydrogen is passed through ferric chloride solution, no change occurs, but if zinc and dilute hydrochloric acid are added to ferric chloride solution, the yellow colour of the ferric salt disappears, and ferr*ous* chloride is formed—

$$FeCl_3 + H = FeCl_2 + HCl.$$

Many similar reactions are known. It was suggested that the atoms of hydrogen in the nascent state have not joined together to form the diatomic molecules of ordinary hydrogen, and that the greater chemical activity of nascent hydrogen is due to this cause. However, the chemical activity of nascent hydrogen varies according to the reaction in which

it is produced, and therefore cannot be due merely to the fact that the hydrogen is in the atomic state. Since "nascent" hydrogen is formed only in exothermic reactions, the phenomena it produces may be due to the fact that it has considerable but varying amounts of energy temporarily at its disposal.

"*Active*" *hydrogen* has been prepared by LANGMUIR by heating filaments of tungsten, palladium or platinum to very high temperatures in hydrogen at low pressures. It is much more chemically active than ordinary hydrogen, and can react directly with oxygen, phosphorus and other substances, at room temperature. It is supposed that this hydrogen is in the atomic state. Langmuir has also shown that by blowing hydrogen into the electric arc the diatomic molecules are split up into single atoms. Combustion of this "atomic" hydrogen yields extremely high temperatures —considerably above that of the electric arc—and atomic hydrogen blowpipes have found application in the welding of metals, etc.

Commercial Uses of Hydrogen.—Hydrogen is used for filling airships and balloons; mixed with carbon monoxide it forms *water-gas*, used as a fuel; the flame of hydrogen burning in oxygen is the *oxyhydrogen* flame, which is produced by means of special blowpipes and is used for many purposes. SABATIER and SENDERENS showed that many oils could be converted into solid fats by reducing them with hydrogen, using reduced nickel (that is, nickel obtained in a fine state of division by reduction of nickel oxide) as a catalyst. This process is used in the manufacture of margarine. Hydrogen is also used in the preparation of quick-drying varnishes and in the manufacture of synthetic ammonia. It is one of the chief constituents of coal-gas.

Position of Hydrogen in the Periodic System.—Hydrogen is a unique element—it has no analogues. Some chemists consider it to be most closely related to the alkali metals, others to the halogens. The former position seems to be the more natural, as the alkali metals are, like hydrogen,

electropositive while the halogens are electronegative. The following table shows the main points to be considered—

	HYDROGEN.	ALKALI METALS.	HALOGENS.
i.	Gas	Solids	Gases (lower members)
ii.	Molecules diatomic	Molecules monatomic	Molecules diatomic
iii.	Oxide stable	Oxides stable	Oxides unstable
iv.	Electropositive	Electropositive	Electronegative
v.		Hydrides unstable	Hydrides stable
vi.		Replaceable by hydrogen in salts	Replaceable by hydrogen in organic compounds, but not in salts
vii.	More gaps are left in the Periodic System if hydrogen is placed above Lithium		

Of these, i, ii and vii are favourable to the view of hydrogen as a halogen, the rest show its similarity to an alkali metal. It has recently been shown that fused lithium hydride, LiH (p. 191), on electrolysis yields hydrogen at the *anode*. This would support the view of those who class hydrogen with the halogens.

QUESTIONS

1. Describe the preparation and properties of hydrogen.
2. How is hydrogen made on the commercial scale? What are its uses?
3. Write an account of the occlusion of hydrogen by metals.
4. Write short notes on (*a*) nascent hydrogen, (*b*) active hydrogen
5. Discuss the position of hydrogen in the Periodic Table.
6. What do you know of the history of hydrogen?

CHAPTER XVIII

GROUP 0

THE INACTIVE GASES

Group in Periodic System: **0**; *valency:* **0.**

Very interesting accounts of the discovery of the inactive gases are to be found in SIR WILLIAM RAMSAY'S book, *The Gases of the Atmosphere*, and in M. W. TRAVERS' *The Discovery of the Rare Gases* (Arnold, 1928), which the student is strongly recommended to read.

In 1785 CAVENDISH published (*Phil. Trans.*, 75, 372, 1785) an account of his work on the conversion of atmospheric nitrogen into oxides of nitrogen by sparking with oxygen. He found that a bubble of gas, about $\frac{1}{120}$th of the original volume of nitrogen taken, defied all efforts made to convert it into nitrogen oxides, and said, "If there is any part of the phlogisticated air of our atmosphere which differs from the rest . . . we may safely conclude that it is not more than $\frac{1}{120}$th part of the whole."

For over a century Cavendish's observation was neglected, but in 1894 RAYLEIGH found that the density of atmospheric nitrogen was always slightly greater (about 0·5 per cent.) than that of nitrogen obtained by the decomposition of nitrogenous compounds. Rayleigh then repeated Cavendish's experiments and found that his results were correct; spectroscopic examination of the residual gas showed that it certainly was not nitrogen.

Rayleigh next began experiments, in collaboration with SIR WILLIAM RAMSAY, to obtain the new gas in larger quantities. This was done by absorbing the oxygen of air by

red-hot copper and the nitrogen by red-hot magnesium. In this way a gas was obtained of density 19·94. The new gas was characterized by its *entire* lack of chemical activity, and was therefore called **argon** (Greek, *idle*). Since argon forms no chemical compounds at all, it has no equivalent; the molecular weight, however, must be twice the vapour density (19·94) and is therefore 39·88. The atomicity of the molecule was found to be 1, by determining the ratio of the specific heats of the gas (p. 41); hence the atomic weight also is 39·88.

Argon was afterwards prepared on a larger scale by the fractional distillation of liquid air, and careful examination of the different fractions led to the discovery of four more gases similar to argon—**helium, neon, krypton** and **xenon.**

Sir Norman Lockyer had many years previously (1868) discovered helium in the sun, by means of the spectroscope, and it was also found by Ramsay in 1894 in the gases evolved, on heating, from the mineral *cleveite.* More recently, helium has been found in large quantities (over 1 per cent.) in the natural gas of certain American (Texas) gas-wells, and has been extracted on a commercial scale for use in airships, since it is very light (V.D. = 2) and non-inflammable.

The α-particles expelled from radium were shown to consist of charged helium atoms, and modern work on the structure of matter (Chap. XVI) affords strong evidence for the theory that the nuclei of all other elements are composed of hydrogen and helium nuclei.

A sixth member of the group is **radon,** or *radium emanation,* a radioactive gas evolved from radium. It is unstable, and disintegrates fairly quickly into helium and other products; this disintegration is not a chemical change in the ordinary sense of the term, but an actual decomposition of radon *atoms.*

The inactive gases (or helium group of elements) fall naturally into the periodic system between the strongly electropositive alkali metals and the strongly electronegative halogens. The atomic weight of argon (39·88) is slightly greater than that of potassium (39·1) and argon therefore appeared to be an anomaly in the system until it was realized that the

atomic numbers (p. 166) of the elements, and not their atomic weights, are the more fundamental characteristics. The atomic number of argon is 18, whereas that of potassium is 19; by taking atomic numbers instead of atomic weights, therefore, the discrepancy disappears.

All the inactive gases are without chemical properties of any kind, and their molecules are all monatomic. The chief physical characteristics are given in the following table:—

Gas.	Atomic Weight.	Atomic Number.	Boiling Point, Absolute.	Melting Point, Absolute.	Ratio of Specific Heats.
Helium .	4·0	2	4·5°	1·5° (?)	1·65
Neon . .	20·2	10	27·1°	?	1·64
Argon .	39·88	18	86°	83·4°	1·65
Krypton .	82·92	36	122°	104°	1·69
Xenon .	130·2	54	163·9°	133°	1·67
Radon[1] .	222·5	86	211°	202°	Undetermined

Helium proved extraordinarily difficult to liquefy; it was first liquefied by ONNES in 1907.

The following *isotopes* (p. 168) of the inactive gases are known; partial separation has been effected in the case of neon:—

Helium, 1, At. wt. 4·0.
Neon, 2, At. wts. 20 and 22.
Argon, 2, At. wts. 40 and 36.
Krypton, 6, At. wts. 84, 86, 82, 83, 80 and 78.
Xenon, 7, At. wts. 128, 129, 130, 131, 132, 134 and 136.

Neon and argon are prepared commercially for use in gas-filled electric lamps; indeed, the cheapest way of obtaining a specimen of neon is to buy a neon lamp. Of recent years, neon electric discharge tubes have played an important part in the illuminated advertisements of our great cities; at night the *Boulevard des Italiens*, Paris—for example—is diffused with the characteristic and beautiful orange-red neon glow.

Neon lighthouses are also used at the principal aerodromes, especially to guide aeroplanes in times of fog, since the light rays at the red end of the spectrum are very penetrating in foggy conditions, as is evidenced by the colour of the sun on a foggy day.

Questions

1. Give an account of the discovery of argon.
2. Describe the general properties of the inactive gases.
3. Discuss the position of the inactive gases in general, and of argon in particular, in the Periodic System.

CHAPTER XIX

GROUP I

Typical Elements: Lithium, Sodium.
Sub-group A (similar to the typical elements): **Potassium,** Rubidium, Cæsium.
Sub-group B: **Copper, Silver, Gold.**

THE ALKALI METALS

Group I in the Periodic Table includes Lithium and Sodium, with Potassium, Rubidium and Cæsium in section A and Copper, Silver and Gold in section B. The first five of these elements are called the Alkali Metals. They form a well-marked group of metals exhibiting great similarity of chemical and physical nature, and this similarity extends to their compounds as well, as shown in the following table :—

	Lithium, Li.	Sodium, Na.	Potassium, K.	Rubidium, Rb.	Cæsium, Cs.
Atomic weight	6·94	23·0	39·1	85·45	132·8
Valency . .	1	1	1	1	1
Specific gravity	0·59	0·97	0·87	1·52	1·89
Atomic volume	11·9	23·7	45·0	56·1	70·7
Melting-point	180°	96°	62·5°	38·5°	26·5°
Atomicity .	1	1	1	1	1
Colour of vapour	Not recorded	Violet	Green	Blue	Not recorded
Simplest oxide	Li_2O	Na_2O	K_2O	Rb_2O	Cs_2O
Peroxide . .	—	Na_2O_2	K_2O_4	Rb_2O_2; Rb_2O_4	Cs_2O_2; Cs_2O_4
Chloride . .	LiCl	NaCl	KCl	RbCl	CsCl
Carbonate .	Li_2CO_3	Na_2CO_3	K_2CO_3	Rb_2CO_3	Cs_2CO_3
Hydride . .	LiH	NaH	KH	RbH	CsH
Action on water	Hydrogen evolved slowly.	Hydrogen evolved quickly. Metal melts.	Hydrogen evolved quickly and ignites. Metal melts.	Hydrogen evolved very quickly and ignites. Metal melts.	Hydrogen evolved very quickly and ignites. Metal melts.

The alkali metals are strongly electropositive, and their chemical activity increases with increase of atomic weight. They readily oxidize in the air and decompose water in the cold forming hydroxides, with evolution of hydrogen—

$$2R + 2H_2O = 2R.OH + H_2.$$

They are soft metals and can easily be cut with a knife or moulded between the fingers. Owing to their affinity for oxygen, they are kept in sealed tins or under rock-oil, a liquid that contains no oxygen.

Lithium

Group in Periodic System: I; *Symbol:* Li; *Valency:* 1; *Atomicity of Vapour:* 1; *Atomic Weight:* 6·94; *Melting-Point:* 180°: *Specific Gravity:* 0·59.

Although lithium is widely distributed in nature, it is found only in small quantities. Its chief ores are *lepidolite* and *spodumene* (double silicates of aluminium and lithium, generally containing sodium and potassium silicates as well). It is also found in the waters of springs at Redruth (Cornwall) and other places.

It is a silvery-white metal which rapidly tarnishes in moist air. It will burn if heated in air or in oxygen, forming lithium monoxide, Li_2O. This is a white solid soluble in water, with which it forms lithium hydroxide—

$$Li_2O + H_2O = 2LiOH.$$

Lithium chloride, LiCl, closely resembles sodium chloride, but lithium carbonate, Li_2CO_3, is only slightly soluble in water and on heating splits up into lithium oxide and carbon dioxide—

$$Li_2CO_3 = Li_2O + CO_2,$$

in these respects differing from the carbonates of the other alkali metals.

Lithium compounds when heated in the Bunsen flame colour it a deep red; this property is made use of for the detection of lithium.

Since lithium urate is the most soluble urate known, a solution of a lithium compound is often taken as a medicine



Nat. Portrait Gallery.

SIR HUMPHRY DAVY

in cases of uric acid diseases (e.g. rheumatism), but it is of doubtful efficacy.

Sodium

Group in Periodic System : I ; *Symbol :* Na ; *Valency :* 1 ; *Atomicity of Vapour :* 1 ; *Atomic Weight :* 23·0 ; *Melting-point :* 96° ; *Specific Gravity :* 0·97.

Occurrence.—The chief naturally occurring compounds of sodium are *sodium chloride*, which is found in the solid state as rock-salt in England, Germany, Galicia and many other countries, and in solution in brine-springs (Droitwich, etc.) and in the sea ; *Chile saltpetre* or *sodium nitrate*, beds of which occur in South America ; and a *sodium carbonate* or *sesqui-carbonate*, found in East Africa, Australia, and in smaller quantities in many other hot countries. *Qali* (whence our word *alkali*) was the crude sodium carbonate obtained by the Arabian alchemists from the ashes of maritime plants.

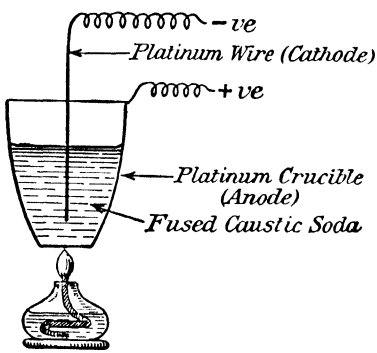


Fig. 45.—Davy's Apparatus for the Preparation of Sodium.

Manufacture.—Sodium was first obtained by Sir Humphry Davy in 1807 by the electrolysis of fused caustic soda (NaOH), and, after an interval during which it was prepared by other means, it is still prepared by an elaboration of Davy's method.

In Castner's process, chiefly used in England and in France, the caustic soda is fused in an iron pot, through a hole in the bottom of which an iron rod, the cathode, rises. This is kept in position by allowing the caustic soda round its base to solidify. The cylindrical anode of nickel surrounds the upper part of the cathode, and between the two there is a cylinder of wire-gauze. The caustic soda is maintained in the fused state partly by the heat developed during electro-

lysis and partly by a ring of gas-burners underneath the pot. Hydrogen and sodium are liberated from the cathode and the molten sodium rises into the receptacle *D*, from which it is ladled out from time to time with a perforated spoon, the holes of which are of such a size that the sodium is retained but that any caustic soda accidentally taken up at the same time runs through into the pot again. The hydrogen, and the oxygen which is evolved at the anode, are valuable by-products and are collected.

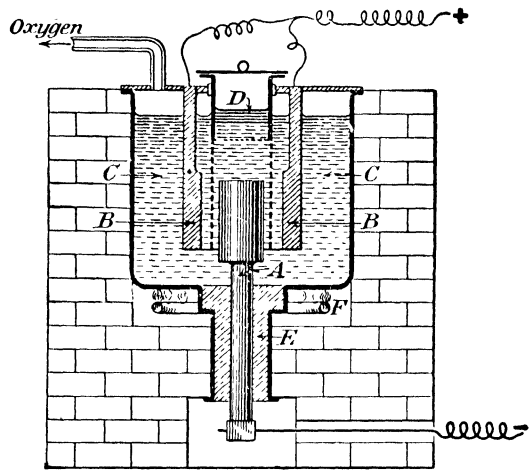


FIG. 46.—Electrolysis of Fused Caustic Soda.

A. Iron cathode. *B*. Nickel anode. *C*. Fused caustic soda. *D*. Sodium. *E*. Solid caustic soda. *F*. Ring of gas burners.

Sodium is used in the manufacture of sodium cyanide (for gold-extraction), sodium peroxide, various dye-stuffs, etc. The annual production runs into thousands of tons.

Properties.—M.P. 96°. B.P. 877°. Sodium is a soft, silvery metal, which is readily attacked by moist air. A thin coating of monoxide (Na_2O) is first formed ; this is then converted into hydroxide (NaOH) by the moisture present, and finally sodium carbonate is formed, owing to the action of atmospheric carbon dioxide upon the hydroxide—

$$2NaOH + CO_2 = Na_2CO_3 + H_2O.$$

When burnt in the air, sodium is converted into sodium peroxide, Na_2O_2.

Sodium readily dissolves in warm mercury, forming *sodium amalgam*, which is liquid at ordinary temperatures when the concentration of sodium in it is small, but forms a crystalline solid with higher concentrations of sodium.

Compounds of Sodium.—Sodium forms two oxides, Na_2O and Na_2O_2.

Sodium monoxide, Na_2O, is a white crystalline solid formed by heating sodium peroxide with sodium or by partially oxidizing sodium in pure oxygen and then distilling off the unchanged metal. It readily combines with water, yielding caustic soda—

$$Na_2O + H_2O = 2NaOH.$$

At 200° it reacts with hydrogen, forming sodium hydroxide and hydride—

$$Na_2O + H_2 = NaOH + NaH.$$

Sodium peroxide, Na_2O_2, is important commercially as an oxidizing agent. It is manufactured by heating sodium on aluminium trays in iron tubes in a current of dry air from which all carbon dioxide has been removed. It is a yellowish solid, readily reacting with water with evolution of oxygen—

$$2Na_2O_2 + 2H_2O = 4NaOH + O_2.$$

It is a powerful oxidizing agent and is used for bleaching and for obtaining a supply of oxygen in closed spaces such as submarines and diving-bells. The commercial name is "oxone." With cold absolute alcohol it yields *sodium hydroperoxide* or *sodyl hydroxide*, Na.O — OH.

Sodium Hydroxide, or Caustic Soda, NaOH.—Caustic soda is made in three ways—

(i) By boiling a 10 per cent. solution of sodium carbonate with lime (*Gossage's method*).

$$Na_2CO_3 + Ca(OH)_2 \rightleftharpoons CaCO_3 + 2NaOH.$$

The calcium carbonate is precipitated. As the action is reversible, the working conditions have to be carefully

adjusted in order to get the best yield. The solution of caustic soda is filtered off as soon as test portions treated with dilute hydrochloric acid give no carbon dioxide, thus showing that all the sodium carbonate has been decomposed. It is then concentrated in specially constructed vacuum evaporators, heated by steam ; the remaining water is driven off by heating in polished cast-iron soda-pots. The temperature required to get rid of the last traces of water is above the melting-point of caustic soda ; the latter is therefore left in the molten state and is run off and either sealed up in metal drums or cast into the sticks or pellets so familiar in the laboratory.

(ii) By heating a mixture of sodium carbonate and iron ore (Fe_2O_3) in revolving cylinders, when sodium ferrite and carbon dioxide are formed :

$$Na_2CO_3 + Fe_2O_3 = 2NaFeO_2 + CO_2.$$

The sodium ferrite is then decomposed with water and the precipitated ferric oxide allowed to settle :

$$2NaFeO_2 + H_2O = 2NaOH + Fe_2O_3.$$

(iii) *By Electrolysis.*—The electrolytic processes may be divided into three classes—

(*a*) Electrolysis of sodium chloride solution, using a diaphragm in the cell.

(*b*) Electrolysis of sodium chloride solution, in a cell without a diaphragm.

(*c*) Electrolysis of fused sodium chloride, and treating the resulting lead-sodium amalgam with water (p. 199).

In each case chlorine is obtained as an equally important product.

(*a*) The Hargreaves-Bird Method.—The sides of the cell in this process are made of compressed asbestos impregnated with sodium silicate, and although liquid diffusion cannot take place through them they are permeable to ions. The cell is filled with salt-solution which enters at the bottom, the liquid after electrolysis escaping through a pipe at the top. The anodes are made of carbon, or of rods of lead carrying lumps of gas-carbon, and dip into the solution in the cell. The cathode consists of a net of copper wire covering the

outer surface of the asbestos sides, which constitute the diaphragm. The whole cell is enclosed in an outer chamber into which steam can be blown. On electrolysis, chlorine is liberated at the anode and escapes through a pipe at the top, while sodium ions pass through the asbestos diaphragm and are discharged at the cathode. The sodium thus formed is converted into a solution of caustic soda by the steam which is blown in.

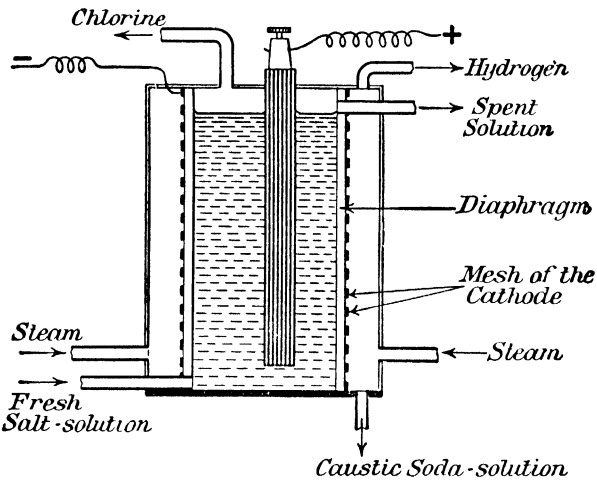


FIG. 47.—Hargreaves-Bird Cell.

Other diaphragm processes have been invented by Le Sueur, etc.

(*b*) THE CASTNER-KELLNER PROCESS.—In this process the cell consists of a rectangular tank divided into three compartments by non-porous partitions which reach nearly but not quite to the floor. On the floor is a layer of mercury of such a depth that the three compartments are completely separated from one another by it.

The middle compartment contains water, into which dip a number of iron rods, forming the cathode. The end chambers are filled with strong salt solution and contain the anodes,

which are made of carbon rods. When the current is passed chlorine is evolved at the anodes and is led away and compressed; sodium ions pass to the mercury where they are discharged, the sodium dissolving in the mercury. By means of an eccentric the cell can be gently rocked, and this movement causes circulation of the sodium amalgam, which when it enters the middle chamber reacts with the water and forms a solution of caustic soda, hydrogen coming off from the cathode. Continuity of this process obviously depends upon continuous circulation of the mercury. In the above case this is brought about by rocking the cell, but other methods also are used.

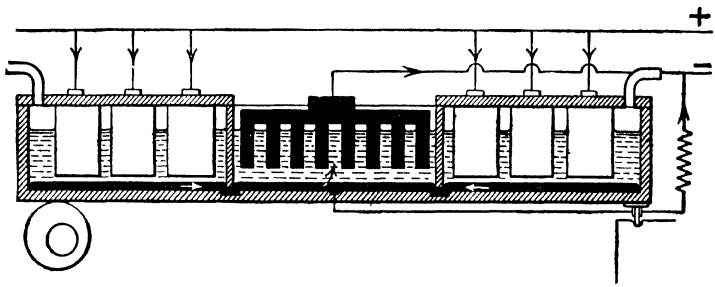


FIG. 48.—Castner-Kellner Cell.

(c) Sodium hydroxide has also been manufactured by the electrolysis of fused sodium chloride, molten lead being used as the cathode. The lead-sodium amalgam thus formed was decomposed by steam. The practical difficulties of this method were very great, largely owing to the high melting-point of sodium chloride.

Properties.—Caustic soda is a white crystalline solid which deliquesces in moist air. On prolonged standing, however, the liquid obtained goes solid again owing to the absorption of carbon dioxide from the air, resulting in the formation of sodium carbonate,

$$2NaOH + CO_2 = Na_2CO_3 + H_2O.$$

Caustic soda is very soluble in water, heat being evolved. The solution is strongly alkaline; caustic soda, indeed, is one

of the strongest bases known, i.e. it has a high degree of ionization in aqueous solution. The solution will precipitate the hydroxides (sometimes the oxides) of heavy metals from solutions of their salts.

In the laboratory, caustic soda is used as a reagent in qualitative analysis (preparation of hydroxides), for the absorption of carbon dioxide and sulphur dioxide from gas mixtures, for the titration of acids in volumetric analysis, and for the saponification or hydrolysis of esters and other organic compounds.

The chief impurity in caustic soda is iron (from the evaporating vessels). Caustic soda may be purified by recrystallization from alcohol, and is then described as " pure by alcohol."

In commerce, caustic soda is largely used for soap-making. Ordinary white soap consists chiefly of sodium stearate and palmitate, while " soft soap " consists of the corresponding potassium salts. Caustic soda finds also many other applications, especially in the dye industry and in the preparation of artificial silk.

Sodium hydride, NaH, is a white crystalline solid prepared by passing dry hydrogen over heated sodium. It is decomposed by water, yielding hydrogen and caustic soda:

$$NaH + H_2O = NaOH + H_2.$$

Sodium carbonate, $Na_2CO_3.10H_2O$.—Sodium carbonate, or " soda," is one of the most important compounds of sodium. In the form of a compound with sodium bicarbonate ($NaHCO_3$), called sodium sesquicarbonate, $Na_2CO_3.NaHCO_3.2H_2O$, it occurs in vast quantities in East Africa, but most of the soda of commerce is manufactured from common salt. The oldest of the processes now or formerly employed was invented by Nicholas Leblanc (1742–1806), who first converted sodium chloride into sodium sulphate and then heated the latter with carbon and calcium carbonate. He was a doctor, and his wealthy patient, the Duke of Orléans, lent him £8,000 to work the process on a commercial scale. Then came the Revolution. The Duke was guillotined in 1793, and Leblanc was ordered to make his process public, as soda supplies in

France were running very short, owing to the blockade. Reduced to poverty, Leblanc lived on in misery till 1806, when he committed suicide.

In England, the manufacture of soda was first established by MUSPRATT in 1824, who used the Leblanc process, but had some difficulty in persuading the public that his product really was soda. (The idea of the chemical individual is still grasped only with the greatest difficulty by the layman, who most often regards the product of the laboratory as an excellent imitation, but not the *real stuff*!)

The Leblanc process now has very serious rivals, and is nearly, if not quite, obsolete. It has, however, been long in dying, since the hydrochloric acid obtained as a by-product is very valuable. It is interesting to remember that in the early days this acid was allowed to escape into the atmosphere, and proved such a nuisance that an Act of Parliament was passed to compel manufacturers to absorb it. It would need an Act of Parliament now to prevent them from absorbing it.

MODERN LEBLANC PROCESS.—(i) A charge of salt is first mixed with an approximately equal weight of concentrated

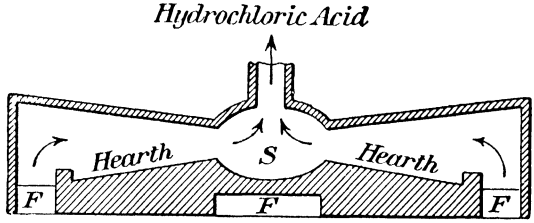


FIG. 49.—Saltcake Furnace—Old Form.

F. Furnace. *S*. Pan for first stage of process. The arrows indicate the path of the hot gases.

sulphuric acid, and heated, when hydrochloric acid and sodium hydrogen sulphate are formed,

$$NaCl + H_2SO_4 = NaHSO_4 + HCl.$$

The residue, consisting of the sodium hydrogen sulphate and unchanged salt, forms a pasty mass which is raked out

on to a hearth heated to a much higher temperature, when sodium sulphate is formed with further liberation of hydrochloric acid—

$$NaHSO_4 + NaCl = Na_2SO_4 + HCl.$$

In the older forms of furnace used for this purpose, the hearth was heated directly by hot furnace gases, but as these

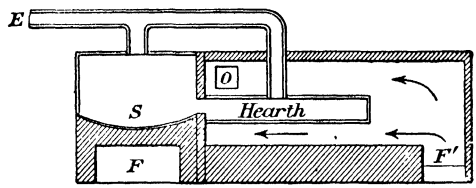


FIG. 50.—Saltcake Furnace—New Form.

S. Pan or first stage of process. *F.* Furnace for heating *S*. *F'*. Furnace for heating hearth. *O.* Exit flue for hot gases from *F'*. *E.* Exit pipe for the hydrochloric acid gas.

mixed with the hydrochloric acid gas formed and thus rendered it impure, the hearth is nowadays arranged in such a way that there is a brick partition between it and the hot gases.

The hydrochloric acid gas is absorbed in towers packed with

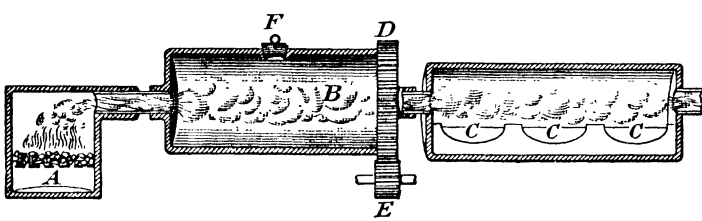


FIG. 51.—Black Ash Revolving Furnace.

A. Furnace for generating hot gases. *B.* Cylindrical revolving furnace. *CC.* Evaporating pans. *DE.* Cog wheels for driving B. *F.* Opening to furnace.

coke over which a stream of water trickles, a solution of hydrochloric acid running out at the bottom. These towers were invented by WILLIAM GOSSAGE in 1836.

(ii) The sodium sulphate, or *salt-cake*, is then mixed with powdered limestone ($CaCO_3$) and small coal, and heated

strongly in cylindrical iron furnaces which revolve around their longitudinal axes. Each furnace will hold about 18 tons, and is heated by hot gases which enter it through an opening at the end. After passage through the furnace, the hot gases are led over the surface of soda solutions in evaporating pans and their heat thus usefully employed in evaporation.

During the operation, the furnace is slowly rotated, thorough mixing and heating being thus ensured. The end of the reaction is marked by the appearance of flames of carbon monoxide, and the semi-liquid mass is then run out through an opening in the furnace into iron trucks below, where it solidifies.

The product is called *black-ash*, and consists of sodium carbonate mixed with excess of limestone and coal, sodium and calcium sulphides, lime, and other substances. The reaction in the furnace may be represented by the following equations—

(i) $Na_2SO_4 + 4C = Na_2S + 4CO$
(ii) $Na_2S + CaCO_3 = CaS + Na_2CO_3$.

The black-ash is crushed and lixiviated or extracted with water, in the cold, in a series of iron tanks which are arranged in such a way that the maximum concentration of solution is obtained, together with complete extraction. The principle of this method will be clear from Fig. 52.

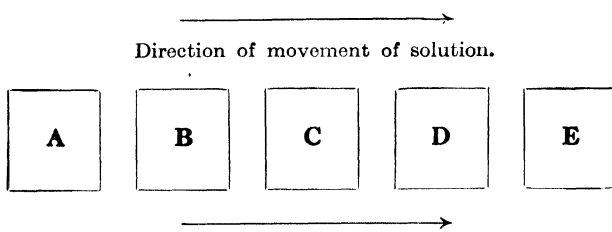


FIG. 52.—Freshness of black-ash.

A–E represent five tanks in which black-ash is placed. Tank A is now filled with water, when sodium carbonate solution is formed, but the solution is not very concentrated.

Tank B is then filled with the soda solution from A, which dissolves more soda. Meanwhile, A is filled with water again, and when tank C is filled with the soda-solution from B, B is filled with the solution from A, and so on. This process is continued until the black-ash in A is completely exhausted of sodium carbonate, when fresh black-ash is put in and the exhausted ash taken out. By this time, the original solution from A has arrived at E and is probably saturated with soda. It is therefore run off for evaporation ; but if not, it is returned to A, which is now charged with the fresh black-ash. Here it will become saturated and may therefore be run off.

Thus the principle used is that of adding fresh water to black-ash which is nearly exhausted (in this way completing the extraction of the sodium carbonate), while the fresher ash is extracted by solutions, the fresher the ash the greater the concentration of the solution used to extract it (in this way obtaining a maximum concentration of the solution). This principle is of very general use in manufacturing chemistry, and is called the Principle of Counter-Currents, since, in this case, for example, the strength of the solution in sodium carbonate increases as we pass from left to right in the diagram, while the richness of the black-ash in sodium carbonate is greater as we pass from right to left.

The solution of sodium carbonate is allowed to stand, in order that insoluble impurities may settle, and is then decanted off and evaporated in shallow pans, when crystals of sodium carbonate decahydrate, or washing soda, $Na_2CO_3.10H_2O$, separate.

The residue left in the extraction tanks is called *alkali waste*, and is commercially valuable on account of the sulphur it contains. It is only by making use of the by-products that the Leblanc process is able successfully to compete with the other main process of manufacturing sodium carbonate ; hence the sulphur is extracted from the alkali-waste by the CHANCE process (see p. 457), and the hydrochloric acid obtained in the salt-cake stage carefully absorbed, as already described.

THE AMMONIA SODA OR SOLVAY PROCESS.—This process

was first used in 1836 by THOM, but is sometimes called the SOLVAY process since it was revived with many improvements by this chemist in 1865. The reaction involved is delightfully simple; here, as in many other cases, it was the practical difficulties of carrying out the principle on a large scale that required much labour and genius to overcome them.

When ammonium bicarbonate is added to a concentrated solution of sodium chloride, sodium bicarbonate is precipitated—

$$NH_4HCO_3 + NaCl \rightleftharpoons NaHCO_3 \downarrow + NH_4Cl.$$

If sodium bicarbonate is heated, sodium carbonate is formed—

$$2NaHCO_3 = Na_2CO_3 + CO_2 + H_2O.$$

In practice, a concentrated solution of salt is taken and saturated with ammonia, when any impurities that are present separate and are allowed to settle. The ammoniacal salt-solution is then pumped into towers ("carbonators") where a stream of carbon dioxide is blown through it. The following reactions then occur—

(i) $2NH_3 + CO_2 + H_2O \rightleftharpoons (NH_4)_2CO_3$
(ii) $(NH_4)_2CO_3 + H_2O + CO_2 \rightleftharpoons 2NH_4HCO_3$
(iii) $NH_4HCO_3 + NaCl \rightleftharpoons NaHCO_3 + NH_4Cl.$

The conditions of these reversible reactions are adjusted so as to give the maximum yield of sodium bicarbonate. Heat is evolved in the reactions and the carbonators are therefore cooled by currents of water on the outside.

The liquid which flows out at the bottom of the towers carries the precipitated sodium bicarbonate with it, and is run over rotating vacuum filters where the sodium bicarbonate is retained. This is scraped off and heated in special furnaces, which differ in construction in different factories, and anhydrous sodium carbonate, or *soda-ash*, is left.

$$2NaHCO_3 = Na_2CO_3 + H_2O + CO_2.$$

One of the chief points of interest in this process is its self-contained nature. Thus, the carbon dioxide is prepared by heating lime-stone in a lime kiln—

$$CaCO_3 = CaO + CO_2.$$

and the other product, lime, is used to regenerate the ammonia from the ammonium chloride formed in the reaction given in equation (iii) above—

$$CaO + 2NH_4Cl = CaCl_2 + 2NH_3 + H_2O.$$

The carbon dioxide evolved when the sodium bicarbonate is heated is of course used again ; the equations show that in a single operation, half the original amount of carbon dioxide is converted into sodium carbonate and the other half regained as gas.

The only waste product is therefore calcium chloride, and in spite of desperate efforts to persuade local authorities to use this to keep their roads damp and free from dust in warm weather, it remains a drug on the market. However, the soda industry is fairly profitable in spite of this intractable substance, for the leading British soda-manufacturers paid a dividend of 100 per cent. for many years.

Sodium carbonate is also manufactured to some extent electrolytically, or rather by the action of carbon dioxide upon solutions of caustic soda obtained electrolytically.

Sodium carbonate is used in the manufacture of glass, soap, and paper, and for softening water. Washing-powders consist mainly of a mixture of sodium carbonate and powdered soap. Bath salts are dyed and scented soda crystals.

Properties.—Anhydrous sodium carbonate is a white solid which readily takes up water to form crystalline hydrates. The decahydrate, $Na_2CO_3.10H_2O$, is washing-soda. In dry weather, washing-soda crystals effloresce ; the resulting white powder is the monohydrate, $Na_2CO_3.H_2O$. In the laboratory, sodium carbonate is used as a mild alkali, since when dissolved in water it is partially hydrolysed—

(i) $Na_2CO_3 \rightleftharpoons Na^{\cdot} + Na^{\cdot} + CO_3''$
(ii) $H_2O \rightleftharpoons H^{\cdot} + OH'$
(iii) $CO_3'' + 2H^{\cdot} + 2OH' \rightleftharpoons H_2CO_3 + 2OH'$.

It first ionizes into sodium ions and CO_3'' ions, but the latter immediately combine with the few hydrogen ions normally present in water, to form un-ionized carbonic acid ; more water

then ionizes to restore the equilibrium $H^{\cdot} + OH' \rightleftharpoons H_2O$, but as soon as hydrogen ions are formed they react with the CO_3'' ions to give more carbonic acid, and this process goes on until equilibrium has been set up between the various substances present. When this occurs, there will be a number of hydroxyl ions (OH') in excess equal to the number of hydrogen ions that have been seized by the CO_3'' ions to form carbonic acid, therefore the solution will have an alkaline reaction.

The strength of a solution of sodium carbonate may be estimated by titration with standard acid, if the solution be kept boiling so that the carbon dioxide produced is driven off, or if an indicator insensitive to carbonic acid (e.g. methyl orange) be used. Of these alternatives, the former is preferable.

Sodium bicarbonate, $NaHCO_3$, is a white crystalline solid with a very slightly alkaline (practically neutral) reaction when dissolved in water. It is used as a baking-powder, since on heating it loses carbon dioxide, which makes the dough "rise." It is also used in making "sherbet" powder.

Sodium chloride, NaCl, or common salt, is a white solid crystallizing in anhydrous cubes. The occurrence of salt is mentioned later, on p. 497. Salt is made from brine by evaporation, usually by steam-heat and under reduced pressure. By arranging the evaporation chambers in a series in such a way that the steam from the boiler passes first into the chamber in which the pressure is highest and thence into chambers in which the pressure is lower, the maximum efficiency is obtained. This arrangement is called the Multiple Effect Vacuum Evaporation Plant.

In hot countries near the sea, salt is obtained by the evaporation of sea-water (e.g. in Spain and the South of France). In cold countries, on the other hand, the sea-water is first frozen, and the residual concentrated brine then evaporated.

Pure sodium chloride may be obtained by passing hydrochloric acid gas into a saturated solution of the impure salt, when the great increase in the active mass of the chlorine ions causes the solubility-product (p. 135) of the salt to be exceeded, while that of the more soluble impurities (chiefly magnesium

chloride) is not reached. Salt is therefore precipitated while the impurities remain in solution.

The uses of salt are well known. It forms the starting-point for the production of practically all the sodium and chlorine and their compounds used in commerce.

Sodium bromide, NaBr, and **sodium iodide,** NaI, resemble the corresponding potassium salts (pp. 525, 213), and may be made in similar ways.

Sodium hypochlorite, NaOCl, is described under hypochlorous acid (page 515).

Sodium sulphate, Na_2SO_4, is obtained commercially as *salt-cake* in the Leblanc sodium carbonate process (p. 202). When an aqueous solution of sodium sulphate is evaporated the salt separates as the decahydrate, $Na_2SO_4.10H_2O$; this is known as GLAUBER'S salt and is used as a purgative. The crystals of the decahydrate gradually effloresce (p. 444) in

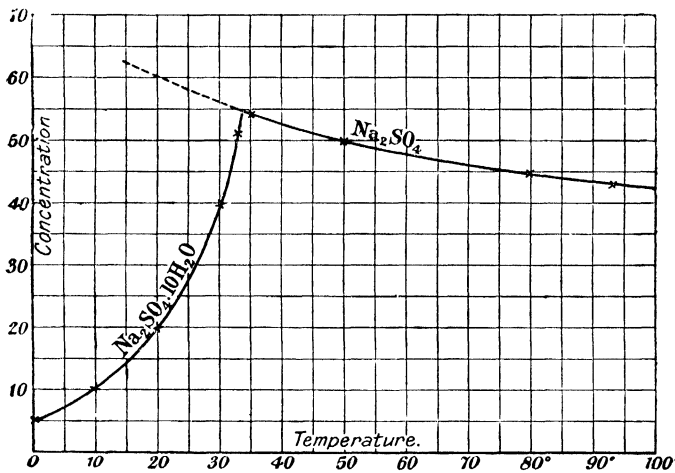


FIG. 53.

dry air. The solubility of Glauber's salt in water gradually increases up to a temperature of 32·5°; at this temperature, however, the solid decahydrate spilts up into water and

anhydrous sodium sulphate which is peculiar in becoming less soluble as the temperature rises. The solubility curve of sodium sulphate therefore exhibits a sharp break at 32·5°.

It should be carefully noted that this curve is really composed of two distinct curves, (i) the solubility curve of the decahydrate from 0° to 32·5°, and (ii) that of the anhydrous salt above 32·5°. There is no sharp break, of course, in the constitution of the *solution* at 32·5°; the only change is in the nature of the *solid* with which the solution is in contact.[1]

Sodium bisulphate, $NaHSO_4$, is a white crystal-line solid with an acid reaction in aqueous solution. It is obtained commercially as a by-product in the manufacture of nitric acid from *caliche* (see below), and is then known as *nitre-cake*. When heated it loses water and is converted into *sodium pyrosulphate*—

$$2NaHSO_4 = Na_2S_2O_7 + H_2O.$$

Sodium thiosulphate, $Na_2S_2O_3.5H_2O$. See p. 478.

Sodium nitrate, $NaNO_3$, occurs in large quantities in South America and is commonly known as *Chile saltpetre*; the crude material is known locally as *caliche*. The sodium nitrate is purified by solution in water and recrystallization; the mother liquors contain *sodium iodate* and are used as a source of iodine (p. 529).

Sodium nitrate is a white deliquescent crystalline solid. When strongly heated it loses oxygen and is converted into *sodium nitrite*, $NaNO_2$—

$$2NaNO_3 = 2NaNO_2 + O_2.$$

Sodium nitrate is very largely used (some millions of tons *per annum*) as a fertilizer for corn lands. It is applied to the growing crop as a top-dressing in the spring; its effects last for one year only, as it is so soluble that it is all leached out of the soil by the winter rains. It is also used in the manufacture of nitric acid.

[1] The left-hand curve represents the equilibrium between the decahydrate and the saturated solution; the right-hand curve represents the equilibrium between the anhydrous salt and the *same* saturated solution.

Sodium nitrite, $NaNO_2$, is chiefly made at the present day by the action of oxides of nitrogen (obtained synthetically from the air, p. 354) upon caustic soda (p. 355). It is also made by fusing sodium nitrate with lead—

$$NaNO_3 + Pb = NaNO_2 + PbO,$$

and by passing a current of sulphur dioxide through a hot concentrated solution of sodium nitrate mixed with lime—

$$NaNO_3 + CaO + SO_2 = NaNO_2 + CaSO_4.$$

It is a pale yellow crystalline solid, somewhat deliquescent and readily soluble in water. It is chiefly employed in the manufacture of aniline dyes. For the properties of nitrous acid and the nitrites see p. 367.

Sodium hydrogen sulphide, NaHS, may be made by passing sulphuretted hydrogen into caustic soda solution until no more will dissolve—

$$NaOH + H_2S = NaHS + H_2O.$$

If to the solution of the sodium hydrogen sulphide an equivalent proportion of caustic soda be added, the *normal sulphide,* Na_2S, is formed—

$$NaHS + NaOH = Na_2S + H_2O,$$

and may be obtained in the form of white hydrated crystals, $Na_2S.9H_2O$, by evaporating the liquid to crystallization.

It is made commercially in the anhydrous state by strongly heating sodium sulphate with powdered coke—

$$Na_2SO_4 + 2C = Na_2S + 2CO_2.$$

Polysulphides of sodium, Na_2S_x, are known.

Other sodium salts have been described in various places in this book. See the index.

Potassium

Group in Periodic System : I ; *Symbol :* K ; *Valency :* 1 ; *Atomicity of Vapour :* 1 ; *Atomic Weight :* 39·10 ; *Melting Point :* 62·3° ; *Specific Gravity :* 0·865.

History.—The Arab chemists gave the name *alkali* (i.e. "the ash") to the ashes obtained by burning plants. Land

plants give an ash containing much potassium carbonate, while the ash of maritime plants contains more of the sodium salt than of the potassium. The distinction in properties between these two alkalis was not clearly observed until the seventeenth century, when the difference between potash and soda was noticed by BOHN. It was later discovered that soda can be made from common salt, and hence it was called *mineral alkali*, while potash was called *vegetable alkali*. Vegetable alkali was purified by extracting wood-ashes with water, allowing insoluble matter to settle, and evaporating the clear solution in pots; hence the name *potash*. The somewhat aristocratic name potassium is therefore of very plebeian origin.

The preparation of *caustic* alkalis from the "mild" vegetable and mineral alkalis by treatment with lime was known in the thirteenth century, and caustic soda and potash were considered to be elements by DALTON. LAVOISIER, however, with his usual wonderful foresight, regarded them as oxygen compounds—a forecast that was brilliantly vindicated by the isolation of metallic sodium and potassium by DAVY in 1807.

Occurrence.—Potassium compounds are widely distributed in nature. Igneous rocks generally contain *potassium silicate* in the form *orthoclase* or *potash felspar*, $KAlSi_3O_8$, or as *leucite*, $KAlSi_2O_6$, or *muscovite*, $KH_2Al_3(SiO_4)_3$. From these minerals, potassium compounds find their way into clays and soil, where they form one of the essential substances for the growth of plants.

The principal source of the potassium salts of commerce is the vast bed of saline deposits at Stassfurt, in Prussia, although the deposits in Alsace are likely to prove of nearly equal importance. The Stassfurt deposits are considered to consist of the salts left by evaporation of an inland sea. The main potassium compound in them is *carnallite*, $KCl.MgCl_2.6H_2O$, from which most of the world's supply of potassium and its compounds is made.

Preparation.—Potassium is of less commercial importance than sodium, and is therefore not extracted on a very large

scale. The process employed for the preparation of the metal is similar to that used in the manufacture of sodium, viz., electrolysis of the fused hydroxide.

Properties.—In general chemical and physical properties potassium closely resembles sodium ; it is, however, distinctly more reactive. Potassium has a specific gravity 0·865, melting-point 62·3°, and boiling-point 757°. The vapour is brilliant green in colour and consists of monatomic molecules.

Compounds of Potassium.

Potassium hydride, KH, is made by passing hydrogen over heated potassium. It is a white crystalline solid, which reacts with water to give caustic potash and hydrogen—

$$KH + H_2O = KOH + H_2,$$

and with carbon dioxide to form potassium formate—

$$KH + CO_2 = H.COOK.$$

Potassium monoxide, K_2O, can be made by heating potassium nitrate with potassium. It dissolves in water to form potassium hydroxide, and in dilute acids to form potassium salts.

Potassium tetroxide, K_2O_4, is formed as a yellow powder when potassium burns in air or oxygen. It reacts vigorously with water, yielding caustic potash and oxygen, and, in the cold, hydrogen peroxide—

$$K_2O_4 + 2H_2O = 2KOH + H_2O_2 + O_2.$$

Potassium hydroxide, KOH, is very similar to caustic soda, and is made in similar ways.

Potassium carbonate, K_2CO_3, is manufactured from carnallite in the following way. The carnallite is first melted and then allowed to cool, when potassium chloride crystallizes out and is removed. A concentrated solution of the potassium chloride is then made and this is mixed with hydrated magnesium carbonate. On passing a stream of carbon dioxide through the liquid a precipitate of a double salt

$$KHCO_3.MgCO_3.4H_2O,$$

is obtained—

$$3(MgCO_3.3H_2O) + 2KCl + CO_2 = 2(KHCO_3.MgCO_3.4H_2O) + MgCl_2.$$

This solid is removed and treated with magnesium oxide, when the hydrated magnesium carbonate is re-formed and potassium carbonate left in solution. After filtration, the solution of potassium carbonate is evaporated to crystallization.

$$2(KHCO_3.MgCO_3.4H_2O) + MgO = 3(MgCO_3.3H_2O) + K_2CO_3.$$

"Commercially pure" potassium carbonate is commonly known as *pearl-ash*.

Potassium carbonate is also manufactured from the potassium chloride (obtained from carnallite) by the Leblanc process (p. 201). The Solvay process (p. 204) cannot be used on account of the high solubility of potassium bicarbonate.

Potassium carbonate is a white *deliquescent* crystalline solid, very soluble in water, from which it crystallizes as the dihydrate, $K_2CO_3.2H_2O$.

Potassium bicarbonate, $KHCO_3$, is made by passing carbon dioxide into a solution of the normal carbonate—

$$K_2CO_3 + H_2O + CO_2 = 2KHCO_3.$$

It is much more soluble than the corresponding sodium salt, which otherwise it very closely resembles.

Potassium chloride, KCl, occurs at Stassfurt and in Alsace as *sylvine*, KCl, and at Stassfurt also as *carnallite*. It is made from carnallite as described under *potassium carbonate*, or by treating the carnallite with the hot mother-liquors from other recrystallizations. On cooling, the potassium chloride separates and is purified by recrystallization.

Potassium bromide, KBr, is a white crystalline solid, used in photography and medicine. For its preparation see p. 525.

Potassium iodide, KI, is very similar to the bromide. Its aqueous solution is a good solvent for iodine (p. 530).

Potassium chlorate, $KClO_3$, is manufactured by the electrolysis of a hot concentrated solution of potassium

chloride.[1] The caustic potash formed at the cathode reacts with the chlorine liberated at the anode, according to the equation—

$$6KOH + 3Cl_2 = 5KCl + KClO_3 + 3H_2O.$$

Potassium chlorate is a white anhydrous crystalline solid. It is a strong oxidizing agent, and is commonly used in the laboratory as a source of oxygen. Its oxidizing powers render it a good germicide ; it is therefore sometimes made up into " chlorate lozenges " for the cure of sore throat. Mixtures of potassium chlorate and sulphur or red phosphorus explode very violently when rubbed or struck.

Potassium sulphate, K_2SO_4, forms *anhydrous* crystals (cf. sodium sulphate). It is largely used as a fertilizer in agriculture, especially for corn, of which it greatly improves the straw, and for potatoes. For the double salt, *alum*, of potassium sulphate and aluminium sulphate, see p. 280.

Potassium nitrate, KNO_3, or nitre, is found in the soil of certain tropical countries, such as India (" Indian saltpetre "). It is made by the bacterial oxidation of nitrogenous animal refuse in the presence of wood-ashes ; this process is a regular industry in India.

It is also manufactured from Chile saltpetre, $NaNO_3$, by adding this compound to a hot concentrated solution of potassium chloride, when " double decomposition " occurs—

$$NaNO_3 + KCl = KNO_3 + NaCl.$$

By regulating the concentrations, the comparatively sparingly-soluble sodium chloride can be made to separate practically completely. After removal of the salt the solution is allowed to cool, when the potassium nitrate crystallizes out.

Potassium nitrate forms white anhydrous crystals which are soluble in water but are not deliquescent and therefore can be used in the manufacture of gunpowder ; sodium nitrate, on the other hand, is very deliquescent and is, naturally, useless for this purpose.

[1] *See also* p. 505.

When potassium nitrate is strongly heated it loses oxygen and is converted into *potassium nitrite*—

$$2KNO_3 = 2KNO_2 + O_2.$$

Potassium cyanide, KCN, is manufactured by passing ammonia into molten potassium carbonate containing powdered carbon—

$$C + K_2CO_3 + 2NH_3 = 2KCN + 3H_2O.$$

It is also prepared, mixed with sodium cyanide, by fusing potassium ferrocyanide with metallic sodium—

$$K_4Fe(CN)_6 + 2Na = 4KCN + 2NaCN + Fe.$$

It is a white crystalline solid, soluble in water and smelling strongly in moist air of *prussic* or *hydrocyanic acid*, HCN. Its aqueous solution is alkaline to litmus, since hydrocyanic acid is a weak acid and hydrolysis of the salt therefore occurs.

Potassium cyanide is used in electro-plating and in the chemical industry. In gold-extraction (p. 236) it has now been replaced by sodium cyanide, which is much cheaper and, bulk for bulk, contains more of the CN radical—the essential part of the molecule. It is extremely poisonous.

Potassium ferrocyanide, $K_4Fe(CN)_6$, or *yellow prussiate of potash*, is made by heating a mixture of nitrogenous organic refuse (such as horns, waste hides and hoofs), scrap iron, and potassium carbonate. Blood, iron and potassium carbonate may be used, whence (so it is said !) the name *prussiate* of potash. The fused mass is treated with water and after insoluble matter has been allowed to settle the clear solution is run off and evaporated, when lemon-yellow crystals of $K_4Fe(CN)_6.3H_2O$ are formed.

When chlorine is passed into a solution of potassium ferrocyanide the latter is oxidized to potassium *ferricyanide*, $K_3Fe(CN)_6$—

$$2K_4Fe(CN)_6 + Cl_2 = 2KCl + 2K_3Fe(CN)_6.$$

Potassium ferricyanide is a dark red crystalline solid, sometimes known as *red prussiate of potash*. It and the ferrocyanide are used in qualitative analysis as tests for iron in solution—

	Ferrous Ions.	Ferric Ions.
Potassium ferrocyanide.	White ppt. rapidly going blue.	Deep blue ppt. "Prussian Blue."
Potassium ferricyanide.	Deep blue ppt. "Turnbull's Blue."	No ppt. Brown colouration.

Potassium thiocyanate, KCNS, is made by heating a mixture of potassium cyanide and sulphur—

$$KCN + S = KCNS.$$

It is a white, deliquescent, crystalline solid readily soluble in water. Its solution with a solution containing ferric ions gives a deep blood-red colour, usually said to be due to the formation of *ferric thiocyanate* but probably caused by the formation of a complex anion. The equation corresponds with the former explanation—

$FeCl_3 + 3KCNS \rightleftharpoons 3KCl + Fe(CNS)_3$. (See p. 121.)

QUESTIONS

1. Show that in the physical and chemical properties of the elements and their compounds the alkali-metals form a natural group.
2. Describe the Leblanc process for the manufacture of sodium carbonate.
3. Describe the Solvay or Ammonia-Soda process for the manufacture of sodium carbonate. Why cannot potassium carbonate be made in a similar way ?
4. Give an account of the manufacture of potassium carbonate and potassium chlorate.
5. Why is a solution of potassium cyanide alkaline to litmus ? How is this salt made, and what are its uses ?
6. How is sodium prepared commercially ?
7. What do you know of the history of sodium and potassium ?

CHAPTER XX

GROUP I, Sub-group B

COPPER, SILVER, GOLD

Practically the only point of resemblance between these three metals and the alkali metals is the fact that they can behave as univalent elements. They show a considerable similarity between themselves, however, and also to the *transition elements* of Group VIII. It is interesting to note that copper, silver and gold, which form a well-defined group in the periodic system, are associated also in daily life from their use in coinage and in electroplating.

Silver is uniformly univalent; copper can be both univalent and bivalent, while gold is sometimes univalent and sometimes tervalent.

They are all very resistant to the action of water, and thus differ as widely as possible, in this respect, from their associates in the group—the alkali metals.

Copper

Group in Periodic System: I; *Symbol:* Cu; *Valency:* 1 and 2; *Atomic Weight:* 63·57; *Melting Point:* 1,083°; *Specific Gravity:* 8·95.

History.—Metallic copper occurs in many parts of the ancient world and has therefore been known to man from immemorial antiquity. The different periods in the development of civilization are roughly described as the Early Stone Age (*Palæolithic*), the Later Stone Age (*Neolithic*), the Bronze Age, and the Iron Age, according to the material used by man

for making his weapons. In the Bronze Age copper and its alloy with tin, *bronze*, had superseded the flint of the Stone Age, but with advance in chemical knowledge they were themselves partially displaced by the more difficultly worked iron and steel.

It seems probable that in the early days of the Bronze Age copper itself was chiefly employed; tin was comparatively rare in the Mediterranean basin and most of it had to be obtained by perilous journeys to Britain, to Persia or to China. However, when tin was discovered in quantity the use of bronze became much more general, and finally pure copper was scarcely ever used except by the chemists for their experimental work.

The copper used by the Egyptians was mined in the peninsula of Sinai, and was called *khomt*; the Greeks and Romans obtained it chiefly from the island of Cyprus, whence the name *aes cyprium* or Brass of Cyprus, modified later into simple *cuprum*. Cyprus was a favourite resort of the goddess Venus, and for this and other reasons copper was often called by the name of the goddess and represented by her sign, ♀. The Latin GEBER (thirteenth century) describes the metal as follows:—

"*Venus* or *Copper* is a *Metallick Body*, livid, partaking of a dusky *Redneſs* ignible (or ſuſtaining Ignition) fuſible, extenſible under the *Hammer*, but refuſing the *Cupel*. . . . It agrees very well with *Tutia* [i.e. it forms an alloy (brass) with zinc], which citrinizeth (or Colours) it with good Yellowneſs. . . . It receives Infection from ſharp and acute things; and to eradicate that, is not an eaſie, but a profound *Art*" [i.e. it is readily attacked by acids, and this property is shown by it even in most of its alloys].

Occurrence.—Enormous quantities of native copper are found near Lake Superior, and smaller quantities in Scandinavia, Russia, Australia, China, and other places. The chief ores are *chalcopyrite* or *copper pyrites*, $CuFeS_2$; *copper glance* or *chalcocite*, Cu_2S; *cuprite* or "red copper ore," Cu_2O; *malachite*, $Cu(OH)_2 . CuCO_3$; and *azurite*, $Cu(OH)_2 . 2CuCO_3$.

In minute traces, copper is widely distributed in soil.

Extraction.—Native copper, when occurring in large boulders, proves rather troublesome to deal with since it is so tough. In cases of difficulty, huge electrolytic cells have been built round the boulders and filled with acidified copper sulphate solution; a thin sheet of pure copper is then made the cathode and the boulder is made the anode. On electrolysis copper passes from the anode to the cathode, where it is deposited. In this way the native copper is extracted and refined at the same time. Smaller masses are melted down with a little carbon and a flux to remove earthy impurities, and the metal then refined by electrolysis.

Oxide and carbonate ores are mixed with a flux and powdered coke and reduced in a reverberatory furnace—

$$Cu_2O + C = 2Cu + CO.$$

Most copper ores, however, contain sulphur, and the extraction of the copper is a difficult matter, for the details of which larger books must be consulted.

The processes employed differ in different localities, but the main principles of most of them are as follow—

(i) The ore is first concentrated by crushing and levigation in a stream of water, when the ore particles are carried on by the water while the earthy matter is left.

(ii) The concentrated ore is then roasted in furnaces shaped like the pyrites burners of the lead chamber process. During the roasting the iron is converted into iron oxide while the copper is left as cuprous sulphide.

$$4CuFeS_2 + 9O_2 = 2Cu_2S + 6SO_2 + 2Fe_2O_3.$$

(iii) The roasted ore is then mixed with sand, quartz or silicates and heated to fusion in a reverberatory furnace, when the silica and iron oxide form a fusible slag of an iron silicate, and the cuprous sulphide, "*matte*" or "*coarse-metal*," is left as a molten mass below the slag. The slag is run off and the matte poured into water, to granulate it.

(iv) Repetition of the above process results in a purer matte, called "*fine-metal.*" This is heated on the hearth of a reverberatory furnace (Fig. 54) with free access of air, or in a Bessemer converter (p. 548) through which hot air can be

blown. Part of the cuprous sulphide is converted into cuprous oxide, which then reacts with the remainder of the sulphide to form copper and sulphur dioxide—

$$2Cu_2S + 3O_2 = 2Cu_2O + 2SO_2$$
$$2Cu_2O + Cu_2S = 6Cu + SO_2.$$

As the mass of copper cools it gives up the sulphur dioxide which was dissolved (or contained) in it; the formation of these bubbles of gas in the copper makes the latter appear to

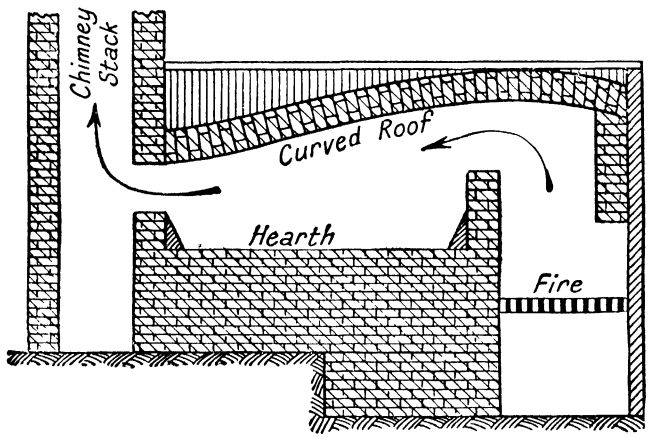


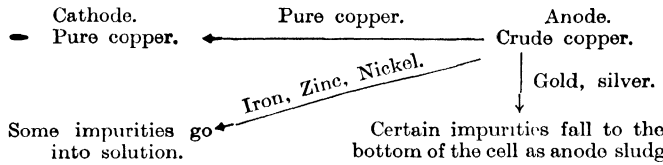
FIG. 54.—Reverberatory Furnace (Short Variety).

be covered with blisters and it is therefore called *blister-copper.*

(v) The blister-copper still contains small quantities (up to 5 per cent.) of sulphur, iron, etc., as impurities. It is melted in a furnace and after removal of the thin layer of slag which rises to the surface, is stirred up with poles of green wood. This reduces any cuprous oxide in the metal to copper; the reduction is completed by addition of a little powdered charcoal.

(vi) The crude copper obtained in this way is refined electrolytically by making it the anode in an electrolytic cell

containing acidified copper sulphate solution and a cathode consisting of a thin sheet of pure copper.



The copper is transferred by the current from the anode to the cathode while the impurities collect on the bottom of the cell as a mud (gold, silver) or pass into solution and are not deposited (iron, nickel, zinc). The anode mud is cupelled (p. 228) to extract the gold and silver.

A considerable quantity of copper is extracted from burnt pyrites by (*a*) " dry chlorination " or (*b*) " wet chlorination " ; the latter is also used to extract copper from ores that are too poor in copper to be worked by the main process described above.

(*a*) *Dry chlorination.*—The burnt pyrites are mixed with about 15 per cent. of common salt and heated in furnaces to a dull red heat. This converts the copper into cupric chloride, $CuCl_2$, which is dissolved out in water. Iron turnings or pieces of scrap iron are then added to the copper chloride solution, when the copper is precipitated—

$$CuCl_2 + Fe = Cu + FeCl_2.$$

(*b*) *Wet chlorination.*—The burnt pyrites or powdered ore is treated with a warm aqueous solution of salt and ferrous sulphate ; the copper passes into solution as cupric chloride, from which it is regained by precipitation with iron as in (*a*).

Properties.—Copper is a metal of a characteristic rosy-pink colour, which is best seen by heating the metal and reducing it in methyl alcohol. It is malleable and ductile at ordinary temperatures, although it becomes very brittle if heated nearly to its melting-point. It is an extremely good conductor of electricity and therefore is widely used in the electrical industry. It has a specific gravity of 8·95 ; it melts at 1,083°

and boils at 2,310°. The vapour is green in colour and probably monatomic.

In dry air copper is stable at ordinary temperatures, but in moist air it is slowly converted into *verdigris*, a basic carbonate. If heated in air or oxygen it is gradually oxidized to black *cupric oxide*, CuO ; it will not, however, burn with a flame—as probably noticed by GEBER or his translator (p. 218), who first wrote *ignible* but modified this to *sustaining ignition*.

Nitric acid readily dissolves copper, with formation of oxides of nitrogen, e.g.—

$$3Cu + 8HNO_3 = 3Cu(NO_3)_2 + 4H_2O + 2NO,$$
$$\text{or } Cu + 4HNO_3 = Cu(NO_3)_2 + 2H_2O + 2NO_2.$$

Concentrated sulphuric acid dissolves copper on heating, yielding sulphur dioxide and a mixture of copper sulphate and sulphides, but the dilute acid has no appreciable action.

In the presence of air, concentrated hydrochloric acid slowly dissolves copper, forming cupric chloride.

Colloidal copper can be prepared by BREDIG'S method, and in other ways.

COMPOUNDS OF COPPER.—Copper forms two oxides, cuprous oxide, Cu_2O, and cupric oxide, CuO ; corresponding to the oxides are the cuprous and cupric salts in which the copper is univalent and bivalent respectively.

Cuprous oxide, Cu_2O, which occurs naturally as *cuprite*, is most conveniently prepared by reducing FEHLING'S solution with grape-sugar. Fehling's solution is made by mixing cupric sulphate and potassium sodium tartrate in solution and adding caustic soda. When heated with grape-sugar it yields a red precipitate of cuprous oxide. This reaction is often used to estimate the strength of a solution of grape-sugar.

Cuprous oxide is a red powder insoluble in water, but soluble in ammonia, with which it forms a complex cuprous-ammonium compound. It dissolves in hydrochloric acid to give a colourless solution of *cuprous chloride*, which rapidly turns blue in the air owing to oxidation—

$$Cu_2O + 2HCl = Cu_2Cl_2 + H_2O.$$

With sulphuric and nitric acid it yields solutions of *cupric* salts—

$$Cu_2O + H_2SO_4 = CuSO_4 + H_2O + Cu.$$
$$Cu_2O + 2HNO_3 = Cu(NO_3)_2 + H_2O + Cu.$$

In the latter case the copper formed is immediately dissolved by the excess of acid, with evolution of nitric oxide.

Cuprous chloride, Cu_2Cl_2, may be made by passing hydrochloric acid *or chlorine* over copper heated in a hard glass tube; we should expect to get cupr*ic* chloride in the latter case, but this compound is unstable, splitting up into cupr*ous* chloride and chlorine at a comparatively low temperature.

Cuprous chloride is generally made by heating a solution of cupric chloride with copper turnings and hydrochloric acid—

$$CuCl_2 + Cu = Cu_2Cl_2.$$

The reaction is a *reduction* of the cupric chloride, and may be effected by many other reducing agents, such as sulphur dioxide—

$$2CuCl_2 + 2H_2O + SO_2 = Cu_2Cl_2 + H_2SO_4 + 2HCl.$$

On pouring the clear solution obtained into an excess of air-free water the cuprous chloride comes down as a white precipitate, rapidly turning green on exposure to air owing to oxidation—

$$Cu_2Cl_2 + \text{oxygen} + H_2O = Cu(OH)_2.CuCl_2.$$

Cupric oxychloride, or basic cupric chloride.

Cuprous chloride is a white solid, melting at 425° and boiling at about 1,100°; the density of its vapour corresponds to the double formula Cu_2Cl_2 and not to the simple one CuCl (cf. mercurous chloride, p. 263). It dissolves in concentrated hydrochloric acid and also in strong ammonia solution, forming colourless liquids that very rapidly oxidize in the air and turn blue. The solution in ammonia is used as a solvent for *carbon monoxide*, with which it forms the colourless compound $Cu_2Cl_2.CO.2H_2O$. When *acetylene* is passed through "ammoniacal cuprous chloride" it gives a chocolate-

brown precipitate of *cuprous acetylide*, Cu_2C_2, which explodes when dried and heated. The explosion is only slight—not at all comparable to the violent detonation of the corresponding *silver acetylide* (p. 298)—though it may be serious enough if large quantities explode, and fatal accidents have been caused by it.

Cuprous cyanide, CuCN or $Cu_2(CN)_2$, is obtained as a white precipitate by adding potassium cyanide to a solution of cupr*ic* sulphate; the first-formed cupric cyanide is unstable and loses cyanogen, leaving the cuprous salt—

(i) $CuSO_4 + 2KCN = Cu(CN)_2 + K_2SO_4$.

(ii) $2Cu(CN)_2 = Cu_2(CN)_2 + C_2N_2$.

Cuprous cyanide. Cyanogen.

Further addition of potassium cyanide dissolves the cuprous cyanide forming a colourless solution of *potassium cuprocyanide*, $K_3Cu(CN)_4$, which ionizes into $K^{\cdot}$, $K^{\cdot}$, $K^{\cdot}$ and $Cu(CN)_4'''$ and therefore shows none of the ionic reactions of copper.

Cuprous sulphide, Cu_2S, is formed when copper burns in the vapour of sulphur, or simply by heating sulphur and copper turnings together. It is a black substance, chiefly of historic interest, since its formation in the above way was observed by the Hindoos of 3,000 years ago, who therefore called sulphur the "enemy of copper," in Sanskrit *sulvari*, whence our *sulphur*.

Cuprous hydride, said to be CuH, is precipitated as a yellow to brown powder on addition of a hypophosphite or hypophosphorous acid (p. 385) to a warm solution of copper sulphate. It dissolves in hydrochloric acid with evolution of hydrogen—

$$2CuH + 2HCl = Cu_2Cl_2 + 2H_2.$$

Cupric oxide, CuO, which is formed by strongly heating copper in air or oxygen, is more conveniently made by ignition of the nitrate—

$$Cu(NO_3)_2 = CuO + 2NO_2 + \text{oxygen}.$$

It is a black *hygroscopic* (not deliquescent) substance, with the usual chemical properties of normal metallic oxides. Its

chief use is in organic analysis, since when heated with carbon compounds it oxidizes their carbon to carbon dioxide and their hydrogen to water, both of which can easily be collected and weighed.

Cupric hydroxide, $Cu(OH)_2$, is precipitated in an impure state by adding caustic soda or potash to a solution of copper sulphate. It is a blue gelatinous substance, readily soluble in ammonia to a deep blue solution called *Schweitzer's* reagent. This liquid dissolves filter-paper, cotton-wool, and other forms of *cellulose* $(C_6H_{10}O_5)_n$; addition of hydrochloric acid reprecipitates the cellulose as a gelatinous mass which can be pressed through fine holes and so obtained in the delicate threads used in making one kind of "artificial silk."

When a suspension of cupric hydroxide in water is boiled a black substance is formed, of the composition $4CuO.H_2O$ (*not* CuO). This may be converted into cupric oxide by strong ignition.

Cupric chloride, $CuCl_2$, may be made by dissolving the oxide, hydroxide or carbonate in dilute hydrochloric acid and evaporating the solution to crystallization. The green crystals of $CuCl_2.2H_2O$ which separate can be converted into the yellowish-brown anhydrous salt by gentle heat.

When more strongly heated the anhydrous salt splits up into cuprous chloride and chlorine.

The difference between the colour of the concentrated aqueous solution (green) and that of the dilute solution (blue) is elegantly explained by the ionic theory. The undissociated salt is *yellow*; the cupric ion $Cu^{\cdot\cdot}$ is *blue*. A concentrated solution, containing both undissociated molecules and ions will be *green* (yellow + blue); on dilution ionization rapidly increases and the solution turns *blue* since undissociated molecules are no longer present in appreciable numbers. If this is the true explanation, then addition of concentrated hydrochloric acid to a dilute, blue, solution should change the colour to green by reducing the ionization; experiment shows that this happens.

Cupric carbonate.—The normal salt is unknown. The natural carbonates and the precipitates obtained by adding

sodium carbonate to solutions of cupric salts are all *basic carbonates*.

Cupric sulphate, $CuSO_4$, may be obtained as the blue crystalline pentahydrate, $CuSO_4.5H_2O$, by dissolving the oxide, hydroxide, or carbonate in dilute sulphuric acid and evaporating the solution until it crystallizes on cooling. It is manufactured by adding dilute sulphuric acid to granulated copper, heating to 90°, and blowing air through the liquid—

$$Cu + H_2SO_4 + \text{oxygen} = CuSO_4 + H_2O.$$

The process is slow, and since the copper employed generally contains iron ordinary commercial copper sulphate usually contains ferrous sulphate as an impurity. This may be removed by boiling a strong solution of the salt with a few drops of concentrated nitric acid and separating the copper and *ferric* sulphates by fractional crystallization. It is impossible to separate copper and *ferrous* sulphates by fractional crystallization, since the two salts are isomorphous and form "mixed crystals."

When the pentahydrated salt is heated at 100° it loses water and is converted into the *monohydrate*, $CuSO_4.H_2O$, a pale blue powder. At 230° the monohydrate loses practically the whole of its water, yielding the *white* anhydrous salt $CuSO_4$. This is used as a test for water, with which it goes blue, owing to formation of the pentahydrate.

Copper sulphate is a very important article of commerce. It is very poisonous, especially to the lower forms of plant life, and is therefore used as a germicide and fungicide. Potatoes are sprayed with "Bordeaux mixture" (copper sulphate and lime or limestone stirred up with water) to kill the fungus, *Phytophthora*, that causes potato-disease. Copper sulphate solution is also used to spray vines, wheat, etc., to check the development of fungi. It is used in the dye industry, and also in electrolytic copper-plating.

Cupric sulphide, CuS, is obtained as a black precipitate when sulphuretted hydrogen is passed through a solution of a cupric salt acidified with hydrochloric acid. It is insoluble in yellow ammonium sulphide.

Cuprammonium Compounds.—The deep blue solutions obtained by addition of ammonia solution to copper compounds contain the copper in the form of a complex cation, *cuprammonium*, $Cu(NH_3)_4^{\cdot\cdot}$. They therefore do not give the reactions of the cupric ion $Cu^{\cdot\cdot}$. By adding excess of ammonia to copper sulphate solution and pouring a layer of alcohol on to the deep blue liquid, crystals of *cuprammonium sulphate* or "cuprammine sulphate" ($Cu(NH_3)_4SO_4.H_2O$), may be obtained.

Copper Alloys.

Alloy.	Average Composition in parts by weight.
Brass	2–4 Cu. 1 Zn.
Bronze	9 Cu. 1 Sn.
Bell-metal	4 Cu. 1 Sn.
German-silver	3 Cu. 1 Ni. 1 Zn.
Speculum-metal	2 Cu. 1 Sn.
Phosphor-bronze	Bronze, 99·5%; P, 0·5%
Delta-metal	55 Cu. 41 Zn. 4 Fe.

Silver

Group in Periodic System: I; *Symbol:* Ag; *Valency:* 1; *Atomic Weight:* 107·88; *Melting Point:* 960·5°; *Specific Gravity:* 10·5.

History.—Silver occurs in nature as the element and is easily obtained from its ores, so that it has been known for thousands of years. The alchemists, obsessed by astrological fancies, regarded it as specially connected with the moon and therefore called it *Luna*. "*Luna*, or *Silver*," says "Geber," "is a *Metallick Body*, white with pure whiteneſs, clean, Hard, Sounding, very durable in the *Cupel*, extenſible under the *Hammer*, and fuſible. . . . Being put over the fume of acute Things, as of *Vinegar*, *Salarmoniac*, *&c.*, it will be of a wonderful *Celeſtine Colour* [probably Geber's silver contained copper]. And it is a noble *Body*, but wants of the *Nobility of Gold*."

Silver nitrate and chloride were both known to the chemists of the Middle Ages. "GEBER" describes the preparation of silver nitrate very clearly—

"Dissolve *Luna* calcined, in ſolutive *Water* [nitric acid], as before; which being done, coct it in a *Phial* with a long *Neck*, the orifice of which muſt be left unstopt, for one day only, until a third part of the *Water* be consumed. This being effected, ſet it with its *Veſſel* in a cold place, and then it converts to ſmall fuſible *Stones*, like *Cryſtall*."

Occurrence.—Native silver is found in lumps of varying size in South America and Mexico, etc. The chief ores are *horn silver* (AgCl), *argentite* (Ag_2S), *pyrargyrite* ($3Ag_2S.Sb_2S_3$), and *strohmeyerite* ($Ag_2S.Cu_2S$).

Extraction.—The methods used for the extraction of silver are numerous, being often conditioned by local considerations of convenience. The following are in common use—

(i) Lead processes.
(ii) Wet processes.
(iii) Amalgamation processes.

(i) *Desilverization of Lead.*—If a lead ore is mixed with a silver ore and the mixture then smelted as for lead (p. 322), the lead obtained carries all the silver with it. Moreover, ordinary lead ores such as *galena* often contain silver, so that the desilverization of lead is of great commercial importance.

The alloy of lead and silver can be treated in various ways for the extraction of the silver, according to whether it is desired to obtain both the lead and the silver or merely the silver.

In the latter case, the alloy is *cupelled*, i.e. it is melted and strongly heated in a current of air on a *cupel* or vessel made of bone-ash [$Ca_3(PO_4)_2$]. The lead oxidizes to litharge, PbO, part of which is carried away by the current of air while the rest is absorbed by the cupel. A "button" of metallic silver is left. This extraction of silver from argentiferous lead caused the alchemists to think that a partial *transmutation* of lead into silver had taken place. Thus ABU'L-QĀSIM AL-'IRĀQĪ (thirteenth century) says in his book *Al-Muktasab*,

" Now if a *part* of the lead can thus be transmuted into silver, what is there to hinder the transmutation of the *whole* ? "

If the lead-silver alloy is poor in silver, it is first concentrated by removal of most of the lead, either by PATTINSON'S process or by PARKES' process. *Pattinson's process* depends upon the fact that when argentiferous lead is allowed to solidify the crystals that separate out first consist of pure lead ; removal of these leaves an alloy richer in silver. Repetition of the process results finally in the production of an alloy containing 2 to 3 per cent. of silver ; this is then cupelled.

Parkes' process depends upon the facts (i) that molten zinc will not mix with molten lead, and (ii) that silver is much more soluble in zinc than it is in lead. Hence, when zinc is added to molten argentiferous lead, most of the silver forms an alloy with the zinc. This alloy floats on the surface of the liquid and can be skimmed off ; it is then strongly heated, when the zinc passes off as vapour, leaving the silver behind. The silver still contains small quantities of lead, which are removed by cupellation.

(ii) *Wet processes.*—The chief wet process is the *cyanide* process. The silver ore is crushed and ground to a fine powder, which is then treated with a dilute solution of sodium cyanide. This dissolves the silver as sodium argentocyanide, $NaAg(CN)_2$—

$$Ag_2S + 4NaCN = 2NaAg(CN)_2 + Na_2S,$$

from the solution of which metallic silver is precipitated on addition of zinc or in other ways.

(iii) *Amalgamation Processes.*—The ore is crushed, and mixed with about 5 per cent. of common salt. The mixture is placed on a stone floor and thoroughly trampled by mules, after which a little burnt pyrites is added, together with more than sufficient mercury to liberate the silver from the silver chloride (formed by the action of the salt upon the silver ore)—

(i) $2NaCl + Ag_2S = Na_2S + 2AgCl.$

(ii) $2Hg + 2AgCl = Hg_2Cl_2 + 2Ag.$

The mixture is trampled again for another six weeks, at the end of which time the silver is present in the mass as an amalgam with the excess of mercury. The amalgam is washed, concentrated by squeezing through canvas bags, and then distilled. The crude silver which is left is purified by cupellation, while the mercury is condensed and used again.

Owing to the loss of mercury (as mercurous chloride) caused by action (ii) above, the amalgamation process is at the present day obsolescent, the cyanide process gradually taking its place.

Silver and gold are both extracted from the anode mud produced during the electrolytic refinement of copper (p. 221). This is cupelled and the gold and silver may then be separated from one another by the action of nitric acid, which dissolves the silver and leaves the gold unaffected.

Properties.—Silver is a lustrous white metal which can take an extremely high polish. Its specific gravity is 10·5, its melting-point 960·5, and its boiling-point 1,955°. The vapour of silver is blue and has a density of 54, hence its molecules are monatomic. Silver is unattacked by air; the tarnish that appears on silver articles in towns is due to the presence in town air of traces of sulphuretted hydrogen, which acts upon silver to form black silver sulphide.

Molten silver absorbs oxygen, which is given up when the metal solidifies. The bubbles of gas which come off cause a considerable commotion in the silver, hence the phenomenon is called the *spitting* of silver.

Silver is practically unattacked by hydrochloric acid but readily dissolves in nitric acid to form silver nitrate. Cold dilute sulphuric acid has no action on the metal, but the concentrated acid dissolves it on heating, with formation of silver sulphate and evolution of sulphur dioxide.

Coinage silver, formerly used for English silver coins, contains 92·5 per cent. silver and 7·5 per cent. copper. It is used for making the "silver" articles of the jeweller and silversmith, since the pure metal is too soft. Modern "silver" coins are made in England of an alloy of silver and nickel in approximately equal weights, with addition of a little copper. Recently it has become customary to add a small proportion

of cadmium to silver used in making jewelry. The silver-cadmium alloy is not so difficult to manipulate as is pure silver.

Electroplated articles are made by depositing silver electrolytically upon copper; if iron objects are to be plated they must first be coated with copper. The electrolytic bath used for the purpose of electroplating consists of a solution of potassium argentocyanide, $KAg(CN)_2$, made by adding potassium cyanide to silver nitrate solution—

$$AgNO_3 + 2KCN = KAg(CN)_2 + KNO_3.$$

The object to be plated is made the cathode, while the anode is made of plates of pure silver.

Sheffield Plate was made, before the invention of electroplating, by welding silver on to copper and rolling the welded bar into sheets, from which the plated articles were made. This process is still employed for the reproduction of "antiques."

COMPOUNDS OF SILVER.—Silver forms one oxide, Ag_2O, and one series of compounds.[1] It is uniformly univalent.

Silver oxide, Ag_2O, is formed as a brownish black precipitate on adding caustic soda to a solution of silver nitrate—

$$2AgNO_3 + 2NaOH = 2NaNO_3 + Ag_2O + H_2O.$$

It splits up into silver and oxygen on heating, and will dissolve in ammonia. If the ammoniacal solution is exposed to air it slowly deposits a black explosive powder of *fulminating silver* or *silver nitride*, Ag_3N.

Silver hydroxide, AgOH, probably does not exist in the free state. Moist silver oxide behaves in most reactions like the hydroxide might be expected to do; thus with ethyl iodide, C_2H_5I, moist silver oxide yields ethyl alcohol and silver iodide—

$$C_2H_5I + \text{"}AgOH\text{"} = C_2H_5OH + AgI.$$

Silver carbonate, Ag_2CO_3, is obtained as a pale yellow precipitate on addition of sodium carbonate to a solution of silver nitrate.

Silver nitrate, $AgNO_4$, or *lunar caustic*, can be obtained

[1] Ag_2O_2, silver peroxide, has been said to exist.

as white tabular crystals by evaporating a solution of silver in nitric acid. It is used in medicine and in photography; its use as an analytical reagent in the laboratory depends upon the fact that most silver salts are insoluble and hence their precipitation from a solution of silver nitrate can be employed as a means of recognition of the corresponding acid anions in the solution under examination.

Silver nitrate is readily reduced to metallic silver in the presence of organic matter; it is therefore used in solution as a *marking-ink*, since writing made with it upon linen rapidly turns black and the silver that is deposited cannot be washed out.

On heating, silver nitrate decomposes according to the equation—

$$2AgNO_3 = 2Ag + 2NO_2 + O_2,$$

a residue of metallic silver being obtained. As the temperature at which this decomposition occurs is much higher than that required to decompose copper nitrate, the latter compound may easily be separated from silver nitrate by gentle heat, followed by treatment with water. The water washes away the unchanged silver nitrate from the residual copper oxide.

Silver chloride, AgCl, occurs naturally as *horn silver*. It can be made by passing chlorine over heated silver, or by adding a soluble metallic chloride to a solution of silver nitrate—

$$\text{e.g., } NaCl + AgNO_3 = AgCl + NaNO_3.$$

Prepared in the latter way it forms a white curdy precipitate which rapidly darkens on exposure to light, finally becoming dark purple.

Silver chloride is insoluble in water and in dilute acids, but dissolves readily in solutions of ammonia, sodium thiosulphate and potassium cyanide, owing to the formation of soluble complex compounds—

$$\text{(i) } 2AgCl + 3NH_3 = \underset{\text{A "silver ammine."}}{2AgCl \cdot 3NH_3}$$

(ii) $Na_2S_2O_3 + AgCl = NaAgS_2O_3 + NaCl$.
Sodium silver thiosulphate.

(iii) $AgCl + 2KCN = KAg(CN)_2 + KCl$.
Potassium argentocyanide.

Silver bromide, AgBr, and **Silver iodide**, AgI, are formed as pale yellow curdy precipitates on addition of potassium bromide or iodide solution to a solution of silver nitrate. In properties they closely resemble the chloride. **Silver fluoride**, AgF, however, is *soluble* in water.

Photography.—The sensitiveness of silver chloride and bromide to light is made use of in photography. The effect upon these salts of a prolonged exposure to light is obvious from the dark colour produced, but even an exposure of a fraction of a second produces a distinct effect which, while not apparent to the naked eye, can be rendered visible by the process of *development*. If an image is thrown, by means of a lens, upon a film of silver bromide, the latter is partially reduced to metallic silver in those parts of the film upon which light falls, and the extent of the reduction is proportional to the intensity of the light. If the film is now immersed in a solution of a reducing agent (" developer "), such as pyrogallol or hydroquinone, further reduction occurs, but most quickly in those parts where the reduction has been already started by the light. The image is thus " developed," but it is a *negative* image, since those parts which were most fully illuminated, on exposure, will have most silver deposited on them, and will therefore be blackest, on development. When the image has attained to a sufficient density, the unchanged silver bromide is dissolved out in a solution of sodium thiosulphate (" *hypo* ") and the image is thus *fixed*. Positive images can then be obtained by " printing off " the negative on paper covered with a film of silver chloride, and fixing as before.

In making a photographic plate the silver bromide is precipitated in a granular form in a solution of gelatine, which serves the double purpose of holding the silver bromide and of

rendering it more sensitive to light. The longer the gelatine is kept in the liquid state the larger become the granules of silver bromide and the greater the sensitiveness of the plate. This process is called *ripening*, and is done before the gelatine is spread over the plate and allowed to set.

The plate prepared in this way is most sensitive to the violet and blue rays, but it may be made more sensitive to rays of other colours by staining the gelatine with various aniline dyes.

Printing papers are covered with a film of gelatine containing a mixture of silver chloride with silver citrate. The latter compound increases the sensitiveness to light of the silver chloride. After the print has attained to a rather deeper shade than that required for the finished photograph, it is *toned* by means of a solution of "gold chloride," the action of which is to replace part of the silver in the print by gold, which gives a better colour. *Gas-light* papers are similar in nature to printing-out papers (except that silver bromide is used instead of silver chloride), but they are exposed for only a short time and the image is then developed as before, and may be toned by means of a solution of sodium sulphide which converts the silver into silver sulphide.

Gold

Group in Periodic System: I; *Symbol:* Au; *Valency:* 1 and 3; *Atomic Weight:* 197·2; *Melting Point:* 1,062·4°; *Specific Gravity:* 19·43.

History.—Gold occurs native in fairly large quantities, so that it has been known from prehistoric times. It was supposed by the alchemists to represent perfection of the metallic species, and one of their aims was to convert the "baser" metals into gold. Alchemical literature is full of descriptions of gold and of suggestions for making it. The account given 600 years ago by the great "Geber" is worth quoting here:

"We say, *Gold* is a *Metallick Body*, *Citrine*, ponderous, mute, fulgid, equally digested in the *Bowels* of the *Earth*, and very long waſhed with *Mineral Water*; under the *Hammer* extenſible, fuſible, and ſuſtaining the Tryal of the *Cupel*, and

Cement. According to this Definition, you may conclude, that nothing is true *Gold*, unleſs it hath all the *Cauſes* and *differencies* of the Definition of *Gold*. Yet, whatſoever *Metal* is radically Citrine, and brings to *Equality*, and cleanſeth, it makes *Gold* of every kind of *Metals*. Therefore, we conſider by the *Work* of *Nature*, and diſcern, that *Copper* may be changed into *Gold* by *Artifice*. For we ſee in *Copper Mines*, a certain *Water* which flows out, and carries with it thin *Scales* of *Copper*, which (by a continual and long continued Courſe) it waſheth and cleanſeth. But after such *Water* ceaſeth to flow, we find theſe thin *ſcales* with the dry *Sand*, in three years time to be digeſted with the *Heat* of the *Sun*; and among theſe Scales the pureſt Gold is found. Therefore, We judg, thoſe *Scales* were cleanſed by the benefit of the *Water*, but were equally digeſted by heat of the *Sun* in the *Dryness* of the *Sand*, and ſo brought to *Equality*. Wherefore, imitating *Nature*, as far as we can, we likewiſe alter; yet in this we cannot follow *Nature*.

"Alſo Gold is of *Metals* the moſt precious and it is the *Tincture of Redneſs*; becauſe it tingeth and transforms every *Body*. It is calcined and diſſolved without profit, and is a *Medicine* rejoycing, and conſerving the *Body* in *Youth*. It is most eaſily broken with *Mercury*, and by the *Odour* [i.e. vapour] of *Lead*. There is not any *Body* that in act more agrees with it in *Subſtance* than *Jupiter* [tin] and *Luna* [silver]: but in *Weight*, *Denſeness*, and *Putreſcibility*, *Saturn* [lead], in *Colour* *Venus* [copper]; in *Potency* indeed *Venus* is more, next *Luna*, then *Jupiter*, and then *Saturn*: but laſtly *Mars* [iron]. And this is one of the *Secrets* of *Nature*. Likewiſe *Spirits* are commixed with it, and by it fixed, but not without very great *Ingenuity*, which comes not to an *Artificer* of a ſtiff neck."

Occurrence.—Native gold is found in quartz veins and, in smaller quantities, in alluvial deposits. The lumps vary in size from huge nuggets (the largest yet recorded weighed nearly two hundredweight!) to minute grains. Gold is widely distributed in the earth, but in only a few districts is enough found to make the extraction worth while. Sea-water con-

tains minute traces, but, in spite of many attempts, no commercially successful method of extracting gold from sea-water has been invented. At the present price of gold, a ton of sea-water contains about sevenpennyworth. The chief gold-producing regions are the Transvaal, Australia, North America (Klondike, etc.), and Russia.

Extraction.—Nuggets need no extraction. Gold-bearing alluvial sand is treated by *levigation*, that is, it is stirred in a current of water which washes away the lighter particles while the heavy grains of gold fall to the bottom. A better process is to treat the auriferous sand or crushed ore with a dilute solution of sodium cyanide (this is where most of the sodium manufactured is used), which dissolves the gold in the form of *sodium aurocyanide*, $NaAu(CN)_2$. The gold may be recovered from this solution by electrolysis, or by precipitation with metallic zinc, which replaces the gold in the complex cyanide. [N.B.—The cyanide employed is *called* "potassium" cyanide, but is really sodium cyanide, as stated.]

Gold is also extracted by a process of amalgamation. The alluvial sand or finely stamped ore is mixed with mercury, which forms an amalgam with the gold. The pulp or slime is then run down a table covered with amalgamated copper plates, the length of the table being some 20 feet and its gradient 1 or 2 inches per foot. The greater portion of the gold is retained on the plates, whence the amalgam is scraped off. The latter is squeezed in chamois-leather bags, to remove excess of mercury, and the residue is then distilled in iron retorts. The gold left in the retorts is purified by cupellation. Any gold not removed from the slime by the amalgamation process is extracted by the cyanide method.

Gold is refined at the present day chiefly by electrolysis. The crude gold (generally containing silver) is made the anode in an electrolytic cell containing a solution of gold chloride acidified with hydrochloric acid. A thin sheet of pure gold is used as cathode, and when the current is passed the anode decreases in bulk while the cathode increases. As a matter of practical importance, it is found advisable to superimpose an alternating current upon the direct current,

since this prevents accumulation of solid silver chloride upon the anode.

Properties.—Gold is a yellow metal with a red reflex. It has a specific gravity of 19·43, and it melts at 1,062·4° to a green liquid. It is more malleable and ductile than any other metal, and is unaffected by air, oxygen, and acids (except *aqua regia*). It is attacked by chlorine, forming gold chloride, and by potassium cyanide in the presence of oxygen, forming the aurocyanide—

$$4Au + 8KCN + 2H_2O + O_2 = 4KAu(CN)_2 + 4KOH.$$

It dissolves in mercury to form an amalgam, and in *aqua regia* to form "gold chloride." (See below.)

The preparation of *colloidal gold*, which is carried out by reducing a solution of gold chloride with formaldehyde (or in other ways), is of interest as representing the realization of a dream of alchemy—the making of "potable gold," or gold in a drinkable form. The "solutions of gold" prepared by the alchemists were solutions of soluble gold compounds. MOSES' chemical experiments on the golden calf possibly consisted in heating the calf with liver of sulphur and thus converting it into the soluble salt NaAuS, which could then have been dissolved in water for the Israelites to drink.

Colloidal gold made in the above way is red, but a blue form is also known; this is made by using hydrazine hydrate instead of formaldehyde as the reducing agent.

Purple of Cassius (colloidal stannic acid containing colloidal gold) is obtained as a purple-violet precipitate by adding a mixture of stannous and stannic chlorides to a dilute solution of gold chloride. It is used for giving a red colour to glass and porcelain and is called after its discoverer, CASSIUS (1685).

Gold is chiefly used for coinage and for jewelry. It is too soft to be used in the pure state and therefore is alloyed with copper or silver. The proportion of gold in the alloy is expresssed in *carats*, pure gold being taken as of 24-carat purity. Thus 18-carat gold is a copper-gold alloy containing $\frac{18}{24}$ of its weight of gold. The English sovereign used to be 22-carat. The fineness of a gold alloy is roughly ascertained

by the *touchstone*, a siliceous mineral. The alloy is rubbed on the stone and leaves a streak of metal behind; this is treated with nitric acid and its behaviour compared with that of another streak made with an alloy of known fineness.

COMPOUNDS OF GOLD.—The compound formed when gold is dissolved in *aqua regia* is not really gold chloride but *hydrochloro-auric acid*, $HAuCl_4$. This may be obtained in the form of trihydrated yellow crystals, $HAuCl_4.3H_2O$, on evaporation. The acid itself and its sodium salt are used in photography, under the general name of "chloride of gold," for toning silver chloride prints. The action is due to the reduction of the "gold chloride" and deposition of metallic gold.

Gold forms two series of compounds, the *aurous* and *auric*. In the first it is univalent and in the second tervalent. Gold compounds are as a rule unstable and yield metallic gold on heating. Auric oxide and hydrochloro-auric acid appear to have been known to the alchemists. *Fulminating gold* is made by adding ammonia to gold chloride solution; it is a greenish powder that explodes violently when struck.

QUESTIONS

1. Give an account of the chemical history of copper, silver and gold. To what chemical reaction do you suppose the alchemists referred in the sentence "*Sol* is devoured by the *Red Dragon*"?
2. Compare the properties of copper with those of (*a*) silver, (*b*) nickel (p. 560).
3. Estimate the success or failure of the periodic system in grouping the alkali metals with copper, silver and gold.
4. Give an account of the metallurgy of copper.
5. Write a short account of the processes employed in the extraction of silver from its ores.
6. Explain the chemistry of photography as far as you can.

CHAPTER XXI

GROUP II

Typical Elements: Beryllium, **Magnesium.**
Sub-group A (similar to the typical elements): **Calcium, Strontium, Barium,** Radium.
Sub-Group B: **Zinc, Cadmium, Mercury.**

MAGNESIUM, CALCIUM, STRONTIUM, BARIUM

The elements magnesium, calcium, strontium and barium are the *alkaline earth* metals. They are all comparatively "light" metals, since the specific gravity of the heaviest of them, barium, is only 3·6. Their valency is uniformly 2.

All of them show considerable chemical activity, and exhibit a close resemblance to one another in their compounds.

Magnesium has many similarities to zinc, as well as to calcium, strontium and barium.

Magnesium

Group in Periodic System: II; *Symbol:* Mg; *Valency:* 2; *Atomic Weight:* 24·32; *Melting Point:* 650°; *Specific Gravity:* 1·74.

History.—Magnesium carbonate was known to the ancient Assyrians, since a votive tablet from the palace of King Sargon was found by Berthelot to consist of this substance. The alchemists gave the name *magnesia* to very many different *alloys* and *oxides*, and became hopelessly confused when trying to describe its properties, as might have been expected. They seem, however, to have distinguished between a *black*

magnesia, which was possibly pyrolusite (manganese dioxide) and a *white* magnesia, which may have been magnesium carbonate, although this substance is comparatively rare in nature in the pure state.

Magnesium sulphate was obtained in 1695 by GREW, from the water of a spring at Epsom, and by addition of sodium carbonate to a solution of this "Epsom salt" a white precipitate of magnesium carbonate was formed. This was called *magnesia alba* and was shown by BLACK (1755) to be a compound of *fixed air* (carbon dioxide) with a peculiar "earth" *magnesia* (MgO). In 1800 DAVY succeeded in isolating a metal, *magnesium*, from magnesia; his product was, however, impure and magnesium was prepared fairly pure only some thirty years later by BUSSY.

Occurrence.—Magnesium occurs chiefly as its carbonate, $MgCO_3$. When it occurs singly this compound is called *magnesite*, but it is found more often combined with calcium carbonate in *dolomite*, $MgCO_3.CaCO_3$, of which the Dolomitic Alps are largely composed. Magnesium occurs also as chloride in the mineral *carnallite*, $KCl.MgCl_2.6H_2O$ (Stassfurt); as silicate in *talc*, $Mg_3H_2(SiO_3)_4$, and *asbestos*, $CaSiO_3.3MgSiO_3$; and as sulphate in *kainite*, $K_2SO_4.MgSO_4.MgCl_2.6H_2O$ and *kieserite*, $MgSO_4.H_2O$. It has been shown by WILLSTÄTTER that the molecule of *chlorophyll*, the green colouring-matter of plants, contains an atom of magnesium.

Extraction.—Magnesium is manufactured from the *carnallite* mined at Stassfurt. When this substance is heated it loses its water of crystallization and then melts to a colourless liquid consisting of fused potassium and magnesium chlorides. This is electrolysed in an iron pot, which is made the cathode the anode being a carbon rod which dips into the molten mass. In practice, a little calcium fluoride is added to the fused electrolyte. Chlorine is evolved from the anode and magnesium is liberated at the cathode. The temperature of the fused chloride is above the melting-point of the magnesium, and the latter therefore melts and rises to the surface, whence it is run off. Owing to the easy oxidation of magnesium, the

air in the apparatus is replaced by an inert gas such as coal-gas (not nitrogen, since magnesium combines with nitrogen to form magnesium nitride).

Properties.—Magnesium is a white silvery metal which is stable in dry air, but slowly oxidizes in moist air, forming magnesium oxide, MgO. It has a specific gravity of 1·74, melts at 650°, and boils at 1,100°. It is ductile and malleable and is usually met with as magnesium *ribbon* or *wire*. In making magnesium wire the metal has to be heated; ribbon is made from the wire by means of heavy rollers.

When heated in the air magnesium takes fire and burns with a brilliant white light rich in the chemically active rays. It is therefore used in photography, star-shells, etc. The product of the combustion of magnesium in air is a mixture of the oxide MgO and nitride Mg_3N_2. Magnesium will burn in steam (p. 181) and also in carbon dioxide; in each case the oxide of the metal is formed and the other element (hydrogen or carbon) liberated.

Magnesium is employed commercially in the preparation of "flashlight powders" ($KClO_3$ + Mg powder, etc.), fireworks, and the alloy (with aluminium) called *magnalium*, which is very light but surprisingly strong and has therefore been used in airship-construction, balance-making, and so on.

Magnesium is readily soluble in dilute acids, but caustic alkalis have no action on it. It dissolves in dry ethereal solutions of *alkyl halides*, etc., forming "GRIGNARD compounds," which are of great importance in organic chemistry—

$$\underset{\text{Methyl iodide.}}{CH_3I} + Mg = \underset{\substack{\text{Methyl magnesium iodide,}\\ \text{a "Grignard compound."}}}{CH_3 - Mg - I}.$$

COMPOUNDS OF MAGNESIUM.

Magnesium oxide or **magnesia**, MgO, is obtained

(i) when magnesium burns in air or oxygen;

(ii) by heating the carbonate—

$$MgCO_3 = MgO + CO_2;$$

(iii) by heating the nitrate—

$$2Mg(NO_3)_2 = 2MgO + 4NO_2 + O_2;$$

(iv) by heating the hydroxide—

$$Mg(OH)_2 = MgO + H_2O.$$

It is a white powder, very slightly soluble in water, with which it slowly combines, forming the hydroxide—

$$MgO + H_2O \rightleftharpoons Mg(OH)_2 \rightleftharpoons Mg^{\cdot\cdot} + 2OH'.$$

The solution has an alkaline reaction. It is readily soluble in acids, yielding magnesium salts. It is employed in medicine and also as a fire-resisting or refractory material for electric furnaces. NERNST electrical lamps, formerly much employed but now obsolescent, consist of a filament of magnesium oxide (mixed with oxides of other metals); on heating this filament it becomes a conductor and is raised to a high temperature on passage of the electric current, giving out a very bright white light.

Magnesium hydroxide, $Mg(OH)_2$, is obtained as a white precipitate by addition of caustic soda, caustic potash or ammonium hydroxide solution to a solution of a magnesium salt—

$$2NaOH + MgSO_4 = Na_2SO_4 + Mg(OH)_2.$$

If ammonium chloride is added to a solution of a magnesium salt, and ammonium hydroxide added afterwards, no precipitate is obtained. This is easily explained by the ionic theory (see p. 135). The ammonium chloride suppresses the ionization of the ammonium hydroxide so much that the solubility-product of magnesium hydroxide is not reached, and therefore no precipitation occurs. For the same reason, magnesium hydroxide is dissolved by a solution of ammonium chloride.

Magnesium peroxide, MgO_2, is obtained in an impure state by adding sodium peroxide to magnesium sulphate solution. It is a white powder with oxidizing powers, and is used as an antiseptic.

Magnesium sulphate, $MgSO_4$, may be made by dissolving the metal, oxide, or carbonate in dilute sulphuric acid and evaporating the solution to crystallization, when colourless crystals of magnesium sulphate heptahydrate, $MgSO_4.7H_2O$,

or *Epsom salt*, separate. On heating, these crystals lose water, forming lower hydrates and finally the anhydrous salt.

It readily forms double salts with the sulphates of sodium and potassium; these double salts have the general formula $M_2SO_4.MgSO_4.6H_2O$, and in solution give all the ionic reactions that would be shown by the two sulphates of which they are composed.

"Epsom salt" is used as a purgative and in the dye industry. It is sometimes used as an artificial manure for certain soils.

Magnesium chloride, $MgCl_2$.—The deliquescent crystals obtained from the solution made by dissolving magnesium or its oxide or carbonate in dilute hydrochloric acid have the composition $MgCl_2.6H_2O$. On heating, this hexahydrated salt loses water and hydrochloric acid, forming an oxychloride, $Mg\begin{<}OH\\Cl\end{>}$, which itself splits up at a higher temperature into magnesium oxide and hydrochloric acid.

Anhydrous magnesium chloride is therefore best prepared by heating magnesium in a stream of hydrochloric acid gas, or by driving off the water and ammonium chloride from the double salt $NH_4Cl.MgCl_2.6H_2O$ by heat—

$$NH_4Cl.MgCl_2.6H_2O = NH_4Cl + 6H_2O + MgCl_2.$$

Magnesium carbonate.—When sodium carbonate is added to a solution of a magnesium salt the precipitate consists not of *normal* magnesium carbonate but of a *basic* carbonate. This may be converted into the normal carbonate by suspending it in water and blowing a current of carbon dioxide through. Excess of carbon dioxide causes the carbonate to dissolve as bicarbonate—

$$MgCO_3 \text{ (insoluble)} + H_2O + CO_2 \rightleftharpoons Mg(HCO_3)_2 \text{ (soluble)}.$$

Calcium

Group in Periodic System: II; *Symbol:* Ca; *Valency:* 2; *Atomic Weight:* 40·07; *Melting Point* · 810°; *Specific Gravity:* 1·55.

History.—LAVOISIER suggested that lime was the oxide of a metallic element, and in 1808 DAVY prepared an impure specimen of calcium by electrolysis. A purer specimen was made by BUNSEN in 1855, and in 1898 MOISSAN obtained the metal by strongly heating calcium iodide with excess of sodium. Compounds of calcium, such as quicklime, slaked lime, and limestone have of course been known and used for thousands of years, since many of them occur naturally in large quantities.

Occurrence.—Calcium carbonate, $CaCO_3$, is the chief calcium mineral. This is found in various crystalline forms, *calcite*, *aragonite*, *marble*, *Iceland spar*, etc., and in the amorphous state as *limestone* and *chalk*. *Dolomite* is a double carbonate of calcium and magnesium, $CaCO_3.MgCO_3$.

Calcium is also found in the form of its sulphate; *gypsum*, *selenite*, and *alabaster* are $CaSO_4.2H_2O$ and *anhydrite* is $CaSO_4$. Phosphates of calcium occur naturally (see *phosphorus*, p. 373).

Calcium is widely distributed in the soil and is found in all plants and animals. Eggshells consist largely of calcium carbonate.

Preparation.—Calcium is becoming of importance in technical chemistry and is therefore prepared on the large scale. In RUFF and PLATO'S method a mixture of 100 parts of anhydrous calcium chloride and 16 parts of calcium fluoride (*fluorspar*) is fused at a temperature of 660° and electrolysed in a pot lined with graphite. The graphite is made the anode and the cathode is a vertical iron wire or rod upon which the calcium is deposited during electrolysis. The calcium obtained in this way is very pure.

Properties.—Calcium is a hard silver-white metal with a slight tinge of yellow. It oxidizes slowly in moist air and attacks water in the cold, with evolution of hydrogen—

$$Ca + 2H_2O = Ca(OH)_2 + H_2.$$

It has a specific gravity of 1·55 and melts at 810° C. If heated in air or oxygen it burns with a reddish flame, forming calcium oxide, CaO. It will also combine with nitrogen if

heated in this gas, being converted into *calcium nitride*, Ca_3N_2. It is a good reducing agent. Metallic calcium is used in the laboratory to free alcohol from traces of water.

COMPOUNDS OF CALCIUM.—**Calcium hydride**, CaH_2, is obtained when calcium is heated in hydrogen.

$$Ca + H_2 = CaH_2.$$

It is a colourless substance, used commercially, under the name of *hydrolith*, for the preparation of hydrogen for airships, etc.—

$$CaH_2 + 2H_2O = Ca(OH)_2 + 2H_2.$$

Calcium fluoride, CaF_2, occurs naturally as *fluorspar*.

Calcium chloride, $CaCl_2$, is the chief waste-product in the SOLVAY process for the manufacture of sodium carbonate. In the laboratory it may be made by dissolving the oxide or carbonate of the metal in dilute hydrochloric acid. On evaporation of the solution calcium chloride hexahydrate, $CaCl_2.6H_2O$, separates in the form of colourless and extremely deliquescent crystals. On heating these crystals they are converted into the dihydrate, $CaCl_2.2H_2O$; further heating results in formation of the anhydrous salt, $CaCl_2$, which is largely used in the laboratory as a drying agent, since it has a great affinity for water and is not very reactive. It cannot, however, be used for drying ammonia (p. 338) as it absorbs this gas, forming compounds which have the general formula $xCaCl_2.yNH_3$; neither must it be used for drying alcoholic solutions, since it dissolves in alcohol. It is also unsuitable as a dehydrating agent for aniline and amines in general.

Calcium oxide or quicklime, CaO, is formed when the metal burns in air and when the nitrate or carbonate is strongly heated. Commercially it is made by heating limestone in a lime-kiln. The crushed limestone is mixed with coal or coke and the kiln filled with the mixture which is then lit at the bottom. The lime, in the form of a powder or small lumps, is removed from the bottom of the kiln and fresh mixture added at the top. Lime prepared in this way contains the ashes of the coal or coke used, but these are rarely

harmful, and are often beneficial in lime which is used for commercial purposes.

Calcium oxide is a white amorphous substance very difficult to fuse. It melts in the electric furnace and can even be boiled; it is not, however, melted by the oxyhydrogen flame but merely made white hot. White-hot quicklime gives a brilliant light, called the *limelight*. Owing to its refractory nature lime is often used in the construction of electric furnaces.

When water is added to quicklime, evolution of heat occurs and **calcium hydroxide or slaked lime,** $Ca(OH)_2$, is formed. If the quicklime is in lumps, these will fall to pieces and the slaked lime will be obtained as a powder. Calcium hydroxide is slightly soluble in water; the solution is called *lime-water*, and is used as a test for carbon dioxide and as a mouth-wash for infants. If excess of lime is stirred up with water the mixture is called *milk of lime*. *Soda-lime* is made by slaking quicklime with caustic soda solution; it behaves like caustic soda in reactions, but has the advantage of being non-deliquescent and not easily fusible, and may therefore be often conveniently employed instead of solid caustic soda (e.g., in the preparation of methane from sodium acetate, p. 294).

Lime finds many applications both in the laboratory and elsewhere. Technically it is employed in the purification of coal-gas, in the manufacture of caustic soda and sodium carbonate, in tanning, in glass-making, in the manufacture of bleaching-powder, in the refinement of sugar, and for many other purposes. It is also the main constituent of *mortar* and *cement*.

Mortar consists of a pasty mixture of slaked lime, sand, and water. The "setting" of mortar is due chiefly to loss of moisture by evaporation, but the lime slowly changes into calcium carbonate by the action of atmospheric carbon dioxide, and part of it combines with the sand to form calcium silicate.

Hydraulic cement is so called because it will set even under water. To make it, limestone containing a little clay is

heated in the lime-kiln, and the quicklime so obtained slaked and mixed with sand and water. It is very useful for building-work which has to stand in water.

Portland cement is made by strongly heating a mixture of limestone, or chalk, and clay. The product is then finely powdered and is ready for use. When mixed thoroughly with water it quickly sets to a hard mass.

Concrete is a mixture of Portland cement and small gravel or finely broken bricks. In *reinforced concrete* the concrete is allowed to set over a skeleton of steel girders or rods.

Calcium carbonate, $CaCO_3$, occurs naturally in many forms, for which see p. 244. It can be obtained as a white precipitate by passing carbon dioxide through lime-water—

$$Ca(OH)_2 + CO_2 = CaCO_3 + H_2O.$$

It is insoluble in water, but dissolves in an aqueous solution of carbon dioxide, owing to the formation of the soluble *bicarbonate*, $Ca(HCO_3)_2$—

$$CaCO_3 + H_2O + CO_2 = Ca(HCO_3)_2.$$

On boiling a solution of the bicarbonate the normal carbonate is re-formed and is precipitated. For the effect of the presence of calcium bicarbonate in water see p. 445, *Hardness of Water*.

Calcium sulphate, $CaSO_4$.—The naturally occurring forms of this substance have already been mentioned, p. 244. When *gypsum*, $CaSO_4.2H_2O$, is carefully heated to 120–130°, it is converted into the hemihydrate, $CaSO_4.\frac{1}{2}H_2O$. This is known as *Plaster of Paris*; when it is made into a thick paste with water it rapidly sets to a mass of gypsum, and as expansion takes place in the process, sharp casts may be obtained by allowing the mixture to set in moulds.

If the gypsum is heated to a high temperature it loses all its water of crystallization and is converted into the anhydrous salt, $CaSO_4$. This will not take up water, and is said to be "dead-burnt."

Calcium bisulphite, $Ca(HSO_3)_2$. See p. 466.

Calcium nitrate, $Ca(NO_3)_2$, and *basic calcium nitrate.* See p. 355. Calcium nitrate forms colourless deliquescent crystals with four molecules of water of crystallization, $Ca(NO_3)_2.4H_2O$. When strongly heated it splits up into quicklime, oxygen, and nitrogen peroxide—

$$2Ca(NO_3)_2 = 2CaO + 4NO_2 + O_2.$$

Calcium carbide, CaC_2, is made by heating a mixture of quicklime and powdered coke in the electric furnace. It is decomposed by water, with evolution of acetylene—

$$CaC_2 + 2H_2O = Ca(OH)_2 + C_2H_2.$$

When calcium carbide is strongly heated in a current of nitrogen *calcium cyanamide,* $CaCN_2$, is formed—

$$CaC_2 + N_2 = CaCN_2 + C.$$

Calcium cyanamide is used as an artificial manure (pp. 342, 371).

Calcium phosphate, $Ca_3(PO_4)_2$. See p. 373.

Calcium "superphosphate," $CaH_4(PO_4)_2$, is manufactured in enormous quantities for use as a fertilizer in agriculture. It is made by adding to crushed calcium phosphate the exact weight of sulphuric acid required according to the equation—

$$Ca_3(PO_4)_2 + 2H_2SO_4 + 4H_2O = 2CaSO_4.2H_2O + CaH_4(PO_4)_2.$$

Commercial "superphosphate" is therefore a mixture of calcium tetrahydrogen phosphate, $CaH_4(PO_4)_2$, with gypsum.

Bleaching-powder, $Ca(OCl)Cl$.—Although absolutely dry chlorine will not act upon specially dried calcium hydroxide, ordinary "dry" slaked lime will readily absorb chlorine, forming a white powder called bleaching-powder. On the commercial scale bleaching-powder is made by passing a stream of chlorine slowly over a layer of slaked lime on the floor of a series of chambers made of stone or lined with lead. The reaction that occurs may be represented by the equation—

$$(CaOH)_2 + Cl_2 = CaOCl_2 + H_2O.$$

Bleaching-powder is, as its name implies, used for bleaching, since with a dilute acid it reacts to yield free chlorine—

$$CaOCl_2 + H_2SO_4 = CaSO_4 + H_2O + Cl_2.$$

Constitution of Bleaching-powder.—The constitution of bleaching-powder proved a very difficult matter to settle. GAY-LUSSAC considered it to be a loose compound of lime and chlorine, "chloride of lime," $CaO.Cl_2$, whereas BALARD regarded it as a mixture of calcium chloride and calcium hypochlorite, $CaCl_2.Ca(OCl)_2$. Against Balard's theory there are the facts that—

(i) Bleaching-powder is not deliquescent, whereas calcium chloride is.

(ii) Calcium chloride is soluble in alcohol, but cannot be dissolved out of bleaching-powder by this solvent.

(iii) Carbon dioxide will act upon bleaching-powder with liberation of practically all the chlorine from the latter compound; carbon dioxide, however, has no action on calcium chloride.

(iv) Bleaching-powder cannot be made by mixing equimolecular proportions of calcium hypochlorite and calcium chloride.

ODLING therefore in 1861 suggested that bleaching-powder was chiefly calcium chlorohypochlorite, $Ca\begin{<}{OCl}{Cl}$, that is, a "mixed salt," half way between calcium chloride, $Ca\begin{<}{Cl}{Cl}$, and calcium hypochlorite, $Ca\begin{<}{OCl}{OCl}$. This formula agrees with all the reactions of the substance, the formula for which, allowing for the water always present, may be written $Ca(OCl)Cl.H_2O$. According to this formula [1] the "available" chlorine (i.e. the chlorine liberated from it by a dilute acid) should be $\frac{71}{145}$, or

[1] Olding's formula does not account for the existence of a *lithium* bleaching-powder, but is the best formula yet suggested.

about 49 per cent., of the weight of bleaching-powder taken. The average percentage of available chlorine is considerably less, generally 35–38 per cent., and diminishes on keeping the powder, possibly owing to the change

$$6CaOCl_2 = 5CaCl_2 + Ca(ClO_3)_2.$$
Calcium chlorate.

Commercial bleaching-powder is therefore bought and sold on the basis of its available chlorine content. This may be estimated by grinding up a known weight of the powder with water in a mortar and making up the fine paste to a known volume with distilled water in a graduated flask. An aliquot portion of the well-shaken suspension is then mixed with excess of potassium iodide solution, acidified with dilute hydrochloric acid, and titrated with standard sodium thiosulphate—

(i) $CaOCl_2 + 2HCl = CaCl_2 + H_2O + Cl_2$.
(ii) $Cl_2 + 2KI = 2KCl + I_2$.
(iii) $I_2 + 2Na_2S_2O_3 = 2NaI + Na_2S_4O_6$.
Sodium tetrathionate.

1 litre N/10 sodium thiosulphate ≡ 12·7 gms. iodine ≡ 3·55 gms. chlorine. For other methods, see BERRY'S *Volumetric Analysis*.

WILKS and others have shown that bromine and iodine probably form similar compounds with slaked lime, *brom-bleaching powder* and *iodine bleaching-powder*, $CaOBr_2$ and $CaOI_2$, thus confirming previous observations by BERZELIUS.

STRONTIUM

Group in Periodic System: II; *Symbol:* Sr; *Valency:* 2; *Atomic Weight:* 87·63; *Melting Point:* 800°; *Specific Gravity:* 2·55.

History.—In 1790 CRAWFORD concluded that the mineral *strontianite* ($SrCO_3$), so called because it is found near Strontian in Argyllshire, contained a new earth; in 1791 HOPE and in 1792 KLAPROTH confirmed Crawford's conclusion, and the metal *strontium* was isolated sixteen years later by DAVY, who electrolysed the fused chloride.

Occurrence.—The chief ores of strontium are *strontianite*, $SrCO_3$, and *celestine*, $SrSO_4$. These are fairly widely distributed, but usually in small quantities.

Preparation.—The metal may be made by Davy's method or by the *thermite* process (see p. 277).

Properties.—Strontium is very similar to calcium in physical and chemical properties. It melts at 800° and has a specific gravity of 2·55. The *oxide*, SrO, and hydroxide, $Sr(OH)_2$, are used in sugar-refining, since they combine with sugar to form a white insoluble substance, $C_{12}H_{22}O_{11}.2SrO$, called *strontium saccharate*. This is washed free from impurities, stirred up in water, and decomposed by a stream of carbon dioxide, which liberates the sugar and precipitates the strontium as carbonate—

$$C_{12}H_{22}O_{11}.2SrO + 2CO_2 = C_{12}H_{22}O_{11} + 2SrCO_3.$$

Cane-sugar.

The insoluble carbonate is allowed to settle and the clear solution of pure sugar evaporated to crystallization. By strongly heating the carbonate it is reconverted into the oxide, available for further use.

Strontium nitrate, $Sr(NO_3)_2$, is used in pyrotechny for making red flares.

Barium

Group in Periodic System: II; *Symbol:* Ba; *Valency:* 2; *Atomic Weight:* 137·37; *Melting Point:* 850°; *Specific Gravity:* 3·6.

History.—The first mention of a barium compound seems to be in 1602, when a shoemaker of Bologna, Casciorolus, drew attention to the fact that if a mineral called *heavy-spar* or *barytes* ($BaSO_4$) was heated strongly with a combustible substance, such as charcoal, the product possessed the power of shining in the dark, after exposure to sunlight. This phosphorescent substance (BaS) was called the *Bolognan Stone*, and when phosphorus was discovered nearly a century later the two were at first considered to be in some way related.

Scheele, however, in 1774, and Gahn, showed that heavy-

spar was the sulphate of an "earth" or metallic oxide, and DAVY succeeded in isolating the metal, in an impure state, in 1808, by electrolysis of the fused chloride.

Occurrence.—Barium occurs chiefly as the sulphate, *heavy-spar* or *barytes*, $BaSO_4$, and also as the carbonate, *witherite*, $BaCO_3$.

Preparation.—Barium can be made by Davy's method (above), or by the *thermite* process (see p. 277).

Properties.—In appearance and general chemical properties, barium closely resembles calcium and strontium. Its specific gravity is 3·6 and its melting-point 850°. Barium *oxide*, BaO, was formerly used in the manufacture of oxygen by Brin's process: on heating in air it is converted into the *peroxide*, BaO_2, which is reconverted into the normal oxide, with loss of oxygen, on further heating or on reducing the pressure—

$$2BaO + O_2 \rightleftharpoons 2BaO_2.$$

Barium *chloride*, $BaCl_2.2H_2O$, is used in solution as a reagent in analysis, especially in testing for sulphates, with which it gives a white insoluble precipitate of the *sulphate*, $BaSO_4$.

Barium *nitrate*, $Ba(NO_3)_2$, is used in the production of green flares, in the firework industry.

Barium *sulphate*, $BaSO_4$, is one of the most insoluble salts known. It is used as a white pigment, under the name of "permanent white."

QUESTIONS

1. Give an account of the occurrence, extraction and uses of magnesium.

2. Compare the chemical properties of magnesium with those of (*a*) calcium, and (*b*) zinc.

3. State the chemical nature of the following: alabaster, plaster of Paris, mortar, gypsum, concrete, fluorspar, Iceland spar.

4. Discuss the constitution of bleaching-powder.

5. What do you know of the history of the alkaline-earth metals?

CHAPTER XXII

GROUP II, Sub-group **B**

ZINC, CADMIUM, MERCURY

Zinc

Group in Periodic System: II; *Symbol:* Zn; *Valency:* 2; *Atomic Weight:* 65·38; *Melting Point:* 419·4°; *Specific Gravity:* 6·9.

History.—In the form of its alloy with copper, *brass*, zinc was known to the chemists of antiquity, who were also acquainted with its oxide and carbonate, which they grouped together under the name of *cadmia*, afterwards changed to *tutia*. Brass was made by heating copper with tutia, as described by many alchemists. The name *zinc* seems to have been given to the metal by Paracelsus (1493–1541), but it was not till 1720 that zinc was obtained in a state of approximate purity by Henckel. Homberg, however, had shown in 1695 that zinc could be extracted from zinc blende, ZnS.

Occurrence.—Zinc does not occur native. Its chief ores are *zinc blende* (ZnS), and *calamine*, $ZnCO_3$. It also occurs as zinc ferrite (*Franklinite*), $Zn(FeO_2)_2$, in the United States. The principal deposits of zinc ores are found in Great Britain, Belgium, Germany, Australia and North America.

Extraction.—The manufacture of zinc was begun in Bristol in 1743, and was practically a Bristol monopoly until 1807, when a zinc works was erected at Liège, followed

by many more in Belgium and in Silesia. The Belgian and Silesian processes differ only in detail.

The ore is strongly heated in air, when (i) zinc blende is oxidized and (ii) calamine loses carbon dioxide, the product in each case being zinc oxide.

(i) $2ZnS + 3O_2 = 2ZnO + 2SO_2$.
(ii) $ZnCO_3 = ZnO + CO_2$.

The sulphur dioxide given off when blende is used is con-

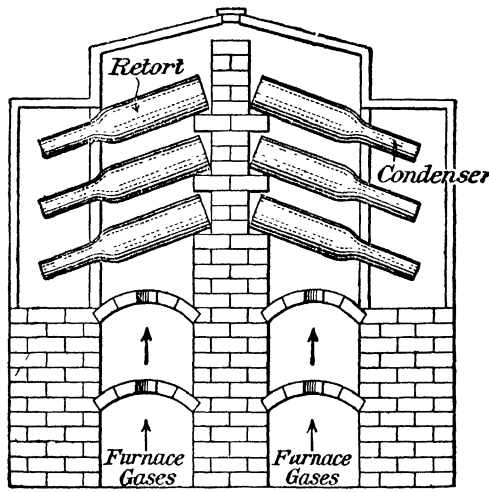


FIG. 55.—Belgian Zinc Plant.

verted into sulphuric acid and is an important factor in the commercial success of the operation.

The zinc oxide obtained in the first operation is then mixed with powdered coal and strongly heated in fireclay retorts by means of producer-gas (p. 301). The Belgian and Silesian processes differ in the shape of the retorts and receivers and in the arrangement of the furnaces; the Silesian method is the better of the two for ores that are not rich in zinc.

The zinc oxide is reduced in the retorts, and zinc vapour comes over—

$$ZnO + C = Zn + CO.$$

Part of the zinc collects as a fine powder (" zinc-dust ") and part condenses to a liquid which is allowed to solidify in moulds. The crude zinc contains many other metals as impurities, chiefly lead, antimony and arsenic; it is purified by heating the molten metal in a reverberatory furnace for a considerable time, when certain of the impurities rise to the surface and can be removed. Electrolytic refinement has recently been introduced, with much success, the metal pre-

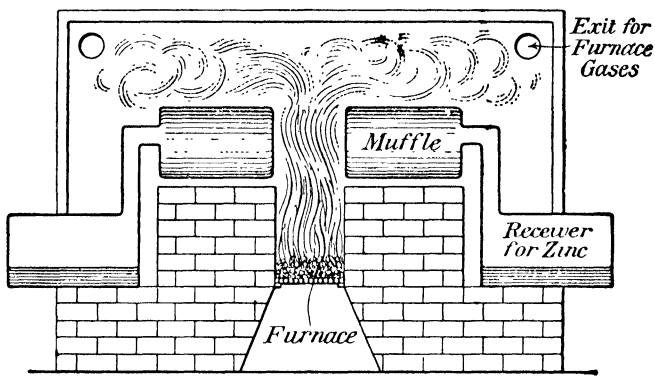


FIG. 56.—Silesian Zinc Plant.

pared in this way having a purity of approximately 99·95 per cent. By the electrolysis of specially purified zinc chloride, zinc of 99·998 per cent. purity may be obtained without difficulty. Commercial zinc (known as *spelter*) always contains lead (0·02–1·5 per cent.) and iron (0·01–0·05 per cent.). A small percentage of lead is advantageous if the metal has to be rolled.

Properties.—Zinc is a hard and rather brittle bluish-white metal; it becomes ductile and malleable when heated from 100° to 150°, but becomes brittle again at 200°, at which temperature it can be powdered. Its specific gravity is 6·9,

melting-point 419·4°, and boiling-point 920°. Zinc is stable in dry air, but in moist air is slowly converted into a white "rust," basic zinc carbonate. If heated strongly in the air zinc burns with a greenish blue flame, forming clouds of the very light zinc oxide (*philosopher's wool*).

The general chemical properties of zinc are well known; the metal readily dissolves in acids, and is soluble also in hot aqueous caustic alkalis—

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

The *pure* metal, however, is usually soluble in a dilute acid only with difficulty, unless a catalyst, such as a few drops of cupric sulphate, is added. The explanation of this phenomenon is probably electrical, since if a plate of pure zinc and a plate of copper are placed in dilute sulphuric acid and connected outside the solution by a wire, the zinc dissolves, hydrogen comes off *from the copper*, and an electric current flows through the wire.

Zinc is used in the laboratory for the preparation of hydrogen and also as a reducing agent. For the former purpose it is generally *granulated* by pouring the molten metal from a height into a tub of cold water, while for the latter purpose *zinc dust* is occasionally used. Zinc dust usually contains about 25 per cent. of zinc oxide, and if it is to be used quantitatively must be estimated first. It is made by blowing a strong blast of air into melted zinc.

Commercially, zinc is chiefly used to coat iron and thus prevent it from rusting. The iron object is first thoroughly cleaned and then dipped into molten zinc, when a thin layer of the latter metal is deposited as a coating on the iron. Iron treated in this way is called (inappropriately) *galvanized iron*. Zinc is also used in the preparation of alloys, e.g. brass and German silver (p. 227), and also in electric batteries.

Compounds of Zinc.

Zinc oxide may be made in any of the usual ways; it is generally prepared by burning zinc in air. It is a white amorphous powder, soluble in acids to form zinc salts, and turning

yellow when heated, but regaining its white colour on cooling. It is used as a paint ("zinc white"), but has not the same covering-power as "white lead" (p. 328); it is not, however, blackened by sulphuretted hydrogen since zinc sulphide also is white.

Zinc oxide is an *amphoteric* substance, since it dissolves in acids to form salts (basic property) and also in caustic alkalis (acidic property); the compounds formed in the latter case are called *zincates* and contain the zinc in the anion.

$$ZnO + 2NaOH = Na_2ZnO_2 + H_2O.$$

Zinc hydroxide is "insoluble" in water, but is not precipitated by ammonium hydroxide if ammonium chloride is present (*Ionic Theory*, p. 135).

Zinc chloride, $ZnCl_2$, is prepared anhydrous by passing hydrochloric acid gas over zinc heated in a tube. It cannot be prepared by heating the hydrated salt in air, as hydrolysis occurs resulting in the formation of zinc oxychloride—

$$ZnCl_2 + H_2O = Zn\begin{<}OH\\Cl\end{>} + HCl\uparrow.$$

The "fused zinc chloride" that is commonly used as a dehydrating agent is made by dissolving zinc in hydrochloric acid and evaporating the solution, after concentration, *in a stream of hydrochloric acid gas*, to prevent hydrolysis.

Zinc sulphate, $ZnSO_4$, is usually met with in the heptahydrated form called *white vitriol*, $ZnSO_4.7H_2O$. Like all soluble zinc compounds, it is very poisonous.

Zinc carbonate, $ZnCO_3$, is made by adding a solution of sodium *bicarbonate* to a solution of a zinc salt; sodium *carbonate* yields a *basic* zinc carbonate.

Zinc sulphide, when not quite pure, is phosphorescent after exposure to light. It is largely used in work on X-rays and radio-activity, as when struck by α-particles, X-rays, etc., it is temporarily luminous (CROOKES, Spinthariscope).

Zinc Alloys.—For the composition of *brass*, see p. 227. High tensile brass is an alloy of copper, nickel and zinc.

Naval brass, resistant to the corrosive action of sea-water, consists of Cu 63, Zn 36, Sn 1, parts by weight. There is reason to believe that copper and zinc form two definite compounds, viz. CuZn and $CuZn_2$ or Cu_2Zn_3.

For certain important *organic compounds of zinc*, see text-books of organic chemistry.

Cadmium

Group in Periodic System: II; *Symbol:* Cd; *Valency:* 2; *Atomic Weight:* 112·40; *Melting Point:* 321°; *Specific Gravity:* 8·6.

History.—The name *cadmia*, according to Dioscorides was given to one of the volatile products formed in the refinement of silver. Possibly owing to the mistake of a scribe in reading *l* for *d* (which letters are somewhat similar in Arabic), the name is met with in Arabian chemical treatises as *calmia*, whence our word *calamine* ($ZnCO_3$). Calmia or cadmia was probably either zinc oxide or sulphide; the name was first used in its modern sense by Strohmeyer (1817), who applied it to a metallic oxide that he found in the condensers of a zinc works. The metal was isolated shortly afterwards and called *cadmium*.

Occurrence.—Cadmium is almost always found in zinc ores, but occurs as sulphide (CdS) in a rare mineral called *Greenockite*.

Extraction.—When zinc ores are being smelted the cadmium, being more volatile, comes over first and collects in the receivers as a brown powder, cadmium *oxide*, CdO. This is reduced with powdered coke. The mixture of oxide and coke is heated to not more than 800° C. in an iron retort, when cadmium vapour distils over and solidifies to a powder in a conical sheet-iron condenser. The metal is then purified by distillation or, more generally, by electrolysis.

Properties.—Cadmium is very similar to zinc; its specific gravity is 8·6, melting-point 321°, and boiling-point 770–780°. Its soluble salts are only very slightly ionized. The *oxide* is a brown powder; the *sulphide*, which comes down in Group

II of the Analysis Tables, is bright yellow and is used as a paint; it is insoluble in yellow ammonium sulphide.

Cadmium is used in the Weston standard electric cell, and has recently found commercial application in cadmium-plating; its importance for this purpose is likely to increase rapidly. It is also alloyed with silver in the jewelry trade, since the cadmium or silver alloy is more malleable and ductile than pure silver and also tarnishes less readily.

MERCURY

Group in Periodic System: II; *Symbol:* Hg; *Valency:* 1, 2; *Atomicity of Vapour:* 1; *Atomic Weight:* 200·6; *Boiling Point:* 357°; *Specific Gravity:* 13·595.

History.—Mercury has been known from time immemorial; the alchemists regarded it as the prime matter or "mother" of the other metals. PLINY distinguishes between the native metal, which he calls *argentum vivum* ("quicksilver") and *hydrargyrum* (liquid silver) prepared from cinnabar (mercuric sulphide, HgS), by powdering the latter with vinegar in a copper vessel. Mercury was also prepared from cinnabar by strongly heating the ore in an iron vessel in a charcoal fire.

The theory that metals are composed of sulphur and mercury was originated by the Arab chemists, and was very popular for many hundreds of years. In the symbolic language of the alchemists mercury was called by many names —*the poison, gambar, permanent water, the dragon*, etc. "GEBER," the unknown author of many thirteenth century chemical treatises, describes it as follows—

"*Argentvive*, which alſo is called *Mercury* by the *Ancients*, is a viſcous *Water* in the *Bowels* of the *Earth*, by moſt temperate *Heat* united, in a total *Union* through its leaſt parts, with the ſubſtance of white ſubtile *Earth*, until the *Humid* be contempered by the *Dry*, and the *Dry* by the *Humid*, equally. Therefore it eaſily runs upon a plain *Superficies*, by reaſon of its *Watery Humidity*; but it adheres not, although it hath a viſcous *Humidity*, by reaſon of the *Dryneſs* of that which contemperates it, and permits it not to adhere. It is alſo (as ſome ſay) the *Matter* of *Metals* with *Sulphur*. And it eaſily

adheres to three *Minerals*, viz. to *Saturn*, and *Jupiter*, and *Sol* [that is, lead, tin, and gold], but to *Luna* [silver] more difficultly. To *Venus* [copper] more difficultly than to *Luna*; but to *Mars* [iron] in no wiſe, unleſs by *Artifice*. Therefore hence you may collect a very great *Secret*. For it is amicable, and pleaſing to *Metals*, and the *Medium* of conjoyning *Tinctures*; and nothing is ſubmerged in *Argentvive*, unleſs it be *Sol*. Yet *Jupiter* and *Saturn*, *Luna* and *Venus*, are diſſolved by it, and mixed; and without it, none of the *Metals* can be gilded. It is fixed, and it is a *Tincture* of *Redneſs* of moſt exuberant *Reflection*, and fulgid *Splendor*; and then it recedes not far from the *Commixtion*, until it is in its own Nature."

Compounds of mercury, especially the oxide (HgO), sulphide (HgS), and chloride ($HgCl_2$, *corrosive sublimate*) have been known for at least 1,000 years. The name *mercury* was given to the metal on account of its fanciful connection with the messenger of the Gods, MERCURY or HERMES, who was also identified with the founder of chemistry, the Egyptian HERMES TRISMEGISTOS. From the earliest days the metallic nature of the element was recognized.

Occurrence.—Mercury is found in small quantities free or as an amalgam with silver. It is obtained chiefly from its ore *cinnabar*, HgS, which is mined in Spain, Mexico, Russia, Peru, China, Japan and other places.

Extraction.—Cinnabar (with or without small admixture of charcoal) is roasted in a current of air and the mercury vapour and sulphur dioxide produced are passed through cooled earthenware receivers called *aludels* (Arabic *al-athāl*). This method has been employed for 2,000 years, with various improvements in detail.

If the cinnabar ore is rich, it is mixed with lime and the mixture strongly heated in cast-iron retorts, when the following reaction occurs:

$$4HgS + 4CaO = 4Hg + CaSO_4 + 3CaS.$$

Properties.—Mercury is the only metallic element liquid at ordinary temperatures. It freezes at −39° C. and boils at 357°, giving a colourless vapour the molecules of which are

monatomic (ratio of specific heats). The commercial metal is preserved in iron bottles (since it "adheres to *Mars* in no wise"), and usually contains a little copper and iron as impurities. Each bottle contains 75 lb. of mercury. The mercury is purified by redistillation, and the traces of foreign metals still present are then removed by allowing the mercury to fall in tiny droplets through a long tube filled with dilute nitric acid, when the impurities are dissolved. If required of very high purity, the mercury is again redistilled in a vacuum or in carbon dioxide at low pressure.

Mercury is not oxidized in the air at ordinary temperatures, but is gradually converted into the red oxide HgO, if heated in air or oxygen to a temperature just below its boiling-point. It is not dissolved by dilute sulphuric or hydrochloric acid; concentrated sulphuric acid dissolves it, forming mercuric sulphate and sulphur dioxide—

$$Hg + 2H_2SO_4 = HgSO_4 + 2H_2O + SO_2,$$

and so does nitric acid, concentrated or dilute, forming mercu*rous* nitrate, $HgNO_3$ (cold dilute acid) or mercu*ric* nitrate, $Hg(NO_3)_2$ (hot concentrated acid). Alkalis and most of the common gases (except chlorine) have no action on mercury.

On account of its high density, low specific heat, low freezing-point and high boiling-point, it is extremely useful in thermometry; the fact that it does not wet glass is an additional advantage. It is also useful for the collection of gases that are soluble in water; it was, indeed, by using mercury in the pneumatic trough that PRIESTLEY was able to collect ammonia. The important rôle played by mercury in the development of the oxygen theory of combustion will be at once remembered.

Amalgams.—Many metals will dissolve in mercury, and the solutions so formed are called *amalgams* (Arabic *al-mulagham*, a mixture). Certain amalgams are used in the laboratory, e.g. sodium amalgam, used as a reducing agent in presence of water. Sodium amalgam is made by gently warming mercury in an evaporating-dish and adding small pieces of sodium on the end of a knife. The sodium dissolves

with evolution of heat and a flash of light. Dilute sodium amalgams are liquid, but more concentrated ones are crystalline. Tin amalgam is used for making mirrors, while amalgams of cadmium, copper, gold, zinc, etc., are employed in dentistry for filling teeth, as they can be obtained as soft and plastic solids which gradually "set" or become hard. Mercury is used to form silver amalgam in the "amalgamation process" for the extraction of the latter metal (p. 229). One of the "artifices" referred to by "GEBER" for forming amalgam of "*Mars*" or iron is to grind iron filings with a paste of mercuric chloride and water. This process was known to the Arab chemists of the twelfth century.

COMPOUNDS OF MERCURY.—Mercury in its compounds can be either univalent or bivalent; it accordingly forms two series of compounds, the *mercurous* and *mercuric*. These may be regarded as derived from the two oxides, mercurous oxide, Hg_2O, and mercuric oxide, HgO.

Mercurous Compounds.

Mercurous oxide, Hg_2O, is a brownish-black powder made by the action of caustic soda solution upon mercurous chloride—

$$Hg_2Cl_2 + 2NaOH = Hg_2O + Hg_2O + 2NaCl.$$

It is unstable, and decomposes when warmed or when exposed to light, forming mercury and mercuric oxide.

Mercurous chloride, Hg_2Cl_2, is a white powder often called *calomel* (Greek, *beautiful black*) because it is changed to a black substance (mixture of metallic mercury with $NH_2.Hg.Cl$) by ammonia. Calomel is prepared by heating an intimate mixture of finely powdered mercuric chloride and mercury in an iron vessel provided with a lid; the calomel sublimes and condenses as a white powder on the lid of the vessel. It still contains a little mercury and mercuric chloride as impurities, and is therefore washed first with dilute nitric acid, to remove the mercury, and then several times with distilled water, to remove the mercuric chloride, and the mercurous nitrate formed in the nitric acid washing.

Mercurous chloride is also obtained, as a white precipi-

tate, by adding a solution of hydrochloric acid or a chloride to a solution of a soluble mercurous salt, e.g. mercurous nitrate.

It is insoluble in water, and is used in medicine (as a purgative) and in the pottery trade. It dissociates on heating into mercury and mercuric chloride; BAKER, however, has shown that perfectly dry calomel does not dissociate, and that the vapour density of the dry salt corresponds to the formula Hg_2Cl_2. Other work (cryoscopic and electrochemical) confirms this double formula. The alchemists prepared calomel mixed with corrosive sublimate by heating a mixture of mercury, salt, and vitriol.

Mercurous nitrate (written $Hg_2(NO_3)_2$ from analogy with the chloride) is obtained when mercury is dissolved in cold dilute nitric acid. It forms colourless crystals with two molecules of water of crystallization, $Hg_2(NO_3)_2.2H_2O$, and is partially hydrolysed by water to a yellowish basic nitrate. The mercurous nitrate solution used as a reagent is therefore mixed with a little nitric acid, to prevent formation of the basic salt.

Mercurous sulphate, Hg_2SO_4, is made by gently heating sulphuric acid with an excess of mercury. It is a practically insoluble crystalline powder, partially hydrolysed by water. It is chiefly of importance from its use in the standard electric cell (WESTON cell, see textbooks of physics).

Mercurous iodide, Hg_2I_2, is a green powder made by rubbing iodine with excess of mercury, and one or two drops of alcohol, in a mortar. In the light it gradually decomposes into mercury and mercuric iodide, HgI_2.

Mercuric Compounds.

Mercuric oxide, HgO, is obtained as a red crystalline powder by heating mercury in the air for several days to a temperature just below its boiling-point. The earliest description of this preparation of *mercuric oxide* appears to be that given by an unknown Spanish Arab of about A.D. 1007, who in his book entitled RUTBAT AL-HAKIM ("The Sage's Step"), says, "I took pure natural quivering quicksilver and placed it in a glass vessel shaped like an egg, and put this in another vessel

shaped like a cooking-pot. I then set the latter on a very gentle fire and heated the apparatus for 40 days; day and night. The original weight of the mercury was ¼ lb. At the end of 40 days I found it was all converted into a soft red powder, but I could detect no change in weight." It is formed as a *yellow* precipitate by addition of caustic soda to a solution of mercuric chloride—

$$HgCl_2 + 2NaOH = HgO + H_2O + 2NaCl.$$

The difference in colour may be due to the difference in size of the particles of the oxide prepared in these two ways. Compare copper sulphate crystals and the *powdered* crystals. Alternatively it may be due to difference in crystalline form.

The red oxide may also be prepared by *cautiously* heating mercuric nitrate—

$$2Hg(NO_3)_2 = 2HgO + 4NO_2 + O_2.$$

Strong heating of the nitrate results in metallic mercury being formed, from decomposition of the oxide.

When mercuric oxide is heated, it turns black and splits up into oxygen and mercury (PRIESTLEY'S experiment on *red calx of mercury*).

$$2HgO = 2Hg + O_2.$$

It is soluble in dilute acids, giving mercuric salts. If it is boiled with a solution of ammonia it gives a yellow solution of a compound called MILLON'S *base, mercurammonium hydroxide*, $NHg_2OH.H_2O$. This is used in testing for proteins.

Mercuric chloride or *corrosive sublimate*, $HgCl_2$, may be made synthetically by passing chlorine over heated mercury. This is the method employed commercially. It may also be made by heating a mixture of mercuric sulphate and common salt, or an intimate mixture of mercury, salt, ferric oxide, alum, and nitre, as used by the alchemists. Thus "GEBER" says: "Sublime *Argentvive* thus: R. of it *lib. i.* of *Vitriol* rubified [i.e. ferric oxide], *lib. ij.* Of *Rock-Allom* calcined, *lib. i.* of *Common Sal, lib. ii.* and of *Salt-Peter* one fourth part. Incor-

porate all together, and ſublime: and gather the *White*, *Denſe*, and *Ponderous*, which ſhall be found about the *Sides* of the *Veſſel*, and keep it, as we have appointed of other Things. But if, in the firſt *Sublimation*, you ſhall find it turbid, or unclean (which may happen, by reason of your own *Negligence*) again ſublime it with the ſame *Feces*, and reſerve it for vſe."

Mercuric chloride is a white crystalline solid, slightly soluble in cold water and more soluble in hot. It is used in medicine, as an antiseptic and germicide, in the form of a very dilute aqueous solution. It is sometimes employed as a perservative for the sleepers of railways, where they are liable to be attacked by insect pests. Like all soluble mercury compounds it is very poisonous.

It is only slightly ionized in solution, and is a mild oxidizing agent; thus, it oxidizes stannous chloride ($SnCl_2$) to stannic chloride ($SnCl_4$), sulphur dioxide in solution to sulphuric acid, and oxalic acid (in presence of a trace of iron salt as catalyst) to carbon dioxide, being itself reduced to mercurous chloride or even to mercury.

Mercuric chloride reacts with ammonia under various conditions to give complex *mercurammonium compounds*, e.g. *white precipitate*, $Hg\begin{<}{Cl}{NH_2}$, made by adding ammonia to mercuric chloride solution.

Mercuric nitrate $[Hg(NO_3)_2]_2.H_2O$ or $Hg(NO_3)_2.\frac{1}{2}H_2O$, is obtained as colourless deliquescent crystals from the liquid produced by dissolving mercury in hot concentrated nitric acid. It is hydrolysed by water, giving a basic nitrate, $Hg(NO_3)_2.2HgO.H_2O$; boiling water carries the hydrolysis still further, to mercuric oxide.

Mercuric iodide, HgI_2, is a characteristic red powder. It is made by adding potassium iodide to mercuric chloride solution—

$$HgCl_2 + 2KI = HgI_2 + 2KCl,$$

and comes down first as a yellow precipitate; the colour, however, rapidly changes to red. On heating to 130° the red

form again changes to yellow; the yellow is unstable at ordinary temperatures and slowly reverts to the red form—rubbing or scratching accelerates the change. Mercuric iodide is soluble in excess of potassium iodide, forming the complex compound *potassium mercuri-iodide*, K_2HgI_4—

$$2KI + HgI_2 = K_2HgI_4.$$

This shows none of the ionic reactions for mercury, since it ionizes into $K^{\cdot}$, $K^{\cdot}$, and HgI_4''. An alkaline solution of potassium mercuri-iodide is called NESSLER'S solution, and is used as a test for ammonia or ammonium salts, with which it gives a yellow precipitate said to be *mercurammonium iodide*, $Hg_2N.I$; the composition of the precipitate is, however, still uncertain.

Mercuric cyanide, $Hg(CN)_2$, may be made by dissolving mercuric oxide in dilute prussic acid and evaporating the solution—

$$HgO + 2HCN = Hg(CN)_2 + H_2O.$$

It forms large colourless crystals which do not ionize in solution and which decompose on heating, yielding *cyanogen* and mercury—

$$Hg(CN)_2 = Hg + C_2N_2.$$

Mercuric sulphide, HgS, occurs naturally as the red mineral *cinnabar*. Formed by passing sulphuretted hydrogen through mercuric chloride solution it is *black*. The black form changes into the red on sublimation. It is made commercially (since it is used as a paint, *vermilion*) (i) by mixing mercury and sulphur with concentrated caustic potash solution and warming to 50°; (ii) by heating mercury and sulphur together, with constant and effective stirring. The crude sulphide is then purified by sublimation.

Mercuric thiocyanate, $Hg(CNS)_2$, is made by adding concentrated potassium thiocyanate solution to mercuric chloride or nitrate solution. It forms a white precipitate, which when mixed with a little gum can be made up into the "eggs" of "PHARAOH'S serpents." When ignited these hatch out into awe-inspiring reptiles of a material which, very appropriately, is extremely poisonous.

QUESTIONS

1. Compare and contrast the properties of magnesium and its compounds with those of (*a*) calcium and calcium compounds, (*b*) zinc and zinc compounds.

2. Describe the manufacture of magnesium.

3. Give an account of the metallurgy of zinc.

4. What calcium compounds are used as fertilizers? Write their formulæ and describe their manufacture.

5. Explain the use of strontium oxide in sugar-refining.

6. Describe the preparation and properties of the chlorides of mercury.

7. Explain the importance of mercury in the chemical theories of the Middle Ages.

8. What are (*a*) the "eggs of Pharaoh's serpents," (*b*) Nessler's solution, (*c*) cinnabar, (*d*) white precipitate? Describe their preparation.

9. What evidence is there for the constitution of bleaching-powder? How would you estimate the available chlorine in this compound?

CHAPTER XXIII

GROUP III

Typical Elements: Boron, Aluminium.
Sub-group A: Scandium, Yttrium, Rare Earths.
Sub-group B: Gallium, Indium, Thallium.

BORON, ALUMINIUM

Boron and aluminium resemble one another very little except in the fact that the formulæ of their compounds are similar, since the valency of each element is 3. The element most closely related in chemical properties to boron is undoubtedly silicon.

Boron is a typical *non-metal*, while aluminium is a true metal.

The "rare earth" metals are numerous and of comparatively little importance chemically; compounds of some of them are, however, used in the manufacture of incandescent gas-mantles and for other purposes.

Scandium and gallium are of interest on account of Mendeléeff's prediction that they existed (p. 156) some years before they were actually discovered.

Boron

Group in Periodic System: III; *Symbol:* B; *Atomic Weight:* 10·82; *Valency:* 3; *Specific Gravity:* 2·6–2·3

History.—The name *buraq*, whence our *borax*, was given by the Arabian chemists to many substances used as fluxes. One variety was *tinkar* or *tinkal*, obtained from Armenia and

also from a salt lake in Tibet, and it is to this substance, $Na_2B_4O_7.10H_2O$, that the name "borax" is at present confined. In 1702 HOMBERG contributed a paper to the French Academy of Sciences, in which he described the preparation of a white flaky substance by adding sulphuric acid to a solution of borax. This new substance was called *sal sedativum*, and was largely used in medicine by the great French scientist LEMERY. Half a century later (1747), BARON showed that borax was a compound of *sal sedativum* and soda, and concluded that Homberg's substance was not a *salt* but an acid, for which the name *boracic acid* was suggested. On LAVOISIER'S oxygen theory of acids, boracic acid would be the oxide of a non-metallic element, and working from this point of view DAVY (1808), and GAY-LUSSAC and THÉNARD in the same year, succeeded in isolating the element *boron*, by heating boracic acid anhydride with potassium.

Occurrence.—Boron has not been found in nature in the free state. It occurs as crystalline boracic (or boric) acid in the mineral *sassolino* (Tuscany), but chiefly as *borax* or *tinkal*, $Na_2B_4O_7.10H_2O$, of which large deposits occur in California. Calcium borate, or *colemanite*, occurs in quantity in South America, while boric acid is found in the natural steam jets or *soffioni* of certain volcanic regions in Tuscany.

Preparation.—Boron proved difficult to isolate in the pure state. The simplest method of getting a reasonably pure specimen is to heat potassium borofluoride (KBF_4) with sodium in a stream of hydrogen—

$$KBF_4 + 3Na = KF + 3NaF + B.$$

Reduction of the oxide (B_2O_3) with magnesium powder has also been recommended (MOISSAN)—

$$B_2O_3 + 3Mg = 3MgO + 2B.$$

In each of these methods the product is treated with hydrochloric acid, to remove the other substances, and the boron is left as a dark brown powder.

Pure boron may be made, according to WEINTRAUB (1909) and PRING and FIELDING (1910), by striking the electric arc

between copper electrodes in a mixture of boron trichloride vapour and excess of hydrogen—

$$2BCl_3 + 3H_2 \rightleftharpoons 2B + 6HCl.$$

Most of the boron is deposited on the electrodes, and finally fuses into small beads, which fall off and solidify.

WARTH (1923) prepared boron of a high purity by reducing boron trichloride with hydrogen at 1,300°–1,850° in the presence of a glowing filament of tungsten.

Properties.—Pure boron is an extremely hard black solid; when broken it shows a *conchoidal* fracture (that is, the broken pieces show *curved* surfaces, and not the plane surfaces characteristic of crystalline bodies) and is therefore amorphous. Its specific gravity is 2·30–2·34 and its boiling-point about 2,300°. A remarkable property of boron is the rapidity with which its electrical resistance falls on rise of temperature. WEINTRAUB showed that a piece of boron which had a resistance of 5,620,000 ohms at 27° C. had a resistance of only 5 ohms at a dull red heat.

Pure boron does not oxidize in the air, even at very high temperatures; it is, however, slowly oxidized to boric acid by concentrated nitric acid. It combines directly with *nitrogen*, if heated, to form boron *nitride*, BN, and with carbon (in the electric furnace) to form the *carbide*, B_4C_3.

The brown powder obtained in the first two ways above described is an impure boron, which differs in many of its properties from pure boron. *Colloidal* boron has been prepared in several ways; some of its colloidal solutions are brown and others are red.

COMPOUNDS OF BORON.—Boron is a non-metallic *tervalent* element; it rarely exhibits a valency of 5.

Boron hydrides.—The simple hydride, BH_3, is not known, but about ten others exist. The chief of these are B_2H_6, diboron hexahydride, and B_4H_{10}, tetraboron decahydride, a mixture of which is prepared by the action of hydrochloric acid on *magnesium boride* (made by heating boron trioxide, B_2O_3, with magnesium powder). B_2H_6 is a colourless gas, while B_4H_{10} is a colourless volatile liquid with a very un-

pleasant smell. B_4H_{10} takes fire spontaneously on exposure to air or oxygen.

Boron fluoride, BF_3, is made by heating a mixture of calcium fluoride and boron trioxide with concentrated sulphuric acid—

$$B_2O_3 + 3CaF_2 + 3H_2SO_4 = 2BF_3 + 3CaSO_4 + 3H_2O.$$

It is a colourless gas with a pungent smell, and must be collected over mercury, as it immediately attacks water, with formation of boric and *hydrofluoboric acids*—

$$4BF_3 + 3H_2O = 3HBF_4 + H_3BO_3.$$

The salts of hydrofluoboric acid are called *borofluorides*; the most important is the potassium salt.

Boron chloride, BCl_3, is made by heating a mixture of boron trioxide and powdered charcoal in a stream of chlorine—

$$B_2O_3 + 3C + 3Cl_2 = 2BCl_3 + 3CO,$$

and passing the issuing gases through a U-tube surrounded by a freezing-mixture, when the boron trichloride condenses as a colourless fuming liquid boiling at 13°. An alternative method (MAZZETTI and DE CARLI) is to heat iron boride ("ferroboron") in a current of dry chlorine at 500°. Water hydrolyses it irreversibly—

$$BCl_3 + 3H_2O = H_3BO_3 + 3HCl.$$

Boron trioxide, B_2O_3 (otherwise known as *boric anhydride* or *boron sesquioxide*), is obtained when boric acid is heated to redness—

$$2H_3BO_3 = B_2O_3 + 3H_2O.$$

It is a glassy colourless solid, very hygroscopic, and soluble in water, with which it combines to form boric acid. Although an acidic oxide, it shows some basic properties as well.

Boric acids.—Two boric acids are known; the ordinary form is *orthoboric acid*, H_3BO_3, and this is converted into *metaboric acid*, HBO_2, at a temperature of 100–140°. Orthoboric acid is volatile in steam, and, as previously mentioned, occurs in the *soffioni* or jets of steam that issue from the ground in certain parts of Italy. The steam is condensed in

large tanks of water and the solution concentrated (largely by the heat of the natural steam) until the boric acid crystallizes out. The origin of the boric acid of the *soffioni* is uncertain ; it has been suggested that the steam may traverse a stratum of rock containing *boron sulphide*, *boron nitride*, or *tourmaline* (a boron mineral), all of which yield boric acid in contact with steam.

In the laboratory, boric acid is conveniently made by addition of sulphuric acid to a hot concentrated solution of borax ; on cooling, the boric acid separates as a pearly crystalline solid, greasy to the touch. It is a very weak acid, so weak that it has no action on methyl orange ; it may, however, be titrated with caustic soda if *excess of glycerol* is added to the solution and phenolphthalein is used as indicator. Under these conditions it behaves as a *monobasic* acid—

$$H_3BO_3 + NaOH = NaBO_2 + 2H_2O.$$

Boric acid or boracic acid finds many uses in everyday life—it is a well-known antiseptic, and was formerly used as a preservative for cream, etc., although it is harmful if taken internally. Its use as a preservative has now been forbidden by Act of Parliament.

Borax, or sodium pyroborate, $Na_2B_4O_7.10H_2O$, occurs naturally as *tinkar* or *tinkal*, but is also made from the South American *colemanite*, $Ca_2B_6O_{11}.5H_2O$, by boiling it for some time with sodium carbonate solution—

$$Ca_2B_6O_{11} + 2Na_2CO_3 = 2CaCO_3 + Na_2B_4O_7 + 2NaBO_2.$$

Carbon dioxide is then blown through the solution, when

$$4NaBO_2 + CO_2 = Na_2CO_3 + Na_2B_4O_7.$$

In this way all the colemanite is converted into borax, which is crystallized out from the filtered solution by evaporation.

Borax is sodium pyroborate decahydrate, $Na_2B_4O_7.10H_2O$. On heating it swells up and loses its water, forming anhydrous borax, which on melting goes to a clear transparent glass. This glassy substance readily dissolves metallic oxides, in many cases with production of characteristic colours. ("Borax Bead" test.)

Borax is still used as a flux, as it has been for the last 1,000 years.

In solution, borax is largely hydrolysed,

$$Na_2B_4O_7 + 7H_2O \rightleftharpoons 2NaOH + 4H_3BO_3.$$

The solution therefore has an alkaline reaction, and since methyl orange is not affected by the weak boric acid, a solution of borax may be titrated with an acid as if it were caustic soda solution, *if methyl orange is used as indicator.*

The green flame produced when boric acid (or a borate), sulphuric acid, and alcohol are heated together and the alcohol vapour ignited, is due to the formation of an organic boron compound, *ethyl borate*, $(C_2H_5)_3BO_3$, which burns with the characteristic greenish flame.

Aluminium

Group in Periodic System: III; *Symbol:* Al; *Atomic Weight:* 27·0; *Valency:* 3; *Melting-point:* 659°; *Specific Gravity:* 2·7.

History.—The word *alum* is derived from the Latin *alumen*, "a mineral salt with an astringent taste." Alum occurs in many parts of the ancient world, and was known to the Arabian chemists, who usually placed it in the group of compounds called by the general name of *buraq* or borax. Other early chemists more correctly classed it with the vitriols with which it has obvious chemical similarities, although it is not isomorphous with them. Paracelsus, however, was unable to extract any metal from alum and therefore stated, in his usual dogmatic fashion, that it was not a vitriol. No further elucidation of the nature of alum was made until 1746, when Pott concluded that it was a compound of a new "earth." Eight years later Marggraf prepared this earth, "alumina," from clay, and showed that it was quite distinct in properties from lime.

Davy attempted to isolate a metal from alumina, which he quite rightly assumed to be a metallic oxide; he was unsuccessful, however, and it was not until 1827 that metallic aluminium was prepared. In that year Wöhler heated

anhydrous aluminium chloride with potassium and obtained aluminium as a white metal of low specific gravity.

Occurrence.—Metallic aluminium is not found in nature, but aluminium compounds are extremely abundant and are found universally in rocks and clays. A few of the chief naturally occurring compounds of aluminium are the following—

Silicates, e.g., clay, slate, mica, felspar ($KAlSi_3O_8$), kaolin ($Al_2Si_2O_7 2H_2O$), garnet, topaz, tourmaline.

Oxides, e.g. bauxite ($Al_2O_3.2H_2O$), corundum (Al_2O_3), diaspore ($Al_2O_3.H_2O$), spinel ($MgAl_2O_4$), chrysoberyl ($BeAl_2O_4$).

Fluoride, e.g. cryolite (Na_3AlF_6); *phosphate*, e.g. turquoise.

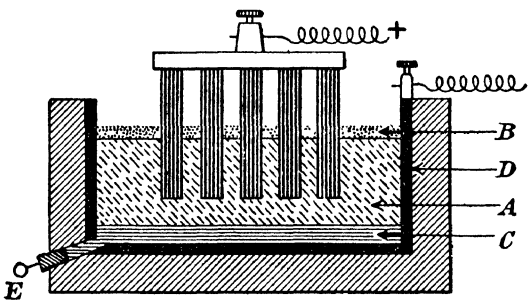


FIG. 57.—Cross Section of Hall Cell for Manufacture of Aluminium.
A. Fused electrolyte. *B*. Layer of powdered coke. *C*. Molten aluminium. *D*. Carbon lining of cell. *E*. Plug for running off the fused metal.

Manufacture.—Aluminium was first manufactured by heating sodium aluminium chloride, $NaAlCl_4$, with sodium, a process devised by DEVILLE in 1854—

$$NaAlCl_4 + 3Na = 4NaCl + Al.$$

Shortly afterwards the fluoride, *cryolite*, Na_3AlF_6, was used instead of the chloride, but the high price (£60 per lb.) of the aluminium made in this way rendered the commercial use of the metal impossible.

In 1886, however, an electrolytic process was invented simultaneously by HALL in America and by HÉROULT in

France. These chemists discovered that alumina (Al_2O_3) would dissolve in fused cryolite and that the solution so obtained could be electrolysed, oxygen coming off from the anode and aluminium being liberated at the cathode. In effect, therefore, the process is an *electrolysis of alumina*, since the cryolite is left unchanged.

Alumina is obtained from the mineral *bauxite* ($Al_2O_3.2H_2O$), which is found in Ireland, France and the United States. Natural bauxite always contains iron oxide and silica as impurities, and since the presence of iron and silicon in aluminium is very harmful (rendering it easily attacked by water, etc.), the bauxite has to be carefully purified before use. Realization of this fact, followed by preparation of a purer aluminium, at once led to a considerable improvement in the financial conditions of aluminium companies.

Purification of the bauxite is carried out in many different ways. In one of these the crushed bauxite is dissolved in hot concentrated caustic soda solution, forming sodium aluminate—

$$Al_2O_3.2H_2O + 2NaOH = 2NaAlO_2 + 3H_2O.$$

The impurities are insoluble and are removed by passing the liquid through a filter-press. To the filtrate a little freshly prepared gelatinous aluminium hydroxide is added, when practically all the sodium aluminate is gradually decomposed and the aluminium precipitated as hydroxide. This is filtered off and converted into alumina by ignition, while the filtrate of caustic soda solution is used again.

The cryolite is obtained from the large deposits that occur in Greenland. It is fused in an iron box lined with gas carbon, which forms the cathode. The anode consists of a number of stout carbon rods which dip into the molten cryolite; the latter forms a shallow layer which in the Hall process is only some 6 inches in depth. Alumina, purified as already described, is dissolved in the fused cryolite, fresh supplies being added from time to time as electrolysis proceeds. Molten aluminium collects on the floor of the cell and is run off as required. The carbon anodes are burnt to carbon

monoxide and dioxide by the oxygen liberated and have to be replaced; as they are expensive, attempts have been made to use other substances for the anodes, but hitherto without success. Analysis of the anode gases indicates that the formation of the aluminium and oxidation of the anode proceed roughly according to the equations—

$$Al_2O_3 + 3C = 3CO + 2Al.$$
$$2Al_2O_3 + 3C = 3CO_2 + 2Al.$$

Properties.—Aluminium is a metal of a bluish white colour. It can be highly polished and is malleable and ductile, although it becomes brittle and can be powdered at a temperature just below its melting-point. It has a low specific gravity, and as it is fairly hard, is extensively used in airship production and for other purposes where "lightness" is a prime requisite. It is also employed on a large scale for the manufacture of domestic utensils such as saucepans. First-grade commercial aluminium is of about 99 per cent. purity; the chief impurities are iron and silicon.

Aluminium melts at 658° and boils at 1,800°; its specific gravity is 2·7. It is stable in the air, apparently owing to the formation of a thin film of oxide which protects the underlying metal from further oxidation. On heating aluminium in the air it burns with a brilliant white flame, forming alumina. Nitric acid has no action upon it; it dissolves, however, in hot concentrated sulphuric acid, forming aluminium sulphate and sulphur dioxide—

$$2Al + 6H_2SO_4 = Al_2(SO_4)_3 + 6H_2O + 3SO_2.$$

It dissolves easily in hydrochloric acid, forming the chloride and hydrogen—

$$2Al + 6HCl = 2AlCl_3 + 3H_2.$$

It also dissolves very quickly in solutions of caustic alkalis, to form *aluminates*, with evolution of hydrogen—

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

Aluminium is a powerful reducing agent; in the form of

powder it readily reduces metallic oxides with evolution of intense heat. A mixture of ferric oxide and aluminium powder is called *thermite*; when ignited by means of a piece of burning magnesium ribbon the whole mass becomes incandescent and molten iron is left. This reaction is employed for welding two pieces of iron together, e.g. tram-rails, without the necessity of removing them from their positions. Thermite was used during the war for filling incendiary bombs, and a mixture of aluminium powder with ammonium nitrate formed the Mills' bomb explosive *ammonal*.

Many *alloys of aluminium* are of importance. The chief are *duralumin* (94 per cent. Al, 0·5 per cent. Mg, 4·5 per cent. Cu, 0·75 per cent. Mn, 0·25 per cent. Fe), *magnalium* (95 per cent. Al, 4·5 per cent. Mg, 0·5 per cent. Sn, etc.), *aluminium bronze* (90 per cent. Cu, 10 per cent. Al), and *aluminium brass* (30 per cent. Zn, 69 per cent. Cu, 1 per cent. Al).

Aluminium amalgam is readily attacked by water, yielding mercury, hydrated alumina or aluminium hydroxide, and hydrogen. The *aluminium-mercury couple* (Al/Hg) consists of aluminium foil covered with a film of aluminium amalgam. With methyl alcohol it forms a reducing agent widely used in organic chemistry, e.g. in the preparation of methane from methyl iodide.

COMPOUNDS OF ALUMINIUM.

Aluminium sesquioxide, or alumina, Al_2O_3, occurs naturally in the anhydrous state as *corundum*, and as hydrates in *diaspore*, $Al_2O_3.H_2O$, *bauxite*, $Al_2O_3.2H_2O$, and *hydrargillite*, $Al_2O_3.3H_2O$. Coloured varieties of corundum are known as *ruby* (red), *oriental topaz* (yellow), *oriental emerald* (green), *oriental sapphire* (blue), and *amethyst* (violet). The colour is due to the presence of small quantities of foreign metallic oxides such as those of chromium, manganese, cobalt, etc. The preparation of artificial rubies and sapphires from aluminium oxide is now an important industry, millions of carats being produced every year. To make rubies, fused alumina is mixed with a little chromium sesquioxide, Cr_2O_3; for the production of sapphires a mixture of magnetic oxide of

iron and titanium dioxide is used instead of the chromium oxide.

Impure corundum is called emery and is used in making "emery-paper."

Pure aluminium oxide may be made by heating the pure hydroxide or nitrate. Alumina is usually soluble in dilute acids, but if it is strongly heated it appears to change into another modification at 850°, and this is insoluble.

Aluminium hydroxide, $Al(OH)_3$, is formed as a white gelatinous precipitate on adding caustic alkali or ammonia to a solution of an aluminium salt; it is insoluble in excess of ammonia but dissolves in excess of soda or potash to form *aluminates*. As it is also soluble in dilute acids, giving aluminium salts, it is an example of the class of *amphoteric* substances; in solution (it is very slightly soluble) it ionizes in two ways—

(i) $Al(OH)_3 \rightleftharpoons Al''' + 3OH'$.
(ii) $Al(OH)_3 \rightleftharpoons 3H^{\cdot} + AlO_3'''$.

It is used in the dye industry as a mordant.

The *aluminates* of sodium and potassium, made by dissolving aluminium or aluminium hydroxide in caustic soda or potash solution, are often represented by the formulæ Na_3AlO_3 and K_3AlO_3. Cryoscopic determinations, however, show that in solution they probably have the formulæ $NaAlO_2$ and $KAlO_2$, and ought therefore more properly to be called *meta*-aluminates. They have been prepared in the solid crystalline state and the crystals have the following compositions: potassium salt, $KAlO_2.1\frac{1}{2}H_2O$, sodium salt, $NaAlO_2.2H_2O$.

Several anhydrous crystalline meta-aluminates occur naturally: they are called *spinels*—

magnesia spinel, $Mg(AlO_2)_2$. *zinc spinel*, $Zn(AlO_2)_2$.
iron spinel, $Fe(AlO_2)_2$.

Minerals of similar constitution, in which the aluminium has been replaced by tervalent iron, chromium, or magnesium, are also called spinels.

Aluminium chloride, $AlCl_3$, **is made anhydrous by heat-**

ing aluminium in a current of dry chlorine or hydrochloric acid gas—

$$2Al + 3Cl_2 = 2AlCl_3;$$

or by heating an intimate mixture of alumina and carbon in chlorine.

It is a white deliquescent solid, often tinged with yellow by ferric chloride present as impurity. When heated, it sublimes at 180°; the molecules of the vapour up to 400° are Al_2Cl_6, but at this temperature rapid dissociation begins and at 700° is complete—

$$Al_2Cl_6 \rightleftharpoons 2AlCl_3.$$

In solution in certain organic solvents such as ether the molecules are $AlCl_3$.

Aluminium chloride is very soluble in water, which partially hydrolyses it—

$$AlCl_3 + 3H_2O \rightleftharpoons Al(OH)_3 + 3HCl.$$

Crystals of aluminium chloride hexahydrate, $AlCl_3.6H_2O$, can be obtained by cautiously evaporating a solution of the metal, oxide, or hydroxide in hydrochloric acid, or by saturating an aqueous solution of the chloride with hydrochloric acid gas. On heating, the hexahydrate loses water and hydrochloric acid and is converted into alumina.

The anhydrous salt is commonly used as a catalyst in certain organic reactions (e.g. *Friedel and Crafts'* reaction).

Aluminium sulphate, $Al_2(SO_4)_3$ can be prepared as a hydrate with $18H_2O$ by evaporating to crystallization a solution of aluminium hydroxide in dilute sulphuric acid—

$$2Al(OH)_3 + 3H_2SO_4 = Al_2(SO_4)_3 + 6H_2O.$$

The crystals of the hydrate lose their water on heating, and the anhydrous sulphate is left.

Aluminium sulphate is of importance commercially since it is employed in the purification of sewage and also in paper-making. It is manufactured by heating china-clay (*kaolin*) or bauxite with sulphuric acid and is put on the market in solid blocks called "*alum-cake.*"

With the sulphates of the alkali-metals, aluminium sul-

phate forms a series of double salts called the *alums*; they have the general formula $R_2SO_4.Al_2(SO_4)_3.24H_2O$, where R = (Li), Na, K, Rb, or Cs. The existence of *lithium alum* is doubtful. Ordinary "alum" is potassium alum.

Similar compounds are known in which the aluminium sulphate is replaced by the sulphate of other tervalent metals such as iron and chromium. *Potassium chrome alum*, for instance, is

$$K_2SO_4.Cr_2(SO_4)_3.24H_2O,$$

and *ammonium ferric alum*

$$(NH_4)_2SO_4.Fe(SO_4)_3.24H_2O.$$

The general formula for all "alums" is therefore

$$R_2SO_4.R'_2(SO_4)_3.24H_2O,$$

where R = a univalent metal, usually an alkali-metal, and
R′ = a tervalent metal, usually iron, chromium or aluminium.

Potassium alum is made from *alum-cake* by dissolving it in water, adding the appropriate weight of potassium sulphate, and crystallizing the solution. It is also made from a mineral called *alunite*, $K_2SO_4.Al_2(SO_4)_3.4Al(OH)_3$, found in France, Hungary and other countries, by treatment with dilute sulphuric acid. Sufficient potassium sulphate is added to convert the excess of aluminium sulphate thus formed into the double salt, and the solution then evaporated.

Another source of alum is *alum-shale*, a slate (or aluminium silicate) containing iron pyrites. The shale is roasted for about a week and then treated in the same way as alunite.

Clay, Porcelain and China.—An account of the clays and their uses in the pottery trade falls outside the scope of this elementary book. The student who is interested in the subject should read the appropriate articles in THORPE'S *Dictionary of Applied Chemistry*, etc.

Ultramarine.—The soft blue mineral known as *lapis-lazuli* is a complex sodium aluminium silicate containing about 13 per cent. of sulphur. It is now manufactured, under the name of "ultramarine," by heating a mixture of china-clay,

charcoal, soda-ash and sulphur. It is used in washing clothes (" blue-bag "), to make them look white.

Questions

1. Give an account of the history of boron.
2. Compare and contrast the properties of boron with those of silicon.
3. Write a description of boric acid and borax. How is borax made commercially ?
4. Mention the chief naturally occurring aluminium compounds.
5. Describe the manufacture of aluminium.
6. Boron and aluminium are classed together in the Periodic System. How far is this classification supported by the chemical relationships of the two elements ?
7. When sodium sulphide is added to a solution of alum, aluminium *hydroxide* is precipitated. Can you explain this ?
8. Describe the preparation and properties of anhydrous aluminium chloride.

CHAPTER XXIV

GROUP IV

Typical Elements, Carbon, Silicon.

Sub-group A: Titanium, Zirconium, Cerium, Thorium.
Sub-group B: Germanium, **Tin, Lead.**

CARBON, SILICON, TIN, LEAD

Although lead and tin show certain resemblances to one another, they are very different from the characteristic non-metals carbon and silicon. Carbon and silicon, again, have the same valency, 4 (and therefore form compounds of similar formulæ), but otherwise differ markedly from one another. In chemical properties silicon is most closely related to boron.

All the elements in Group IV are quadrivalent, and many of them may be bivalent as well.

Chemically, cerium should be classed with the rare-earth elements of Group III.

Carbon

Group in Periodic System: IV; *Symbol:* C; *Valency:* 4; *Atomic Weight:* 12·00.

History.—The history of carbon was fairly uneventful until the beginning of the nineteenth century, when, with the aid of the Atomic Theory, the constitution of "organic" or carbon compounds was first successfully studied. Since that time the chemistry of the compounds of carbon has become an entire subject in itself and is called *Organic Chemistry.*

In the form of *coal,* which crops out at the surface of the

earth in many places, carbon has been known for at least 2,000 years. A Roman altar, excavated at Bath, was found to have coal ashes upon it, and there are many mentions of coal in the ancient writers. It was not until 1775 that the *diamond* was proved to be a form of carbon; in that year, however, LAVOISIER, and twenty-two years later TENNANT, showed that when the diamond is burnt carbon dioxide is produced, the latter proving in addition that the *weight* of carbon dioxide formed from a given weight of diamond is the same as that which would be given by the combustion of an equal weight of charcoal.

In 1800 MACKENZIE proved that *graphite*, formerly confused with molybdenum sulphide under the name of "blacklead," was another crystalline form of carbon.

Occurrence.—Carbon is found free in nature in three allotropic forms—*diamond* (crystalline), *graphite* (crystalline), and *coal* (impure amorphous form). In combination it is found in metallic *carbonates* (limestone, marble, dolomite, etc.); as *carbon dioxide*, in the air; as *hydrocarbons* (compounds of carbon and hydrogen only) in petroleum and natural gas; and in the form of more complex bodies in all living tissue, of which, indeed, it is the prime constituent.

Properties.—The three allotropic forms will be considered in turn.

(i) *Diamond*

Diamonds are found in many parts of the world. In olden days they came chiefly from India, but most of them are now obtained from South Africa, Brazil, and Australia, although a few are still extracted in India and Borneo. In South Africa diamonds are found occasionally in alluvial river sand, but chiefly in "pipes" or inverted cones of a blue clay lying vertically in the earth and supposed to have been formed by volcanic activity in a remote geological age. To mine this clay, a shaft is sunk through the rock at one side of the "pipe," and horizontal tunnels are then made from the shaft into the "earth." The "earth" is brought to the surface and exposed to the weather for several months, during which

it falls to a coarse powder. This powder is then agitated in a stream of water, which removes the lighter particles, and the concentrated earth is then washed over a layer of grease, to which the diamonds adhere.

Natural diamonds differ considerably in size, colour, and value. The largest diamond ever discovered was the Cullinan, which was found in the Transvaal in 1905 and before cutting weighed 3,025¾ carats—over a pound and a quarter (1 *carat* = 3·17 grains or 0·2054 gm.). Colourless diamonds are the most valuable; the "black diamonds" (*carbonado*) are used for making glass-cutters, etc., and for cutting and polishing the colourless stones.

For purposes of jewelry, the natural diamonds are cut in such a way that as much internal reflection as possible is caused; this process requires great skill, and many valuable stones have been spoilt through inexpert cutting. There is always bound to be some loss in weight on cutting a stone, of course, but in some cases it is found necessary to cut the stones down severely. Thus the *Koh-i-noor* ("mountain of light") which originally weighed 186 carats, had to be cut down to 106 carats.

The density of the diamond is 3·5 and its refractive index 2·45; it is the hardest substance known. It is extremely stable towards chemical reagents; acids have no effect upon it, but it is slowly attacked by fused sodium carbonate, forming carbon monoxide—

$$Na_2CO_3 + C = Na_2O + 2CO.$$

When a diamond is heated in air to about 800° it takes fire and burns brilliantly, forming carbon dioxide. If heated in the electric furnace in absence of air it swells up, and changes, partially at least, into graphite.

It is generally believed, from a study of the rocks and clay in which they occur, that diamonds have been formed by the crystallization of carbon from a solution of that element in iron, or perhaps in a silicate, possibly under great pressure. This conclusion is supported by the chemical researches of the versatile French chemist MOISSAN. Many chemists had

previously been attracted to the fascinating problem of the artificial production of diamonds, but success was first attained by Moissan in 1893. He took a small tube of soft iron fitted with a screw cap, filled the tube with pure sugar-carbon (p. 294), and screwed down the cap so that the carbon inside was strongly compressed. He dropped this tube into a crucible of molten iron heated in the electric furnace; the crucible and contents were then removed and quickly cooled by immersion in melted lead. Under these conditions the iron on the outside of the mass solidified while that inside was still liquid. Now iron, like water, expands on solidification, so that when the interior of the mass solidified it did so under the extremely high pressure caused by the central iron trying to expand inside the hard solid crust.

When cold, the iron was dissolved away in hydrochloric acid, and a number of crystals of carbon were left. Some of these proved to be graphite, but others were diamonds, both black and colourless. The diamonds obtained in this way are, however, very small (the largest was scarcely more than half a millimetre in diameter), and the process is therefore not a commercial success, as the cost of making the diamonds is about three times their market value when made.

The experiments of Sir Charles Parsons (1907, 1918, etc.) appear to show that retention of carbon monoxide, and not production of high pressure, is the essential part played by the outer crust of iron in Moissan's process; experiments made to melt carbon under enormous pressures in the electric furnace always gave negative results.

(ii) *Graphite*

The name "graphite" was given to this substance on account of its use as a writing material (*γράφω*, I write). It was called *plumbago* or *black lead* possibly because, like lead, it marks paper, or because it was supposed to be a lead compound. Graphite occurs in large quantities in many different localities: Cumberland, Bohemia, Ceylon, Siberia and California are the chief.

It is manufactured on a large scale at Niagara by a process

invented by ACHESON (who also discovered *carborundum*, p. 313). About three tons of a mixture of powdered coke with a little sand and some pitch are placed in a brick furnace the bottom of which is protected by a layer of sand. Through the walls of the furnace project two stout carbon rods, connected to a dynamo. On passing a powerful current through the mass for 24 to 30 hours a very high temperature is maintained and the coke is converted into a pure and soft graphite, called *Acheson's graphite*. This can be finely powdered and is then used in the preparation of *aquadag* and *oildag*.

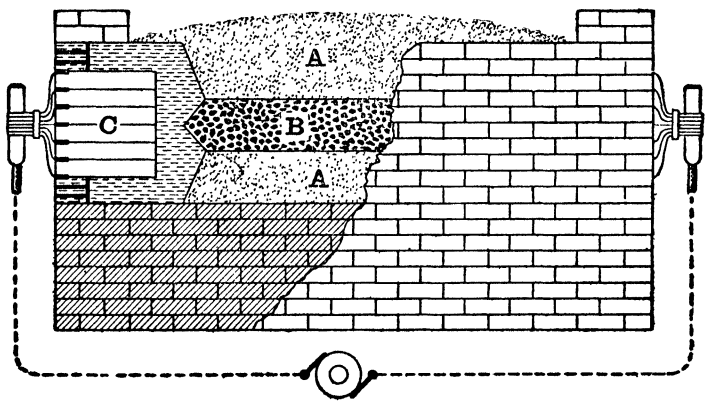


FIG. 58.—Furnace for the Manufacture of Graphite.

Aquadag (an *aqueous* solution of *de*flocculated *A*cheson graphite) is a colloidal suspension (p. 145) of graphite in a dilute solution of tannin. The tannin is a *protective* and prevents the precipitation of the graphite. Aquadag is used as a lubricant.

Oildag is made by filtering aquadag through *rubber* (ordinary filters are useless for filtering colloids) and mixing the paste of colloidal graphite obtained in this way with lubricating oil. This yields a colloidal solution of graphite in oil, called oildag, extensively used as a lubricant.

Finely powdered graphite itself may also be used as a lubricant; many people "blacklead" their bicycle chains instead of putting oil on them, while if the vulcanite mouth-

piece of a pipe fits very stiffly into the wooden stem a smoker will rub his " lead " pencil on the part of the vulcanite which fits into the wood, and so ease it.

Graphite crystallizes in lustrous black hexagonal plates that feel greasy to the touch ; it is a good conductor of heat and electricity, and is very stable to chemical reagents. A mixture of nitric acid and potassium chlorate will act slowly upon graphite (BRODIE, 1855), to form a green substance which on treatment with acidified potassium permanganate is converted into an amorphous yellow compound called *graphitic acid.* Graphitic acid is usually given the formula $C_{11}H_4O_5$ but it is really a complex mixture. Nitric acid has no action on diamonds, and converts amorphous carbon into *mellitic acid.*

The specific gravity of graphite is variable ; it is usually about 2·3. Graphite finds many applications. Powdered graphite mixed with clay is used for making pencils. A mixture of sand and graphite is made up into refractory crucibles capable of withstanding a high temperature and the action of many acids.

Graphite is also used to protect iron and steel (e.g. fenders, stoves, and grates) from rust, and as a polish for gunpowder. On account of its comparatively good conductivity it is often used in electrolytic processes.

(iii) *Amorphous Carbon*

Coal.—Coal has been formed by the decomposition of plant remains by bacteria and saprophytic fungi, in absence of air and under high pressures. Recent experiments (BERGIUS, 1913–1925) have shown that a substance very similar to coal may be made by heating peat, cellulose and water to 300–400° under a pressure of 5,000 atmospheres ; it is therefore possible that heat changes in the earth's crust may have had something to do with coal-formation.

Various stages in the conversion of vegetable matter into coal are shown by the substances called *peat, lignite, bituminous coal, cannel coal* (or " parrot " coal), and *anthracite.* Ordinary coal is the bituminous variety.

The approximate composition of these substances is given in the following table—

Substance.	Carbon, Per Cent.	Hydrogen, Per Cent.	Nitrogen and Oxygen, Per Cent.	Ash, Per Cent.
Peat	57	6	32	5
Lignite	60	5	30	5
Bituminous coal	80	5	12	3
Cannel coal	83	5	10	2
Anthracite	93	3	2	2

The figures in the table are rough only, and variation within fairly wide limits is found in practice. The table serves, however, to show two important facts—

(i) The percentage of carbon from peat to anthracite steadily increases.

(ii) The percentage of hydrogen falls off much less rapidly than that of the nitrogen and oxygen (the figures given in the last column but one represent chiefly oxygen ; the percentage of nitrogen remains fairly constant at about 1 to 2).

Peat is a brown substance composed of the partially decomposed remains of bog plants. It is used as a fuel and is cut in many parts of the country, as on Sedgmoor for instance. It represents in all probability the first stage in the formation of coal.

Lignite or brown coal is generally considered to represent the next stage. It is harder than peat and usually contains a slightly higher percentage of carbon. It differs from peat and coal in that it is mainly composed of *fossil wood* ; however, there seems to be no doubt that in the course of ages it would have become converted into a coal.

Bituminous coal is composed of the remains of cryptogamic or flowerless plants (thus resembling peat, chiefly composed of decayed *mosses*) which flourished in an amazing manner in the Carboniferous Age. These flowerless plants are now represented on the earth only by insignificant descendants such as the ferns, horse-tails and club-mosses.

The problem of the chemical constitution of coal is now engaging the attention of chemists; it is too complicated a subject to be discussed here. Coal certainly contains free amorphous carbon, but it contains in addition many complex carbon compounds. According to STOPES, four distinct constituents may be detected in coal by examination of thin sections under the microscope; these are called *durain*, *clarain*, *fusain* and *vitrain*. In general, coal appears to consist of a colloidal mass in which are embedded (i) woody substances, (ii) the decayed spores of flowerless plants, (iii) resinous matter and (iv) a heterogeneous débris formed of i, ii and iii. Further light has been thrown on the subject by a chemical examination of the substances dissolved out of coal by heating it with benzene under pressure.

Cannel coal is so called because a piece of it if lit will burn like a *candle*. It is chiefly used for making coal-gas.

Anthracite is a hard coal which may contain as much as 97 per cent. of carbon. It is used for heating boilers (hence the name *steam-coal*) and also in anthracite stoves. Anthracite is difficult to ignite, but when ignited goes on burning very steadily, without flame, and with production of intense heat; anthracite stoves are therefore economical in use and require very little attention. Much of the world's anthracite is mined in South Wales; the Admiralty pits produce anthracite for the Navy, the ships of which are now, however, largely oil-driven.

Distillation of Coal.—The destructive distillation of coal is more conveniently dealt with in the study of Organic Chemistry; the student is therefore referred to the author's *Outlines of Organic Chemistry* (London, Edward Arnold & Co.).

When coal is heated in iron retorts with exclusion of air, four main products are formed—

(i) Coke (left in the retorts).

(ii) An aqueous liquid from which the ammonium sulphate of commerce is made; the "*ammoniacal liquor*."

(iii) Coal-tar.

(iv) Coal-gas.

(i) **Coke.**—This consists chiefly of carbon (about 70–80 per cent.); it also retains some of the nitrogen of the original coal, the rest appearing in the form of the ammonia of the ammoniacal liquor. Coke is used as a fuel and as a source of *gaseous fuels* (water-gas and producer-gas, pp. 301–3); its use in metallurgical operations is referred to many times in the course of this book.

(ii) **Ammoniacal liquor.**—For the treatment of this liquid see p. 339.

(iii) **Coal-tar.**—Tar is a black liquid containing many important substances such as benzene, toluene, naphthalene and phenol. It is redistilled, and the distillate, which is collected in fractions, is worked up in various ways that are described in the books on organic chemistry.

(iv) **Coal-gas.**—The crude gas which passes on from the receivers in which the ammoniacal liquor and tar are condensed still contains traces of these and other substances, and has to undergo purification. It is first passed through a number of vertical pipes, the *condensers*, in which most of the remaining tar and ammoniacal liquor are condensed and collect at the bottom. It is then usually sent through a *tar-extractor*, in which any tar that may have escaped condensation is removed.

From the extractor the gas passes into the *exhauster*, where the pressure of the gas is adjusted by means of pumps, and thence into the *scrubbers*, which are iron towers packed with broken bricks or coke down through which water trickles. In the scrubbers the last of the ammonia is removed, and some of the sulphuretted hydrogen and carbon dioxide is retained.

The gas now passes through the *purifiers*, which are iron chambers containing trays filled with moist ferric oxide ("bog ore," from Holland and Belgium). Here the sulphuretted hydrogen is removed, since it reacts with the ferric oxide to form ferric sulphide, ferrous sulphide, and sulphur—

$$2Fe_2O_3 + 2H_2O + 6H_2S = Fe_2S_3 + 2FeS + S + 8H_2O.$$

When the ferric oxide has all been changed according to the

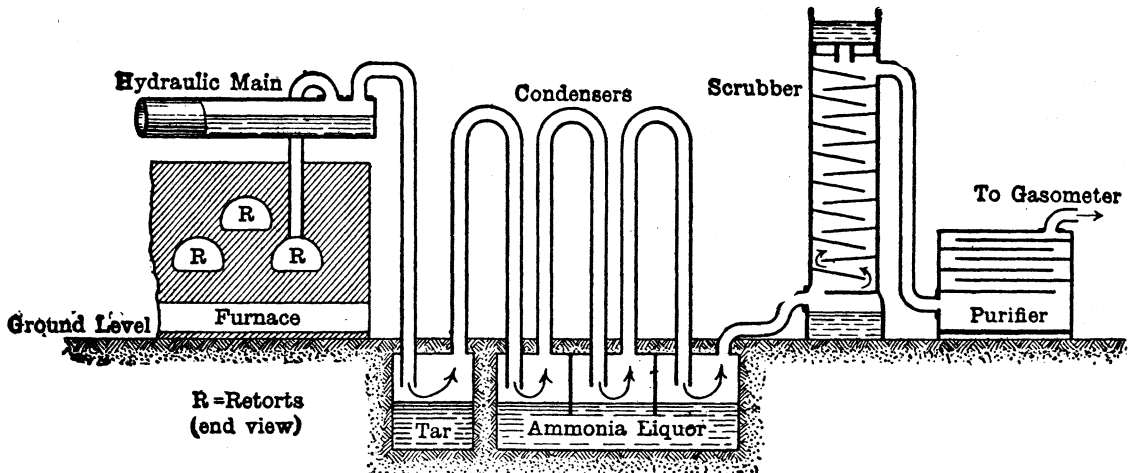


FIG. 59.—The Manufacture of Coal Gas.
(N.B.—The retorts are now usually arranged vertically.)

above equation, the product is called "*spent oxide.*" This is taken out and exposed to the air, water being added if necessary. Oxidation with separation of sulphur occurs and the spent oxide is now said to be "*revivified*"—

$$2Fe_2S_3 + 3O_2 = 2Fe_2O_3 + 6S.$$
$$4FeS + 3O_2 = 2Fe_2O_3 + 4S.$$

The mixture of iron oxide and sulphur is returned to the purifiers and used repeatedly until it contains about 50–60 per cent. of sulphur; it is then sold to a lead-chamber sulphuric acid works and used as a source of sulphur dioxide.

Carbon disulphide, which is always present as an impurity in coal-gas, is sometimes removed and sometimes allowed to remain. It can be absorbed by using slaked lime instead of ferric oxide in the purifiers, since it combines with the calcium hydrosulphide formed by the action of sulphuretted hydrogen on the lime—

$$Ca(OH)_2 + 2H_2S = Ca(HS)_2 + 2H_2O.$$
$$Ca(HS)_2 + CS_2 = CaCS_3 + H_2S.$$

The product, *calcium thiocarbonate*, $CaCS_3$, has no commercial application and is difficult to deal with. It has been shown, however, that by passing coal-gas over finely divided nickel at 250–300° reduction of the carbon disulphide by the hydrogen present is brought about—

$$CS_2 + 2H_2 = 2H_2S + C.$$

This is another interesting application of SABATIER and SENDERENS' reducing agent (reduced nickel and hydrogen: the nickel is a catalyst).

From the purifiers the gas passes into the gasometers. It consists chiefly of *hydrogen*, *methane* and *carbon monoxide*, by the combustion of which most of the heat of a coal-gas flame is produced, together with small quantities of *acetylene*, *benzene* and *ethylene*, to which the luminosity of the flame is due. There are also present varying amounts of gaseous impurities. The following table (BUTTERFIELD, 1913) gives the analysis of typical specimens of coal-gas—

Gas.	Percentage.
Hydrogen	43·0–55·0
Methane	25·0–35·0
Carbon monoxide	4·0–11·0
Unsaturated hydrocarbons (acetylene, etc.)	2·5– 5·0
Nitrogen	2·0–12·0
Carbon dioxide	0·0– 3·0
Oxygen	0·0– 1·5

Of recent years it has become the practice to add a certain amount of water-gas (p. 301) to the pure coal-gas.

Gas-carbon is a very hard form of carbon deposited as a lining on the retorts in gas-works. It is formed by the decomposition of hydrocarbons by heat, and as it is a good conductor of electricity is used for making the "carbons" for arc-lamps.

Soot and lampblack are also forms of amorphous carbon. Lampblack contains oil and other substances as impurities. It is used in making *printer's ink*.

Animal charcoal or **bone-black** is a mixture of calcium phosphate and about 10 per cent. amorphous carbon made by the destructive distillation of bones. It is used in sugar refining, since when boiled with a coloured solution it will often absorb the colouring matter and leave the solution colourless; the brown solution of crude sugar is decolourized in this way.

Wood charcoal is a porous form of amorphous carbon made by burning wood with insufficient air ("charcoal-burning"). It is important in the laboratory chiefly on account of its remarkable power of absorbing gases; thus 1 c.c. of charcoal will absorb nearly 200 c.c. of ammonia at ordinary temperature and pressure, and almost as much sulphur dioxide.

Moreover, Sir James Dewar discovered that this absorptive power of charcoal was greatly increased at low temperatures, a fact which has found several useful applications, e.g.

production of high vacua, separation and purification of the rare gases.

Pure carbon is prepared by heating pure sugar in air until it is completely charred and reheating the charred mass first in a current of chlorine and then in a current of hydrogen. The product is called sugar-carbon and is extremely pure.

COMPOUNDS OF CARBON.—Over 1,000,000 compounds of carbon have been described, and there seems to be no limit to the number which might be prepared. The study of these compounds is the province of organic chemistry; we shall describe here only a few of the most important.

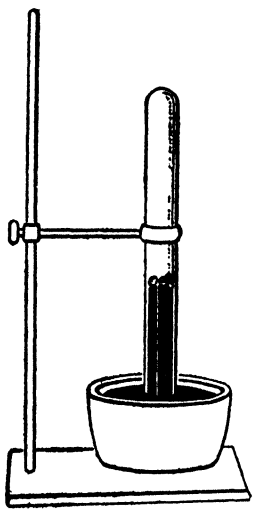


FIG. 60.—Absorption of Gases by Carbon.

HYDROCARBONS are compounds consisting of hydrogen and carbon only. Three of the simplest are methane, ethylene and acetylene.

Methane, or marsh-gas, CH_4, is produced by bacterial action upon vegetable matter at the bottom of ponds, marshes, etc., hence one of its names. It also occurs in coal-mines and is there called *fire-damp*. In the laboratory it is often prepared (in an impure state) by heating anhydrous sodium acetate with sodalime (p. 246).

$$CH_3.COONa + NaOH = Na_2CO_3 + CH_4.$$

A purer gas may be made by adding water to aluminium carbide—

$$Al_4C_3 + 12H_2O = 4Al(OH)_3 + 3CH_4.$$

Another convenient method of obtaining the pure gas is to dissolve dry magnesium in a dry ethereal solution of methyl iodide, forming methyl magnesium iodide ($CH_3.Mg.I$), and then to decompose the latter substance with dilute hydrochloric acid:

$$CH_3I + Mg = CH_3.Mg.I$$
$$2CH_3.Mg.I + 2HCl = 2CH_4 + MgI_2 + MgCl_2.$$

Methane is a colourless gas, with no taste or smell; it is insoluble in water and burns with a practically non-luminous flame—

$$CH_4 + 2O_2 = CO_2 + 2H_2O.$$

A mixture of methane with air or oxygen in certain proportions will explode if ignited.

A mixture of 1 volume of methane with 1 volume of chlorine may explode if exposed to bright sunlight, the products

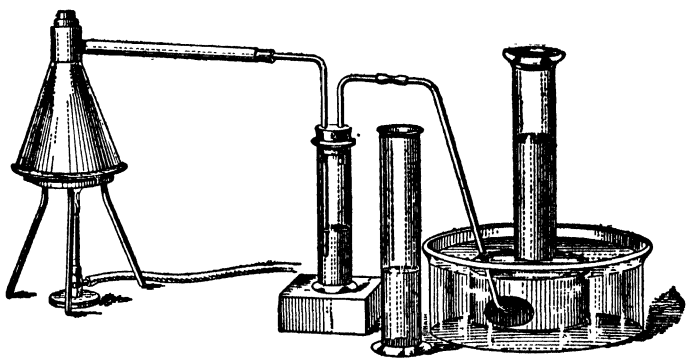


FIG. 61.—Preparation of Methane.

being *methyl chloride* (a gas) and hydrochloric acid. Slow reaction takes place in ordinary daylight.

$$CH_4 + Cl_2 = CH_3Cl + HCl.$$

Under suitable conditions, this *substitution* process may be continued until all the hydrogen of the methane has been replaced by chlorine—

$CH_3Cl + Cl_2 = HCl + CH_2Cl_2$, *dichloromethane.*
$CH_2Cl_2 + Cl_2 = HCl + CHCl_3$, *trichloromethane* or *chloroform.*
$CHCl_3 + Cl_2 = HCl + CCl_4$, *tetrachloromethane* or *carbon tetrachloride.*

Ethylene, C_2H_4, is obtained as a colourless gas when ethyl alcohol, C_2H_5OH, is heated with strong sulphuric acid; *sulphovinic acid*, $C_2H_5HSO_4$, is first formed but immediately splits up, on heating, into ethylene and sulphuric acid—

$$C_2H_5OH + H_2SO_4 = C_2H_5HSO_4 + H_2O.$$
$$C_2H_5HSO_4 = C_2H_4 + H_2SO_4.$$

It will be noted that, theoretically, there is no loss of sulphuric acid in the reaction, which resolves itself into the

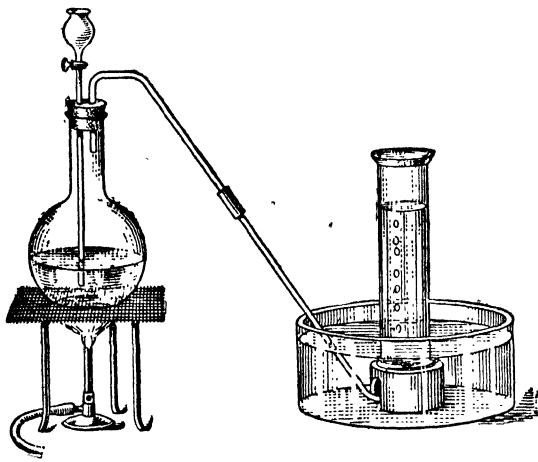


FIG. 62.—Preparation of Ethylene.

decomposition of the alcohol by the acid into ethylene, C_2H_4, and water—

$$C_2H_5OH = C_2H_4 + H_2O.$$

[You should be careful to avoid the inexcusable blunder of saying that the acid *dehydrates* the alcohol, i.e. takes water out of it. Alcohol does not contain water, and therefore water cannot be removed from it. It contains the *elements* of water, but that is a different thing. A factory does not *contain* a house, yet if you take the factory to pieces you may be able to *build up* a house from certain of them. Remember that in science looseness of expression is a serious fault.]

Ethylene is more conveniently made by passing the vapour of ethyl alcohol over aluminium oxide heated to 360°; the alumina acts as a catalyst—

$$C_2H_5.OH = C_2H_4 + H_2O.$$

Ethylene is a colourless gas with a sweetish taste and smell. It burns with a luminous flame and yields an explosive mixture with air. One of its most characteristic properties is that it will combine directly with bromine or chlorine to form colourless oils, *ethylene dibromide* and *ethylene dichloride.*

$$C_2H_4 + Br_2 = C_2H_4Br_2; \quad C_2H_4 + Cl_2 = C_2H_4Cl_2.$$

These substances are *additive* compounds, and should be contrasted with the *substitution* compounds formed by methane. Substances that will form addition compounds are called *unsaturated* (e.g. ammonia, which "adds on" hydrochloric acid—$NH_3 + HCl = NH_4Cl$).

Acetylene, C_2H_2, is well-known as the gas made by the action of water on calcium carbide—

$$CaC_2 + 2H_2O = Ca(OH)_2 + C_2H_2.$$

As usually prepared it has an objectionable smell, due to the presence of traces of phosphine (from the calcium phosphide in the carbon); the pure gas has a sweetish smell, not unlike that of ethylene. It may be synthesized by passing an electric current between two carbon electrodes in an atmosphere of hydrogen (Fig. 63).

Acetylene is an unsaturated compound—more so than ethylene, since 1 molecule of it will combine directly with 2 molecules of bromine or chlorine—

$$C_2H_2 + 2Cl_2 = C_2H_2Cl_4.$$

It burns with a smoky flame unless burnt in special burners, designed to supply plenty of air to the flame; from these burners it is delivered either as a fine jet or as a thin sheet and then burns with an intensely hot and brilliant flame. The flame of acetylene burning in oxygen is as hot as the electric arc (3,500°) and is used for welding and steel-cutting (*oxy-acetylene flame*). Acetylene is of growing commercial import-

ance as the starting-point in the synthetic production of many organic substances.

A mixture of acetylene and oxygen explodes with great violence when ignited. Acetylene is an *endothermic* compound.

When acetylene is passed through ammoniacal cuprous chloride it gives a chocolate brown precipitate of *cuprous acetylide*, Cu_2C_2; ammoniacal silver nitrate with acetylene gives the corresponding *silver acetylide*, Ag_2C_2. Both these compounds are explosive, especially the silver one.

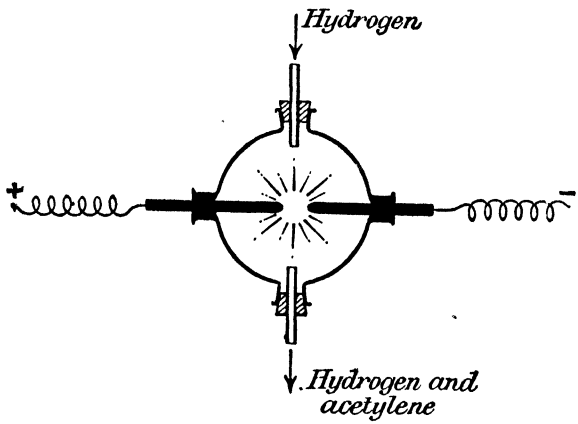


FIG. 63.—Synthesis of Acetylene.

Oxides of Carbon.—Carbon forms several oxides, of which the chief are *carbon sub-oxide*, C_3O_2, *carbon monoxide* CO, and *carbon dioxide*, CO_2.

Carbon suboxide, C_3O_2, is a colourless gas made by the action of phosphorus pentoxide upon an organic compound called *ethyl malonate*—

$$\begin{matrix} \diagup COOC_2H_5 \\ CH_2 \\ \diagdown COOC_2H_5 \end{matrix} + 2P_2O_5 = C_3O_2 + 2C_2H_4 + 4HPO_3.$$

It will burn in air, forming carbon dioxide, and dissolves in

water to form malonic acid, of which it is therefore an anhydride—

$$C_3O_2 + 2H_2O = \begin{matrix} COOH \\ CH_2 \\ COOH \end{matrix}$$

Carbon monoxide, CO, may be made in many ways, such as the following—

(i) Carbon dioxide is passed over red-hot coke (Fig. 64)—

$$CO_2 + C = 2CO.$$

(ii) Steam is passed over red-hot coke—

$$C + H_2O = CO + H_2.$$

The mixture of carbon monoxide and hydrogen obtained in this way is called *water-gas* (p. 301).

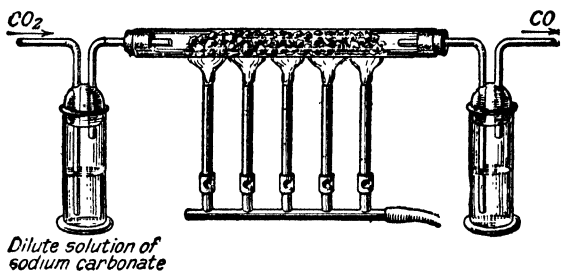


FIG. 64.

(iii) *Formic acid* is heated with concentrated sulphuric acid—

$$H.COOH = H_2O + CO.$$

Sodium formate may be used instead of formic acid.

(iv) *Oxalic acid* is heated with concentrated sulphuric acid and the evolved gases passed through a Drechsel bottle containing caustic soda solution to absorb the carbon dioxide that is also formed—

$$\begin{matrix} COOH \\ | \\ COOH \end{matrix} = CO + CO_2 + H_2O.$$

(v) *Potassium ferrocyanide* is heated with *concentrated* sulphuric acid (**care !** *dilute* acid gives *prussic acid*, HCN).

$$K_4Fe(CN)_6 + 6H_2O + 6H_2SO_4 = 2K_2SO_4 + 3(NH_4)_2SO_4 + FeSO_4 + 6CO.$$

Methods iii and iv are most convenient for laboratory purposes. Carbon monoxide is very often formed when a metallic oxide is reduced with carbon, e.g.—

$$ZnO + C = Zn + CO.$$

Carbon monoxide is a colourless gas with a practically unnoticeable smell; as it is extremely poisonous and constantly present in coal-gas its lack of smell makes it a source of considerable danger. Many cases of carbon monoxide poisoning are reported in the newspapers. The poisonous action of the gas is due to the fact that carbon monoxide combines with the red colouring-matter (*hæmoglobin*) of the blood, forming a bright red compound called *carboxy hæmoglobin*. The hæmoglobin is therefore rendered incapable of carrying on its function as a distributor of oxygen to all parts of the body, and death results from a kind of suffocation.

Carbon monoxide is a colourless gas which can be liquefied by cold and pressure to a colourless liquid boiling at −190° and freezing to white crystals at −200°. It will burn in the air with a blue lambent flame, forming carbon dioxide. A mixture of 2 volumes of carbon monoxide and 1 volume of oxygen will explode if sparked, giving 2 volumes of carbon dioxide. Hence, by Avogadro's Hypothesis, 2 molecules of carbon monoxide + 1 molecule of oxygen give 2 molecules of carbon dioxide. But the molecule of carbon dioxide is CO_2 and that of oxygen is O_2,

$\therefore$ molecule of carbon monoxide must be CO.

Carbon monoxide is an unsaturated compound, since the carbon atom in its molecule is only bivalent whereas the normal valency of carbon is *four*. Carbon monoxide will therefore readily combine with chlorine or oxygen and is thus a powerful *reducing agent* (cf. manufacture of iron, p. 545).

If passed into an ammoniacal solution of cuprous chloride, carbon monoxide is absorbed, with formation of the compound $CuCl.CO.2H_2O$; this has been isolated in the form of unstable white crystals.

A characteristic property of carbon monoxide is its power of forming addition compounds, *carbonyls*, with gently heated metals. Certain of these, such as *nickel carbonyl*, $Ni(CO)_4$ (p. 562), are of considerable importance. They are generally liquids which split up again into metal and carbon monoxide at higher temperatures.

When carbon monoxide is passed over solid caustic soda heated to 200° the two combine to form *sodium formate* (cf. method iii, p. 299).

$$NaOH + CO = H.COONa.$$

This is a commercial method of obtaining sodium formate and thence formic acid itself.

The heat of formation of carbon monoxide is 29,000 calories, and its heat of combustion 67,960 calories. It is clear that carbon monoxide will therefore be a very efficient *gaseous fuel* and as such is very widely used.

Carbon Monoxide as a Fuel.

Producer Gas is a mixture of carbon monoxide (30 per cent.) and nitrogen (62 per cent.) made by sending a blast of air through white-hot coke. If used directly for combustion, both the heat of formation and heat of combustion of the gas are available, but if the gas is allowed to cool first the heat of formation is naturally dissipated and only the heat of combustion will then be available; there will thus be a loss of heat in the proportion of $\frac{29,000}{96,960}$, or about 30 per cent.

Water Gas is the name given to a mixture of gases, chiefly hydrogen (49 per cent.), carbon monoxide (42 per cent.) and carbon dioxide (4 per cent.), made by passing steam over white-hot coke—

$$C + H_2O = CO + H_2.$$

This action is strongly *endothermic* (−29,000 calories); the

coke therefore cools down rapidly. After the steam-blast has been on for 5 or 6 minutes it is cut off and an *air-blast* turned on, when producer-gas is formed with evolution of heat and the coke becomes incandescent again. The water-gas and producer-gas are usually stored in separate gasometers.

In an alternative process sufficient air is used in the air-blast to form carbon *dioxide*; this is of course useless, but the loss in coke is more than counterbalanced by the extra evolution of heat—

$$C + \text{oxygen} \longrightarrow CO + 29{,}000 \text{ calories.}$$
$$C + O_2 \longrightarrow CO_2 + 96{,}960 \text{ calories.}$$

Semi-water Gas is a mixture containing hydrogen (17 per cent.), carbon monoxide (27 per cent.), and nitrogen (52 per cent.), made by passing air and steam *together* over white-hot coke. The heat evolved in the reaction is sufficient to keep the coke at a suitable temperature.

Carburetted Water Gas is made by spraying paraffin into the steam-blast used in the water-gas process. It burns with a luminous flame, whereas water-gas burns with a blue non-luminous flame.

Coal-gas is often mixed with water-gas at the present day; the practice has the disadvantages, from the consumer's point of view, that the gas is thereby made much more dangerously poisonous, and that the heat produced by combustion of the gas is much less than that given out by the combustion of an equal volume of pure coal-gas. The latter difficulty has been overcome by selling gas on the basis of its heating-power (i.e., at so much per *therm*) instead of by volume.

Water-gas has recently been used for the commercial preparation of *hydrogen*. A mixture of water-gas and steam is passed over reduced nickel, iron or copper at a temperature of 400–500°, sometimes under slightly increased pressure; the following reaction then occurs, the metal acting as a catalyst—

$$CO + H_2O = CO_2 + H_2.$$

The hydrogen is freed from the carbon dioxide by absorbing the latter in lime. Water-gas is also largely employed in the manufacture of methanol (methyl alcohol, CH_3OH). It

is mixed with half its volume of hydrogen and the mixture is heated to 450°, under a pressure of 200 atmospheres, in the presence of certain metallic oxides that act as catalysts:

$$CO + 2H_2 = CH_3OH.$$

[For a useful account of the manufacture of coal-gas, water-gas and carburetted water-gas, see H. HOLLINGS, *The Manufacture of Gas*, School Science Review, September and December, 1927.]

Carbon dioxide, CO_2.—Carbon dioxide was discovered by VAN HELMONT (1577–1644), who called it *gas sylvestre* ("the wild gas of the woods"). It is interesting to note that the word *gas* was coined by van Helmont and is defined by one of his English disciples, GEORGE THOMSON (*Direct Method of Curing Chymically*, London, 1675), as "a wild invisible spirit, not to be imprisoned or pent up, without damage of what conteins it, arising from the Fermentation of the concourse of some Bodies, as it were eructating or rasping this untamable Matter." Two more of Thomson's definitions seem to be worth quoting—

"*Chymist* is one who imitates Nature in Separating the Pure Juice from the Dross and Filth for the use of Medicine Mechanicks, and the advancement of Mettals." "*Chymicophant*, one who seems to be a *Chymist*, but is not really."

Carbon dioxide was rediscovered in 1754 by JOSEPH BLACK, who called it *fixed air* and showed that it was liberated from chalk by the action of a dilute acid. Its synthesis from carbon and oxygen, and therefore its composition, were first shown by LAVOISIER in 1781. Lavoisier re-named it *acide carbonique*, although it is, of course, not an acid but the *anhydride* of an acid.

Carbon dioxide is constantly present in the atmosphere, of which it forms about 0·03 per cent. by volume. It is also found in solution in all natural waters, and is found in large quantities in ravines in certain volcanic districts, e.g. the *Grotto del cane* at Naples and the *Valley of Poison* in Java. It is a product of combustion of coal and other carbonaceous fuels, and also of the respiration of plants and animals.

Preparation.—Although carbon dioxide is formed when

carbon is burnt in air or oxygen, it is usually prepared in the laboratory by the action of dilute hydrochloric acid upon marble or other carbonates—

$$CaCO_3 + 2HCl = CaCl_2 + H_2O + CO_2.$$

It may be dried by sulphuric acid and collected by downward displacement, or over mercury. A convenient apparatus for this purpose is that known as Kipp's Apparatus (Fig. 65).

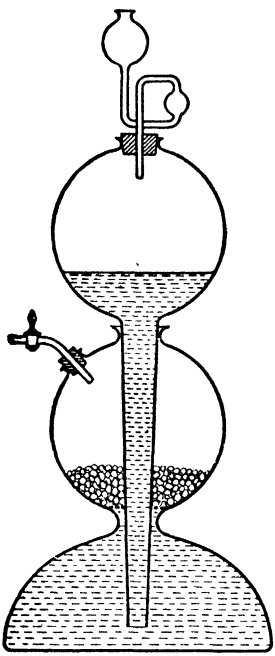


Fig. 65.

It is formed by strongly heating the carbonates of heavy metals, e.g.—

$$CaCO_3 \rightleftharpoons CaO + CO_2$$

and also during the fermentation of sugar solution by means of *yeast*—

i. $C_{12}H_{22}O_{11} + H_2O = C_6H_{12}O_6 + C_6H_{12}O_6$.

ii. $C_6H_{12}O_6 = 2CO_2 + 2C_2H_5OH$.

Alcohol remains in solution.

Properties.—Carbon dioxide is a colourless gas usually said to be odourless; it has, however, a distinct but faint smell. It will not burn and will not allow things to burn in it. Although it is not poisonous it will not support life; the unpleasant effects of "stuffy" rooms, however, are not due to the accumulation of carbon dioxide in them, but rather to the stagnation of the atmosphere. Even a comparatively high concentration of carbon dioxide causes little discomfort if the air is kept in motion by a fan.

Carbon dioxide can easily be liquefied. The liquid is colourless and under atmospheric pressure at once solidifies to a white crystalline mass of solid carbon dioxide. At

atmospheric pressure, then, carbon dioxide has no melting-point or boiling-point; rise of temperature merely causes *sublimation* of the solid, and not *fusion*. A mixture of solid carbon dioxide and ether is a good freezing-mixture, giving a temperature of −79°. If carbon dioxide is allowed to escape, from a cylinder of the compressed gas, into a flannel bag, the bag quickly fills with solid carbon dioxide, the so-called "carbon dioxide snow." This is used in ice-cream factories and carts.

Carbon dioxide is soluble in water, one volume of water dissolving an equal volume of the gas at 15°. The solution is weakly acid and contains a little *carbonic acid*, H_2CO_3, which has never yet been isolated—

$$H_2O + CO_2 \rightleftharpoons H_2CO_3 \rightleftharpoons H^{\cdot} + HCO_3' \rightleftharpoons H^{\cdot} + H^{\cdot} + CO_3''.$$

Carbonic acid is an extremely weak acid; thus an aqueous solution of carbon dioxide turns litmus only to a "port-wine" colour and has no effect upon methyl orange. It will, however, decolourize pink phenolphthalein. Carbonic acid is a dibasic acid and forms both normal carbonates and bicarbonates. When carbon dioxide is passed into a solution of an alkali it forms first the normal carbonate and then the bicarbonate—

(i) $2NaOH + CO_2 = Na_2CO_3 + H_2O$.
(ii) $Na_2CO_3 + H_2O + CO_2 = 2NaHCO_3$.

Sodium *bicarbonate* is *neutral* in solution, since it ionizes into $Na^{\cdot}$ and HCO_3', and the further dissociation of HCO_3' into $H^{\cdot}$ and CO_3'' is negligibly small. Sodium *carbonate*, on the other hand, is *alkaline* in solution, owing to hydrolysis—

(i) $H_2O \rightleftharpoons H^{\cdot} + OH'$.
(ii) $Na_2CO_3 \rightleftharpoons Na^{\cdot} + Na^{\cdot} + CO_3''$.
(iii) $CO_3'' + H^{\cdot} \rightleftharpoons HCO_3'$, thus leaving free hydroxyl ions, which render the solution alkaline.

Or, $Na_2CO_3 + H_2O \rightleftharpoons NaOH + NaHCO_3$.

All bicarbonates are soluble in water and yield the normal carbonates on heating—

$$2NaHCO_3 = Na_2CO_3 + H_2O + CO_2.$$

When carbon dioxide is passed into lime-water it gives first a milky precipitate of calcium carbonate—

$$Ca(OH)_2 + CO_2 = CaCO_3 + H_2O.$$

Further action of carbon dioxide will turn the milky liquid clear again owing to the formation of soluble calcium bicarbonate—

$$CaCO_3 + H_2O + CO_2 = Ca(HCO_3)_2.$$

The presence of calcium bicarbonate in natural water makes the water "temporarily hard" (p. 446).

Dissociation of Calcium Carbonate.—When calcium carbonate is heated it splits up into calcium oxide and carbon dioxide. If the reaction is carried out in a closed vessel (so that the carbon dioxide cannot escape), connected with a pressure-gauge or manometer, it is found that a state of equilibrium is set up, which may be represented by the equation—

$$CaCO_3 \rightleftharpoons CaO + CO_2.$$

In terms of the phase rule (p. 146), we have 3 phases (CaO, $CaCO_3$, CO_2), and two components (CaO, CO_2).

$$P + F = C + 2, \text{ or } 3 + F = 2 + 2.$$

$\therefore F = 1$, or the system is univariant. Therefore at any given temperature there will be a definite dissociation-pressure of carbon dioxide.

In terms of Le Chatelier's principle, since an increase of volume takes place on dissociation we should expect increase of pressure to diminish the dissociation; this is found to be the case.

Percarbonates.—Electrolysis of a cooled saturated solution of potassium carbonate yields a bluish-white, amorphous, deliquescent precipitate of *potassium percarbonate*, $K_2C_2O_6$. This is a strong oxidizing agent. Other percarbonates are known.

Composition of Carbon Dioxide.—If a weighed quantity of carbon is burnt in oxygen and the weight of carbon dioxide

produced is estimated, by absorbing the gas in a weighed bulb containing caustic potash solution and finding the increase in weight, the gravimetric composition of carbon dioxide can be calculated. Experiments have shown that the ratio of carbon to oxygen in carbon dioxide is exactly 3 : 8. The vapour density of the gas is 22, ∴ its molecular weight is 44. The atomic weight of carbon is 12 and that of oxygen is 16, ∴ the formula of the gas must be CO_2.

Volumetrically the composition of carbon dioxide may be determined by burning a piece of carbon in a measured volume of oxygen (Fig. 66). After cooling it will be found that there is no change in volume; hence 1 volume of oxygen is contained in 1 volume of carbon dioxide.

∴ by Avogadro's Hypothesis, 1 molecule of carbon dioxide contains 1 molecule of oxygen,

∴ formula is C_xO_2.

x is found from the vapour density of the gas and the atomic weight of carbon.

Carbon dioxide in the Air. See p. 451.

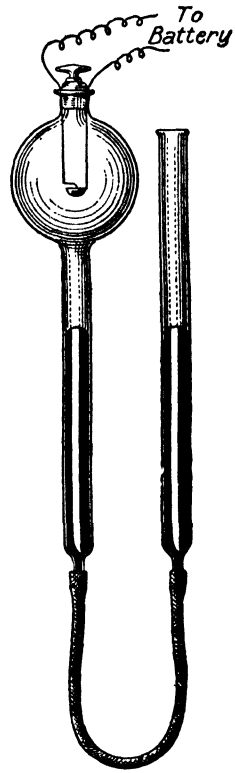


FIG. 66.

Carbonyl chloride, $COCl_2$, or *phosgene,* is made by passing a mixture of equal volumes of carbon monoxide and chlorine over gently heated animal charcoal—

$$CO + Cl_2 = COCl_2.$$

It is a colourless and very poisonous gas which reacts with water to form carbon dioxide and hydrochloric acid—

$$COCl_2 + H_2O = CO_2 + 2HCl.$$

It can be regarded as the acid chloride of carbonic acid—



Carbonic acid. Carbonyl chloride.

Carbon disulphide, CS_2, is formed by passing sulphur vapour over red-hot coke, or by heating sulphur and coke together in an electric furnace—

$$C + 2S = CS_2.$$

It is a colourless, volatile, and very inflammable liquid which has a pleasant sweetish odour when pure. It generally contains impurities, however, which give it a very evil smell. It boils at 46° and melts at −110°.

Carbon disulphide vapour is poisonous and has been used as an insecticide and rat-killer, but its inflammable nature makes its use a matter of no little risk. It is a very good solvent for rubber and other organic substances, but has been displaced very largely of late years by the non-inflammable acetylene tetrachloride, $C_2H_2Cl_4$, and carbon tetrachloride, CCl_4.

Silicon

Group in Periodic System: IV; *Symbol:* Si; *Atomic Weight:* 28·3; *Valency:* 4; *Specific Gravity:* 2·35–2·5.

History.—Silica (SiO_2) was regarded by Becher (1655) as an "earth" [i.e. a basic substance, like lime], which he called *terra vitrescibilis* owing to its use in glass making. Tachenius, however, in 1660, showed that it would dissolve in fused caustic alkalis, and therefore must possess an acidic nature. Lavoisier regarded silica as the oxide of a new element, a hypothesis which was supported by Scheele's work on silicon fluoride (SiF_4) and the silicic acids. Gay-Lussac and Thénard, working on Lavoisier's theory and Scheele's facts, in 1811 passed the gaseous silicon fluoride over heated potassium and succeeded in preparing elementary ***silicon.***

Occurrence.—Silicon is very widely distributed, and forms more of the earth's crust than any other element except oxygen. It is always found as the oxide, *silica*, SiO_2. This may occur in the free state as *quartz* (" rock-crystal ") (12 per cent. of the earth's crust) or as *silicates*, which are compounds of silica with basic metallic oxides. The most widely-distributed silicate is that of aluminium, which is the chief constituent of many rocks and also of clay. Many specimens of *quartz* show delightful colours and are prized as gems, e.g. *jasper* (red), *carnelian* (red), *amethyst*, *chrysoprase* (green), *cairngorm* (yellow). The *opal* consists of amorphous silica, while *agate* is a variety of quartz. *Flints* are composed of a mixture of quartz and amorphous silica (hence the name *silica*, from *silex*, a flint). *Sand* is a form of silica.

Preparation.—Silicon may be obtained in the amorphous state by heating potassium silicofluoride, K_2SiF_6, with potassium—

$$K_2SiF_6 + 4K = 6KF + Si \text{ (Berzelius, 1823),}$$

or by heating finely-powdered sand (SiO_2) with magnesium powder—

$$SiO_2 + 2Mg = Si + 2MgO.$$

The crystalline variety may be made by melting the amorphous form and allowing the liquid to crystallize, or directly by passing silicon tetrachloride vapour over fused aluminium and dissolving out the residual excess of aluminium in hydrochloric acid—

$$3SiCl_4 + 4Al = 3Si + 4AlCl_3.$$

Other methods have been described, of which perhaps the most important is that of heating sand and carbon in the electric furnace. If too much carbon is present, silicon carbide or carborundum is formed.

Properties.—*Amorphous* silicon is a brown powder, which melts at about 1,550° and can be boiled in the electric furnace. It can be made to burn in the air if strongly heated, and burns readily in oxygen, forming silica, SiO_2. It combines with many elements at a high temperature, forming *silicides*. The specific gravity of amorphous silicon is 2·35.

It is insoluble in acids (except hydrofluoric mixed with a little nitric), but dissolves in fused or aqueous caustic alkalis to form a silicate and hydrogen—

$$Si + 2NaOH + H_2O = Na_2SiO_3 + 2H_2.$$

Crystalline silicon is a yellow or brown solid ; it is not so reactive as the amorphous variety.

All specimens of silicon hitherto prepared have been impure, so that its true properties are not known with accuracy or certainty.

COMPOUNDS OF SILICON.

Silicon dioxide, SiO_2, is the most important silicon compound. It occurs naturally in the crystalline form as *rock-crystal*; other varieties have been mentioned previously. Silica is also found in plants and animals—the sharp cutting edge of blades of grass is often strengthened with silica, while skeletons of tiny plants called *diatoms* form large deposits of the " siliceous earth " known as *kieselguhr*, used in the manufacture of dynamite, etc. (p. 360).

Silica occurs in three crystalline forms and also in the amorphous state. The crystalline varieties are known as *quartz*, *tridymite*, and *cristobalite*. When an acid is added to a solution of sodium silicate, a white gelatinous precipitate of a silicic acid is obtained ; if this precipitate is heated it loses water and yields *amorphous* silica.

Silica is an acidic oxide, and in combination with water forms the *silicic acids*. Of late years it has become very important in the manufacture of " quartz glass " ; when silica is heated it becomes soft and can be made into tubes, basins, crucibles, etc., and since silica has a very low coefficient of expansion, quartz-glass vessels can withstand great and sudden changes of temperature without cracking. A silica basin, for example, may be made red hot and cooled under the tap. Fused silica may also be drawn out into very fine threads used in mirror-galvanometers, etc.

Vitreosil is an opalescent form of quartz glass, made by passing a powerful electric current through a rod or plate of

carbon packed in sand. It is cheaper than the transparent form but equally good for most purposes, although of course it does not look so attractive.

Silicic acids.—It is supposed that *metasilicic acid*, H_2SiO_3, and *orthosilicic acid*, H_4SiO_4, exist, but the existence of neither has been definitely proved. When hydrochloric acid is added to an aqueous solution of sodium metasilicate, Na_2SiO_3, a white gelatinous precipitate is obtained, which after drying in a desiccator has a composition approximating to that of metasilicic acid, H_2SiO_3. A substance which has roughly the composition H_4SiO_4 or $Si(OH)_4$, *orthosilicic acid*, is formed, according to NORTON and ROTH (1879), by hydrolysing silicon chloride, $SiCl_4$, with water and washing the precipitate with benzene and dry ether.

The silicates are more important than the silicic acids. They are in general very complicated substances, many of them occurring naturally in rocks and clays. The chief is *aluminium silicate*, the main constituent of clay, and possibly of the constitution $\left[Si(OH)\begin{smallmatrix}O\\ \diagup\diagdown\\ O\end{smallmatrix}Al(OH)\right]_2O$ or $Al_2Si_2O_7.2H_2O$.

Sodium metasilicate, Na_2SiO_3, made by dissolving silica in caustic soda, is soluble in water. The commercial product is called *water-glass* and contains more silica than corresponds to the above formula; it is used in solution as a preservative for eggs, since it clogs up the pores of the shell with calcium silicate and thus prevents the ingress of air and bacteria. It has also been successfully employed in preserving certain of the wooden boats and other objects excavated from the Glastonbury Lake Village, etc.

Glass is a mixture of the silicates of calcium and sodium or potassium. Ordinary *soda-glass* is made by fusing a mixture of sand, limestone and soda-ash; *hard-glass* is made in a similar way except that potash is used instead of soda; while *flint glass* is made from sand, limestone, litharge and soda or potash. Flint-glass is more highly refractive than soda- or potash-glass and is therefore used for making lenses; it is,

however, soft and easily scratched, therefore microscope objectives, etc., should always be cleaned with silk or chamois leather and not with the rougher cotton or linen cloths.

Coloured glass is made by adding certain metallic oxides to the original mixture or preferably to the glass after fusion. *Blue* glass is made by adding cobalt oxide ; *amethyst* or *purple*, from manganese dioxide ; *red*, from *purple of Cassius* (p. 237) ; *opalescent*, from bone-ash.

Glass is regarded not as a solid but as a very viscous liquid, cooled so far below its freezing-point that it crystallizes only very slowly. This phenomenon of " super-cooling " is quite common ; all supercooled liquids crystallize after a time and in the case of glass this process is called *devitrification*. Soda-glass devitrifies more quickly than the other kinds. Devitrified glass is brittle and useless.

Silicon hydrides.—Silicon resembles carbon in forming many hydrides. These, however, while similar in constitution to the corresponding carbon compounds, are very different in properties.

Silicomethane, SiH_4, is made by the action of hydrochloric acid on magnesium silicide (prepared by heating silica with magnesium powder)—

$$Mg_2Si + 4HCl = SiH_4 + 2MgCl_2.$$

The gas made in this way is not pure, being mixed with other silicon hydrides and hydrogen. Silicomethane is a colourless gas which readily takes fire in the air and as generally prepared is spontaneously inflammable. The products of oxidation are silica and water—

$$SiH_4 + 2O_2 = SiO_2 + 2H_2O.$$

Silicomethane reacts with chlorine to form silicon tetrachloride and hydrochloric acid—

$$SiH_4 + 4Cl_2 = SiCl_4 + 4HCl.$$

(Cf. methane, p. 295).

Silicoethane, Si_2H_6, *silicopropane*, Si_3H_3, and *silicobutane*,

Si_4H_{10}, are also known. *Silicoacetylene*, $(Si_2H_2)_n$, was made as a yellow crystalline powder in 1900 by BRADLEY.

Silicon fluoride, SiF_4, is made by acting upon a mixture of silica and calcium fluoride with strong sulphuric acid—

$$2CaF_2 + 2H_2SO_4 + SiO_2 = 2CaSO_4 + 2H_2O + SiF_4.$$

The excess of acid takes up the water formed.

Silicon fluoride is a colourless fuming gas with a pungent smell. It is decomposed by water, forming silicic and *hydrofluosilicic* acids—

$$3SiF_4 + 3H_2O = H_2SiO_3 + 2H_2SiF_6.$$

The action of hydrofluoric acid upon glass (p. 495) results in the formation of silicon fluoride, which is then decomposed by the water present.

Silicon tetrachloride, $SiCl_4$, is a colourless fuming liquid conveniently made by passing chlorine over an intimate mixture of silica and carbon heated strongly in a furnace—

$$SiO_2 + 2C + 2Cl_2 = SiCl_4 + 2CO.$$

It is hydrolysed by water, giving a gelatinous precipitate of what may be *orthosilicic acid* (p. 311)—

$$SiCl_4 + 4H_2O = H_4SiO_4 + 4HCl.$$

Silicochloroform, $SiHCl_3$, is a colourless mobile liquid which fumes in the air and is hydrolysed by water to silicic acid at ordinary temperatures, but to *silicoformic anhydride*, $\begin{matrix}H.SiO\\H.SiO\end{matrix}\!\!>\!O$, at 0°—

$$2SiHCl_3 + 3H_2O = \begin{matrix}H.SiO\\H.SiO\end{matrix}\!\!>\!O + 6HCl.$$

Silicochloroform is made by passing hydrochloric acid gas over heated silicon—

$$Si + 3HCl = SiHCl_3 + H_2.$$

Silicon carbide, SiC, one particular variety being known as *carborundum*, is made by heating a mixture of sand and excess of powdered coke in the electric furnace—

$$SiO_2 + 3C = SiC + 2CO.$$

It is an extremely hard crystalline solid, colourless when pure, but black as usually prepared. It is used instead of emery for grinding and polishing, etc.

Optical Activity.—The resemblance of silicon to carbon is further illustrated by KIPPING's discovery (1907) that the silicon atom can act as a " centre of asymmetry " and form optically active compounds. (See textbooks of organic chemistry.)

TIN

Group in Periodic System: IV; *Symbol:* Sn; *Valency:* 2 and 4; *Atomic Weight:* 118·7; *Melting Point:* 232°; *Specific Gravity:* 7·2.

History.—The use of bronze, which is an alloy of copper and tin, by Neolithic man proves that tin must have been known in those very remote times. The Hebrew word *bedil*, which occurs in the Old Testament, probably means tin (as in *Numbers* xxxi. 22), although sometimes it is used for any base metal, such as lead or tin, which occurs in a silver ore (as in *Isaiah* i. 25) and is *separated* (*badala*) from the silver in refinement. CÆSAR (*De bello gallico*, 5, 12) says, " *Nascitur* (*in Britannia*) *plumbum album in mediis regionibus.*" PLINY first carefully distinguished between this *plumbum album* (tin) and *plumbum nigrum* (lead). He says that tin was obtained from the *Cassiterides* or *Tin* Islands (British Isles), the name κασσίτερος having been given to the metal by the Greeks, who possibly derived it from the Arabic *qaṣdīr*, tin, although the opposite is more likely.

The apparent similarity between lead and tin was the cause of their being known very frequently as the " two leads." According to the alchemists, tin was especially under the influence of the planet Jupiter and was therefore often called by the same name. Thus " GEBER " says " Of *Jupiter* or *Tin*. We ſignifie to the *Sons* of *Learning*, that *Tin* is a *Metallick Body*, white, not pure [white], livid, and ſounding little, partaking of little *Earthineſs*; poſſeſſing in its *Root Harſhness*, *Softneſs*, and ſwiftness of *Liquefaction*, without *Ignition*, and not abiding the *Cupel*, or *Cement*, but Extenſible under the

Hammer. . . . Its vice is, that it breaks every [metallic] *Body*, but *Saturn* [lead], and moſt pure *Sol* [gold] [i.e. when alloyed with them it makes them brittle]."

When sheets of tin are bent, they emit a peculiar noise, called the "cry of tin," and hence tin was sometimes called by the alchemists the "*metallic devil*."

The allotropic modification known as *grey tin* was first noticed by ARISTOTLE. (*De mirabilibus auscultationibus*, 50.)

The Latin name *stannum* was given to the metal about 1,500 years ago.

Occurrence.—Traces of native tin have been found, but the metal generally occurs as the oxide, *tinstone*. This is found in Cornwall, Germany, the East Indies, the Malay Peninsula, Australia, China, and South America (Bolivia and Peru), as well as in other places. *Stream tin* is tinstone in small granules, found in alluvial deposits.

Extraction.—Tin is prepared by reduction of its oxide with carbon in the form of charcoal or anthracite—

$$SnO_2 + 2C = Sn + 2CO.$$

Tinstone is generally mixed with earthy impurities, pyrites, wolfram ($FeWO_4$) and other substances, and therefore has to be purified before reduction. The ore is first crushed, and levigated in a stream of water, when the earthy matter is swept away. The impure stannic oxide is then roasted in a current of air, which oxidizes the pyrites, sulphur dioxide and arsenious oxide volatilizing away. The calcined ore, which contains oxides of iron, etc., as impurities, is again levigated, when most of the impurities are carried off by the current of water and the heavier tin oxide sinks to the bottom.

The purified tin oxide is then smelted with anthracite in small blast-furnaces (e.g. in the Dutch East Indies) or in reverberatory furnaces (e.g. in Australia, England, Malay), when

$$SnO_2 + 2C = Sn + 2CO.$$

The charge for a reverberatory furnace may be as much as 4 tons of ore with half a ton to a ton of anthracite.

The crude tin has to be refined, since it contains more or

less lead, iron, and arsenic. It is therefore *liquated*, or heated gently until the easily fusible tin ["poſſeſſing ſwiftneſs of *Liquefaction*"] melts and can be run off from the *liquation-dross*, consisting of the less fusible metals. The tin is still further purified by "*poling*" or stirring the molten metal with green wood (see *Copper*, p. 220); the gases which come off from the heated wood carry any impurities to the top, where they collect as a scum which can be removed.

The slag still contains large quantities of tin, and is smelted a second time.

The final purification of tin is effected by electrolysis in wooden vats lined with asphalt. The electrolyte is an aqueous solution of hydrofluosilicic acid (H_2SiF_6) in which tin has been dissolved.

Properties.—Tin is a lustrous white metal which melts at 232° and boils at 2,270°. It is stable in moist air at ordinary temperatures, but molten tin slowly oxidizes in air, forming stannic oxide, SnO_2. If heated to whiteness (1,500–1,600°) tin burns in air with a bright flame—

$$Sn + O_2 = SnO_2.$$

It is soluble in hydrochloric acid, dissolving slowly in the cold dilute acid but very quickly in the hot concentrated acid, forming stann*ous* chloride and hydrogen—

$$Sn + 2HCl = SnCl_2 + H_2.$$

Concentrated sulphuric acid dissolves the metal on heating, sulphur dioxide being evolved and stannous sulphate left—

$$Sn + 2H_2SO_4 = SnSO_4 + 2H_2O + SO_2.$$

Dilute nitric acid slowly dissolves tin, yielding stannous nitrate and ammonium nitrate—

$$4Sn + 10HNO_3 = 4Sn(NO_3)_2 + NH_4NO_3 + 3H_2O.$$

The concentrated acid, if absolutely pure, has no action on tin, but in the presence of a little water a vigorous reaction occurs and the tin is converted into *metastannic acid*, a hydrated stannic oxide of variable composition, with evolution of volumes of brown fumes. If the residue of metastannic acid is strongly heated, stannic oxide is left.

Caustic alkalis dissolve tin on heating, to form *stannates* and hydrogen, e.g.—

$$H_2O + Sn + 2NaOH = Na_2SnO_3 + 2H_2.$$
Sodium stannate.

Allotropic Forms.—Tin exists in three allotropic forms. Ordinary tin is called *white tin*, and is stable between the limits of temperature 18° and 170°. Below 18°, white tin gradually passes into *grey tin*, which is a grey powder. 18° is therefore the *transition point* of these two forms; *at* 18° both forms are equally stable, *above* it white tin is the stable form, and *below* it, grey tin. This transformation of white tin into a grey powder was noticed by ARISTOTLE and was rediscovered by ERDMANN in 1851. It was forcibly brought home to the Russian Government in 1867, when a consignment of block tin that had been kept in cellars at St. Petersburg (*bolshevikė* Leningrad) during the winter was found to have disappeared when the cellars were opened in the following spring, the floor being covered with a grey powder. The grey form may easily be reconverted into ordinary white tin by fusion and subsequent solidification.

The rate of transformation of white tin into grey tin depends upon two factors: (i) distance of the temperature of transformation from the transition point; (ii) the ordinary effect of changes of temperature upon the rate of chemical change. Factor (i) shows that the lowering of the temperature below 18° will accelerate the change, while factor (ii) will act in the opposite way. Hence there is a temperature of *maximum velocity* of the change, and this is found experimentally to be — 50°. The change takes place much more quickly in the presence of a solution of "pink salt" [$(NH_4)_2SnCl_6$, p. 320].

If white tin is heated to a temperature of about 170°, it slowly changes into a third allotropic form, called *rhombic tin*. The exact temperature of the transition point is not known; 170° is a mean value.

The following diagram shows the relationships between the three forms—

Grey tin $\rightleftharpoons$ ordinary tin $\rightleftharpoons$ rhombic tin.
Transition point 18° C. Transition point, about 160°–170° C.

Uses.—Tin finds many important applications, since it is stable in moist air. *Tin-foil* is used for wrapping chocolates and cigarettes, though a good deal of so-called "tin-foil" nowadays is aluminium foil; *tin-plate* is sheet-iron covered with tin; while tin is a constituent of many *alloys* such as *bronze*, *phosphor-bronze*, *pewter*, *solder*, and *Britannia metal*.

For the composition of *bronze* and *phosphor-bronze*, see p. 227. *Pewter* consists of 4Sn to 1Pb and a little antimony, though some varieties have a smaller proportion of tin. Too little tin is undesirable, as lead poisoning may occur from drinking from vessels with a high proportion of lead. *Solders* are of many varieties, but usually consist of 34–50 per cent. of tin and the rest lead. Fine-solder is a mixture of 1 part of lead with 2 parts of tin. *Britannia metal* contains tin, antimony and copper, while certain *antifriction alloys*, used for bearings, contain the same metals in varying proportions.

Tin-plating is carried out by thoroughly cleaning steel or iron plates in dilute hydrochloric acid and then passing them into a bath of molten tin preserved from oxidation by a layer of oil or grease. The plates are afterwards sent through rollers to remove excess of tin and are then left with a bright and even coating of the metal.

Large quantities of tin are used in this way, and since tin is an expensive metal, many methods have been suggested for recovering it from scrap tin-plate. Electrolytic methods are sometimes used, but chlorine is now so cheap that the scrap tin-plate is usually treated with this gas, which converts the tin into the volatile *stannic chloride*, $SnCl_4$. This can be hydrolysed into hydrated stannic oxide, from which the tin may be recovered.

Compounds of Tin.

Tin forms two oxides, SnO, stannous oxide, and SnO_2, stannic oxide, and two corresponding series of salts. In stannous salts the metal is bivalent and in stannic salts quadrivalent.

Stannous oxide, SnO, is obtained as a dark green, almost

black, powder by heating stannous oxalate out of contact with air—

$$SnC_2O_4 = SnO + CO_2 + CO,$$

and in other ways. It takes fire if heated in air, forming the dioxide, and dissolves in dilute acids to give stannous salts.

Stannic oxide, SnO_2, occurs naturally in the crystalline form as *tinstone* or *cassiterite*. It is formed as a white powder by burning tin in air or by heating the metastannic acid produced by the action of concentrated nitric acid on the metal.

Stannic oxide has practically no basic properties and will not dissolve in acids; it is slightly *acidic*, and if fused with caustic alkalis forms *salts*, the *stannates*—

$$SnO_2 + 2KOH = K_2SnO_3 + H_2O.$$

Many hydrates of stannic oxide are known; they exhibit feebly acidic properties and are called *stannic acids*. Metastannic acid, or *β-stannic acid*, is made, as stated above, by the action on tin of concentrated nitric acid. Its formula is not definitely known, but the sodium salt, made by the action of cold caustic solution upon the acid, has the formula $Na_2Sn_5O_{11}.4H_2O$, so that the acid may be $H_2Sn_5O_{11}$ or $H_2Sn_5O_{11}.4H_2O$.

α-stannic acid, H_2SnO_3, is obtained as a gelatinous precipitate by adding dilute hydrochloric acid to a solution of sodium α-stannate, Na_2SnO_3, made by dissolving stannic oxide in fused caustic soda.

Sodium α-stannate is used as a mordant in dyeing, under the name of "preparing-salt."

Stannous chloride, $SnCl_2$, is formed when tin is dissolved in concentrated hydrochloric acid. By evaporation of the solution, white crystals of $SnCl_2.2H_2O$ are formed—

$$Sn + 2HCl = SnCl_2 + H_2.$$

The hydrated salt *on heating is converted into a basic salt*, with loss of hydrochloric acid, so that the anhydrous salt must be obtained in other ways, e.g. by heating tin in a stream of hydrochloric acid gas.

Stannous chloride is partially hydrolysed by water to a white insoluble basic chloride—

$$2SnCl_2 + 2H_2O = SnCl_2.Sn(OH)_2 + 2HCl;$$

its solution is always made up therefore in dilute hydrochloric acid, which prevents hydrolysis, and not in pure water.

A solution of stannous chloride in hydrochloric acid is largely used as a powerful reducing agent, owing to the readiness with which the tin passes to the stannic state. Thus, it reduces ferric salts to ferrous, mercuric salts first to mercurous salts and then to mercury, nitric acid to hydroxylamine, etc.—

$$SnCl_2 + 2FeCl_3 = SnCl_4 + 2FeCl_2.$$

$$\left\{\begin{array}{ll} \text{(i)} & SnCl_2 + 2HgCl_2 = SnCl_4 + Hg_2Cl_2. \\ \text{(ii)} & SnCl_2 + Hg_2Cl_2 = SnCl_4 + 2Hg. \end{array}\right.$$

$$4SnCl_2 + 8HCl + HNO_3 = NH_2.OH + 4SnCl_4 + 3H_2O.$$

It is used as a mordant, under the name of "tin-salt," and also in the preparation of *purple of Cassius* (p. 237).

Vapour density determinations show that some of the molecules of the vapour are Sn_2Cl_4 and some $SnCl_2$, but CASTORO has shown (1898) that the depression of the freezing-point of urethane (an organic compound) caused by solution in it of stannous chloride corresponds to the formula $SnCl_2$.

Stannic chloride, $SnCl_4$, was discovered in 1605 by LIBAVIUS, and is still sometimes called *spiritus fumans Libavii*. It is prepared by heating tin in a current of dry chlorine—

$$Sn + 2Cl_2 = SnCl_4.$$

It is a colourless fuming *liquid*, which readily combines with water to form solid hydrates, e.g. $SnCl_4.5H_2O$, which is used as a mordant in dyeing and is commercially known as "butter of tin." With excess of water stannic chloride is partially hydrolysed. It will combine directly with ammonium chloride to form $(NH_4)_2SnCl_6$, *ammonium stannichloride*, which was formerly used as a mordant for certain red dyes and was therefore called *pink salt*. It is the ammonium salt of *hydrochlorostannic acid*, H_2SnCl_6.

Stannous sulphide, SnS, is formed when tin is heated with sulphur, and when sulphuretted hydrogen is passed through

a solution of stannous chloride in the presence of hydrochloric acid—

$$SnCl_2 + H_2S \rightleftharpoons SnS + 2HCl.$$

It is a brownish-black substance which dissolves in dilute acids, forming stannous salts, and in yellow ammonium sulphide, forming *ammonium thiostannate*, $(NH_4)_2SnS_3$—

$$SnS + (NH_4)_2S_2 = (NH_4)_2SnS_3.$$

Stannic sulphide, SnS_2, is made by heating a mixture of tin amalgam, sulphur and ammonium chloride, when it is left in the form of golden-yellow crystalline plates, called *mosaic gold*. When sulphuretted hydrogen is passed through an acidified solution of stannic chloride, stannic sulphide is obtained in an impure state as a dirty yellow precipitate, soluble in yellow ammonium sulphide, forming ammonium thiostannate.

Organic Compounds of Tin.—The similarity of tin to carbon is well shown by the fact that many organic tin compounds are known, in which the tin is quadrivalent. Thus *tin ethyl*, $(C_2H_5)_4Sn$, corresponding to tetra-ethyl methane has been prepared, and so has $\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!Sn = O$, *dimethyl stannone*, corresponding to acetone, $\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!C = O$.

The compound $\begin{matrix}CH_3\\C_2H_5\end{matrix}\!\!>\!Sn.\!<\!\begin{matrix}CH_2.CH_2.CH_3\\I\end{matrix}$ has been obtained in optically active forms by POPE and PEACHEY (1900).

LEAD

Group in Periodic System: IV; *Symbol:* Pb; *Valency:* 1, 2, and 4; *Atomicity of Vapour:* 1; *Atomic Weight:* 207·2; *Melting Point:* 326°; *Specific Gravity:* 11·25–11·4.

History.—Lead has been known from very remote times, and was early distinguished as *plumbum nigrum* from *plumbum album* (tin). The Arabian chemists, while recognizing the similarity of the two metals, realized that they were distinct, and called lead *usrub* while they gave the name *qaṣdīr* to tin.

Astrologically lead was connected with the planet Saturn and is very often referred to by the name of that planet in alchemical treatises. "GEBER" says that "*Lead* is a *Metallick Body*, livid, earthy, ponderous, mute, partaking of a little *Whiteness*, with much paleneſs, refuſing the *Cineritium* and *Cement*, eaſily in all its dimenſions with ſmall *Compreſſion extenſible*, and readily fuſible, without *Ignition*. . . . *Lead* is in like Manner burnt, and made *Minium*; and it is put over the *Vapours* of *Vinegar*, and made *Ceruſs*. . . . *Lead* alſo is the *Tryal* of *Silver* in the *Cupel*."

Occurrence.—The chief ore of lead is *galena*, lead sulphide, PbS. It also occurs in the form of carbonate, $PbCO_3$, in the mineral *cerussite*.

Extraction.—Practically all the lead of commerce is made from galena, which occurs in England, New South Wales, and many other countries. The galena is first roasted in a current of air, which converts part of it into lead oxide and part into sulphate—

(i) $2PbS + 3O_2 = 2PbO + 2SO_2$.
(ii) $PbS + 2O_2 = PbSO_4$.

The roasted ore is then mixed with more galena and the temperature raised; at the same time the current of air is cut off. The following reactions then occur—

(i) $2PbO + PbS = 3Pb + SO_2$.
(ii) $PbSO_4 + PbS = 2Pb + 2SO_2$.

The molten lead collects at the bottom of the furnace and is run off. It contains impurities, chiefly antimony, tin, copper, and bismuth, which are removed by heating the lead to redness in a small reverberatory furnace until the impurities are oxidized and collect on the surface of the metal as a scum which is removed from time to time. If much copper is present this is removed by *liquation*, i.e. heating the impure lead until it melts, when it may be run off from the less fusible copper.

The lead purified in this way still contains silver, which is often present in sufficiently large quantities to be worth extraction. (See *desilverization of lead*, p. 228.)

Properties.—According to LAMBERT and CULLIS (1915)

absolutely pure lead is a silvery white metal, but as usually obtained it has a bluish grey colour. It rapidly tarnishes in the air, owing to the formation of a thin film of lead suboxide, Pb_2O. The specific gravity of the metal is 11·3, its melting-point 326° and its boiling-point over 1,200°.

Lead is a soft metal, and leaves a mark if rubbed across paper. It can be cut with a knife, and is readily malleable. It can easily be moulded into pipes or pressed into sheets, and as it oxidizes only superficially in air it finds many applications. Alloys of lead with antimony and tin are used as *type-metal*, while the "lead" of accumulator plates frequently consists of an alloy of 24 parts of lead with 1 of tin.

It is soluble in nitric acid, forming lead nitrate and nitrogen peroxide, etc.—

$$Pb + 4HNO_3 = Pb(NO_3)_2 + 2NO_2 + 2H_2O,$$

or perhaps $3Pb + 8HNO_3 = 3Pb(NO_3)_2 + 4H_2O + 2NO$.

Hot concentrated sulphuric acid rapidly dissolves lead, with formation of lead sulphate and sulphur dioxide. The dilute acid has no action, neither has hydrochloric acid.

By heating lead tartrate, the metal is obtained in a very finely divided condition and is then called *pyrophoric lead*, since it takes fire spontaneously in the air.

The *atomic weight* of ordinary lead is 207·2, but lead exists in isotopic forms, two, of atomic weights 206 and 208 respectively, being of considerable interest in that they were the first isotopes the existence of which was experimentally proved.

Lead and its soluble compounds are poisonous, and are all the more dangerous in that the effect is cumulative; i.e. the poisonous substances are not eliminated from the system. Lead poisoning is common among painters and others who work with lead or compounds containing it.

Compounds of Lead.—Lead forms five oxides—

Pb_2O, lead suboxide.

PbO, lead monoxide or litharge.

Pb_3O_4, triplumbic tetroxide, red lead, or minium.

Pb_2O_3, lead sesqui-oxide.

PbO_2, lead peroxide.

[Several more have been reported, but their individuality is doubtful.]

Lead suboxide and **sesqui-oxide** are unimportant. The former is obtained by gently heating lead oxalate in absence of air—

$$2PbC_2O_4 = Pb_2O + 3CO_2 + CO,$$

and is a black powder. It forms, under suitable conditions, the corresponding sub-salts. *Lead sesqui-oxide*, Pb_2O_3, is a reddish yellow powder, discovered by SCHAFFNER (1844), who made it by adding sodium hypochlorite to a cold solution of litharge in caustic soda.

Lead monoxide, massicot, or litharge, PbO, is formed when lead is strongly heated in air, or by the action of heat on lead nitrate—

$$2Pb(NO_3)_2 = 2PbO + 4NO_2 + O_2.$$

It is a yellow powder, commonly known as *massicot*; on fusion and cooling it is converted into the reddish crystalline variety, called *litharge*, since it is obtained in the purification of *silver*. (Litharge = "silver stone.") Lead monoxide is readily reduced to the metal; it dissolves in acids to give lead salts, and also in concentrated caustic alkalis, to form salts, the *plumbites*—it is therefore both *basic* and *acidic*, although more the former than the latter.

It is used in glass manufacture and as a source of more important compounds of lead such as "red lead" and "white lead"; under carefully regulated conditions and in specially licensed factories it is used for glazing pottery. (Precautions have to be taken since lead compounds are poisonous.) It is also used for "drying" paints and varnishes, or making them "set"; this is an oxidation process and therefore hastened by the ready "reducibility" of litharge, although it is said that the action is also catalytic.

Litharge is slightly soluble in water, with which it partly combines, to form lead hydroxide. The solution has a perceptibly alkaline reaction—

$$PbO + H_2O \rightleftharpoons Pb(OH)_2 \rightleftharpoons Pb^{\cdot\cdot} + 2OH'.$$

Lead hydroxide, $Pb(OH)_2$, is precipitated as a white solid on addition of caustic alkali solution to a solution of a soluble lead salt. It is both basic and acidic.

Red lead or **minium,** Pb_3O_4, has been used for centuries as a red paint. It is said that "miniature" really means "a picture painted by a '*miniatore*'," i.e. one who used red lead. Red lead is made by heating litharge in air for some hours at a temperature of 400–450°. It seems to be a compound of the basic *litharge*, PbO, with the acidic *lead peroxide*, PbO_2, and is therefore sometimes called *lead orthoplumbate*, the lead salt (Pb_2PbO_4) of orthoplumbic acid, $Pb(OH)_4$ or H_4PbO_4. It reacts with acids giving ordinary lead salts and a deposit of lead peroxide—

$$Pb_3O_4 + 4HNO_3 = 2Pb(NO_3)_2 + 2H_2O + PbO_2.$$

Lead dioxide or **peroxide,** PbO_2, is a chocolate-brown powder obtained by the action of an oxidizing agent, such as potassium chlorate, upon litharge, but most conveniently prepared from red lead by the reaction given above. It is formed as a brown deposit on the anode when a solution of a lead salt is electrolysed between lead electrodes, or by the electrolysis of dilute sulphuric acid, using a lead anode. In the latter case the SO_4'' ions after discharge at the anode act on the water present and liberate oxygen—

$$2SO_4 + 2H_2O = 2H_2SO_4 + 2O;$$

the oxygen then oxidizes the lead anode to lead peroxide—

$$Pb + 2O = PbO_2.$$

This reaction is used in *accumulators* (Fig. 67). A discharged accumulator consists essentially of two lead plates coated with lead sulphate and immersed in dilute (20 per cent.) sulphuric acid. To charge the cell, one of the plates is connected to the positive pole of a dynamo, and thus made the anode, while the other is made the cathode. On electrolysis, SO_4'' ions pass to the anode, where they are discharged, lead peroxide being deposited—

$$SO_4 + PbSO_4 + 2H_2O \rightleftharpoons PbO_2 + 2H_2SO_4.$$

At the cathode, the hydrogen ions are discharged and the lead sulphate is reduced to lead—

$$PbSO_4 + 2H \rightleftharpoons Pb + H_2SO_4.$$

Charging is therefore continued until gases begin to appear on the plates, showing that the above changes are complete.

The cell will now give a current (flowing in the opposite direction to the charging current) if the two plates are connected by a wire. The charges that occur during discharge are the reverse of those that take place during charging—

$PbO_2 + 2H_2SO_4 \rightarrow PbSO_4 + 2H_2O + SO_4''$ at the positive pole,

and $Pb + H_2SO_4 \rightarrow PbSO_4 + 2H^{\cdot}$ at the negative pole.

After discharge, therefore, both plates are covered with lead sulphate.

The principle of the accumulator is thus the conversion of electrical energy into chemical energy (charging), followed by the re-conversion of this chemical energy into electrical energy (discharging). Expressed in one equation the changes that take place are—

(i) *Charge.* $2PbSO_4 + 2H_2O = PbO_2 + 2H_2SO_4 + Pb$, with *absorption* of energy, supplied by the dynamo.

(ii) *Discharge.* $PbO_2 + 2H_2SO_4 + Pb = 2PbSO_4 + 2H_2O$, with *liberation* of energy, given out in the form of an electric current.

Lead peroxide is used as an oxidizing agent; thus it oxidizes hot hydrochloric acid to chlorine—

$$PbO_2 + 4HCl = PbCl_2 + 2H_2O + Cl_2,$$

and combines with sulphur dioxide, to form lead sulphate, with so much evolution of heat that it becomes incandescent—

$$PbO_2 + SO_2 = PbSO_4.$$

A mixture of sulphur and lead peroxide inflames, and a mixture of red phosphorus and lead peroxide explodes, when rubbed in a mortar.

Lead peroxide exhibits both basic and acidic properties;

it dissolves in *cold* concentrated hydrochloric acid to give a dark solution containing *lead tetrachloride*, $PbCl_4$, probably in the form of hydrochloroplumbic acid, $H_2PbCl_6 (= PbCl_4.2HCl)$. It also dissolves in hot concentrated caustic alkalis to form salts, the *plumbates* e.g.—

$$2NaOH + PbO_2 = \underset{\text{Sodium plumbate.}}{Na_2PbO_3} + H_2O.$$

Other plumbates are known ; they are the salts of the *plumbic acids*—

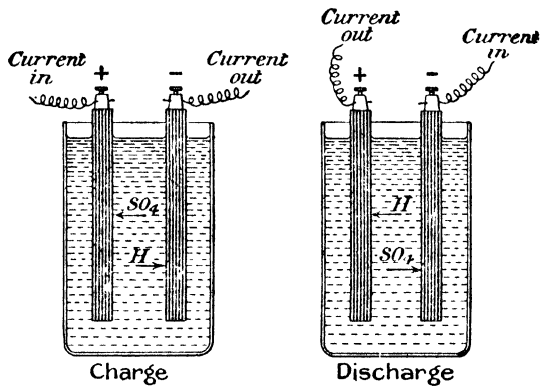


FIG. 67.

$PbO_2.2H_2O$, $Pb(OH)_4$, or H_4PbO_4, *ortho*plumbic acid, known in the form of its calcium salt, Ca_2PbO_4; and

$PbO_2.H_2O$, $Pb\begin{matrix}OH\\ \diagup\\ \diagdown\\ O\end{matrix}$—OH, or H_2PbO_3, *meta*plumbic acid,

which has been prepared in the free state.

Lead dichloride, $PbCl_2$, is generally made as a white crystalline precipitate by adding a solution of a soluble chloride to a solution of lead nitrate or acetate (the two common *soluble* salts of lead)—

$$Pb(NO_3)_2 + 2NaCl = PbCl_2 \downarrow + 2NaNO_3.$$

It may also be made by heating lead in chlorine, since the higher chloride, $PbCl_4$, which would be expected, dissociates on heating.

Lead chloride, as it is commonly called, is only slightly soluble in water, but sufficiently so for a part of the lead in qualitative analysis to be left over from Group I and to make its appearance as lead sulphide in Group II.

It is more soluble in hot water than in cold.

Lead tetrachloride, $PbCl_4$, is prepared from the solution of hydrochloroplumbic acid described under lead dioxide. Ammonium chloride is first added, when a yellow precipitate of the ammonium salt, $(NH_4)_2PbCl_6$, is obtained. If this precipitate is then added to well-cooled concentrated sulphuric acid, hydrochloric acid gas is evolved and a yellow oil, *lead tetrachloride*, $PbCl_4$, separates—

$$(NH_4)_2PbCl_6 + H_2SO_4 = (NH_4)_2SO_4 + 2HCl + PbCl_4.$$

It fumes in moist air, is readily hydrolysed by water, and decomposes on slight warming, into the dichloride and chlorine.

Lead carbonate, $PbCO_3$, is obtained as a white precipitate by adding a solution of sodium *bi*carbonate to a solution of lead nitrate or acetate. Sodium carbonate precipitates not the normal lead carbonate, but a *basic* carbonate, $2PbCO_3 . Pb(OH)_2$, called *white lead*. This substance is extensively used for making paints, and is therefore made on a large scale commercially. Many processes are employed, but the best is still that described by "GEBER" in the thirteenth century and now called the *Dutch Process*. Rolls of lead sheets are placed in earthenware pots, towards the bottom of which are shelves or ledges upon which the lead rests. The part of the pots below the ledges is filled with vinegar, and the pots then covered with lead plates and placed, to the number of a gross or more, in heaps of horse-dung. Fermentation of the dung serves two purposes, (i) it keeps the pots rather warm ("temperature of putrefaction," one of the "fixed points" on the old alchemical scale of temperature), and (ii) it liberates carbon dioxide. After a time, which varies from four to

twelve weeks, the lead is converted into white lead of a very good (indeed, the best) quality.

Possible reactions—

(i) The acetic acid vapour, in the presence of air, converts the lead into a basic lead acetate—

$$2Pb + 2CH_3.COOH + O_2 = Pb(OH)_2.(CH_3.COO)_2Pb.$$

(ii) The carbon dioxide then reacts with the basic acetate to form the basic carbonate and acetic acid—

$$3Pb(OH)_2.(CH_3.COO)_2Pb + 4CO_2 + 2H_2O = 2Pb(OH)_2.2PbCO_3 + 6CH_3.COOH.$$

The liberated acetic acid attacks more lead and so the process is continuous as long as any lead is left. Any soluble lead acetate remaining in the white lead is removed by washing with water. The white lead is then dried by heating under reduced pressure, or by mixing it with oil in a "pug-mill," when most of the water separates and the white lead remains in association with the oil.

In England, old tannery bark is often used instead of horse-dung. White lead is also made by hanging straps of lead in a chamber over dilute acetic acid, and blowing in carbon dioxide, but attempts to hurry matters in this and other ways result in the formation of an inferior quality of the product, owing to the particles of white lead being rather larger in size and therefore possessing a smaller "covering-power."

Lead carbonate as a paint suffers from the defect that it is blackened by sulphuretted hydrogen; the white paint in chemical laboratories, etc., is therefore made from *zinc* carbonate, which possesses less covering-power but is unchanged in colour by sulphuretted hydrogen, since zinc sulphide is white.

Lead sulphate, $PbSO_4$, is a heavy white substance, obtained by adding sulphuric acid or a solution of a sulphate to a solution of a soluble lead salt. It is soluble in hot concentrated sulphuric acid, but most of it separates out again on cooling. It is a common impurity in commercial lead-chamber sulphuric acid.

Lead nitrate, $Pb(NO_3)_2$, is a white crystalline solid that decrepitates on heating and is decomposed into litharge, oxygen and nitrogen peroxide—

$$2Pb(NO_3)_2 = 2PbO + 4NO_2 + O_2.$$

Lead acetate or sugar of lead, $(CH_3COO)_2Pb.3H_2O$, is made by dissolving litharge in dilute acetic acid and evaporating the solution to crystallization. It is a poisonous substance with a sweet taste, and is readily soluble in water. Filter-paper impregnated with lead acetate smoulders when ignited, owing to the formation of the spontaneously-combustible pyrophoric lead. Basic acetates of lead also exist.

Lead chromate, $PbCrO_4$, comes down as a yellow precipitate on the addition of potassium chromate to lead acetate solution. It is used as a pigment under the name of " chrome yellow."

Organic compounds of lead, such as *lead tetraethyl*, $Pb(C_2H_5)_4$, are known. These generally contain quadrivalent lead. Lead tetraethyl is the " anti-knock " agent in the now familiar " ethyl petrol."

QUESTIONS

1. How far is the inclusion of carbon, silicon, tin and lead in a single group justified from a consideration of the chemical and physical properties of these elements ?
2. Describe the artificial preparation of the diamond.
3. How is graphite manufactured ? What are its properties and uses ?
4. Give an account of the manufacture of coal-gas.
5. Describe the preparation and properties of methane, ethylene and acetylene.
6. How is carbon monoxide prepared in the laboratory ? What are its properties ?
7. Write a short account of gaseous fuels, excluding coal-gas.
8. Discuss the equilibrium $2NaHCO_3 \rightleftharpoons Na_2CO_3 + H_2O + CO_2$ in terms of (*a*) Le Chatelier's principle, and (*b*) the phase rule.
   (Solid. Solid. Gas. Gas.)
9. A solution of sodium carbonate is alkaline to litmus and a solution of sodium bicarbonate is neutral. Explain these phenomena in terms of the ionic theory.
10. Write an account of the silicic acids and silicates.
11. What do you know of the history of tin ?

12. Describe the metallurgy of tin.

13. Discuss the equilibria between tin allotropes.

14. Describe the process of tin-plating and state how tin is recovered from scrap tin-plate.

15. How would you prepare (i) anhydrous stannic chloride, (ii) anhydrous stannous chloride ? For what purposes is stannous chloride used ?

16. Describe the preparation and properties of the oxides of lead.

17. Explain the chemistry of the accumulator.

18. How is " white lead " made commercially ?

CHAPTER XXV

GROUP V

TYPICAL ELEMENTS: **Nitrogen, Phosphorus.**
Sub-group A: Vanadium, Niobium, Tantalum.
Sub-group B (similar to typical elements): **Arsenic, Antimony, Bismuth.**

NITROGEN, PHOSPHORUS, ARSENIC, ANTIMONY, BISMUTH

For a group in the Periodic System, which, as we have seen, often classifies together elements of widely-diverging character, the elements nitrogen, phosphorus, arsenic, antimony and bismuth form a remarkably homogeneous family.

They are all tervalent or quinquevalent, and they show a gradual change in physical and chemical properties from the characteristic gaseous non-metal nitrogen, through the metalloid arsenic, to the true metal bismuth.

NITROGEN

Group in Periodic System: V; *Symbol:* N; *Valency:* 3 and 5; *Atomicity:* 2; *Atomic Weight:* 14·01.

History.—Nitrogen was discovered in 1772 by RUTHERFORD, Professor of Botany at Edinburgh University. He obtained it from air in the course of experiments on the respiration of animals, and called it *mephitic air* since it would not support life. SCHEELE also obtained it from air and called it *foul air*, and it seems to have been independently discovered by PRIESTLEY, who gave it the name of *phlogisticated air*. LAVOISIER renamed the gas *azote*, by which name

it is still known in France, while the name *nitrogen* was given to it on account of the fact that it occurs in nitre.

Occurrence.—In the uncombined state nitrogen forms about 79 per cent. by volume and 77 per cent. by weight of the air. It is found combined in large quantities as sodium nitrate or *Chile saltpetre* ($NaNO_3$), and is widely distributed in smaller quantity in the soil as ammonium salts and nitrates of sodium, potassium and calcium. It is an essential constituent of living matter.

Preparation.—It is difficult to obtain pure nitrogen from the air, since although the water-vapour, carbon dioxide, and oxygen may readily be removed, the residual nitrogen still

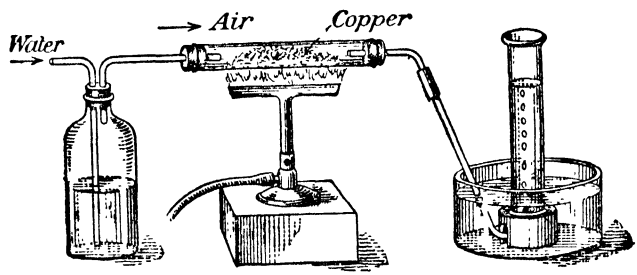


FIG. 68.

contains argon and the other rare gases of the atmosphere (p. 187), from which it cannot be purified except by long and tedious processes, e.g. liquefaction followed by fractional distillation. However, for ordinary chemical purposes the presence of the inactive gases in nitrogen is no drawback, as these substances naturally do not interfere with any of the chemical reactions for which the nitrogen may be required. It is only when the nitrogen is required for the purpose of determining its physical constants, etc., that it is essential to obtain it free from all impurities.

"Atmospheric" nitrogen, then (i.e. nitrogen containing about 1 per cent. of the inactive gases), may be prepared by removing the oxygen from air which has been previously freed from (*a*) carbon dioxide (by passing through caustic soda

solution), and (*b*) water-vapour (by passing through concentrated sulphuric acid). The oxygen may be removed in various ways—

(i) By passing the air over heated copper, when copper oxide is formed and the nitrogen left. (Fig. 68.)

(ii) By burning phosphorus in the air.

It is clear that a great number of similar methods is available. Moist nitrogen is readily obtained from air by shaking the air up with an alkaline solution of pyrogallol. This absorbs both the carbon dioxide and the oxygen, going brown in the process (owing to the formation of oxidation products), and leaves the moist nitrogen.

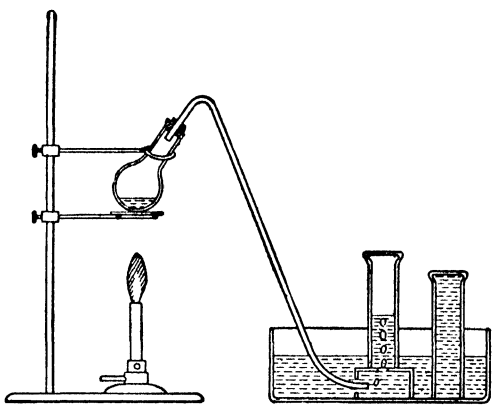


FIG. 69.

"Chemical" nitrogen is prepared by the decomposition of nitrogenous compounds, and is therefore free from the inactive gases. (i) The usual laboratory method is to heat a solution of ammonium nitrite (Fig. 69)—

$$NH_4NO_2 = N_2 + 2H_2O.$$

As, however, ammonium nitrite is an unstable compound it is never put on the market in the solid state, and even in solution is but rarely met with. It is better to use a mixture of equimolecular proportions of ammonium chloride and sodium nitrite, which in solution react to give ammonium nitrite and sodium chloride—

$$NH_4Cl + NaNO_2 \rightleftharpoons NaCl + NH_4NO_2.$$

(ii) By passing chlorine into a concentrated solution of ammonia—

$$8NH_3 + 3Cl_2 = 6NH_4Cl + N_2.$$

The chlorine removes hydrogen from some of the ammonia, forming hydrochloric acid and nitrogen; the hydrochloric acid then combines with excess of ammonia to form ammonium chloride. Care must be taken not to pass the chlorine for too long a time, or the highly explosive nitrogen trichloride, NCl_3, will be formed.

(iii) By the action of heat on ammonium dichromate—

$$(NH_4)_2Cr_2O_7 = N_2 + Cr_2O_3 + 4H_2O.$$

Nitrogen and steam are given off and a green solid, chromium sesqui-oxide, is left. The reaction is too vigorous for convenience unless the dichromate is mixed with about twice its volume of dry sand. A little ammonia is formed as a by-product.

Commercially, nitrogen is prepared from the atmosphere by the fractional distillation of liquid air. It was formerly a waste-product, but is now largely employed in the manufacture of certain nitrogen compounds (p. 340, etc.).

Properties.—Nitrogen is a colourless, odourless gas. It will not burn nor support combustion. It is very slightly soluble in water, less so than oxygen. It boils at $-194°$ and the liquid nitrogen freezes to a white solid at $-214°$. Under ordinary conditions nitrogen behaves as a rather inert element, but of recent years much work has been done on the combination of nitrogen with other elements and the necessary conditions discovered. The compounds of nitrogen are very numerous, interesting and important. Explosives, dyes, drugs, and artificial manures are mostly nitrogenous compounds, and nitrogen compounds are necessary to the life of plants and animals.

Nitrogen will combine directly with many metals, on heating, forming *nitrides*—

$$3Mg + N_2 = Mg_3N_2, \text{ magnesium nitride.}$$
$$6Li + N_2 = 2Li_3N, \text{ lithium nitride.}$$

Fig. 70 shows an apparatus that may be used for demonstrating the absorption of nitrogen by heating magnesium. It is interesting to note that when magnesium burns in the air it burns in *both the oxygen and the nitrogen*, the product being a mixture of magnesium oxide with a little magnesium nitride. This may easily be proved by adding a little water and then some Nessler's solution (p. 350). When a metallic nitride is acted upon by water, ammonia is formed—

$$Mg_3N_2 + 6H_2O = 3Mg(OH)_2 + 2NH_3,$$

and Nessler's solution with ammonia gives a yellowish precipitate or coloration. Magnesium nitride is a highly magnetic substance.

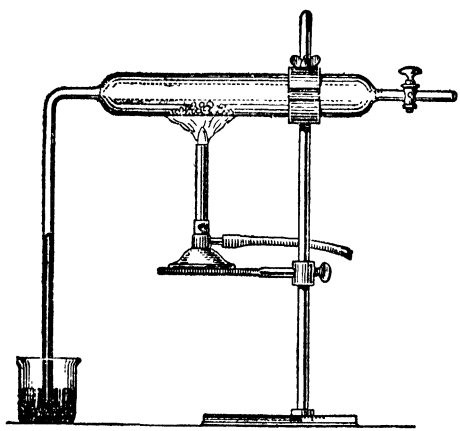


FIG. 70.

Nitrogen and oxygen, and nitrogen and hydrogen, combine together if sparked—

$$2N + O_2 \rightleftharpoons 2NO$$

and

$$2N + 3H_2 \rightleftharpoons 2NH_3,$$

but the reactions are reversible and the equilibrium mixtures obtained in this way contain only traces of oxides of nitrogen and ammonia respectively. However, the fact that a little combination does occur is of great importance, as we shall see later.

Nitrogen will combine directly with many metallic carbides if heated, e.g.—

$$CaC_2 + N_2 = CaCN_2 + C.$$

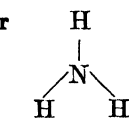
$CaCN_2$ is calcium cyanamide and is of technical importance (p. 248).

Active Nitrogen is an allotropic form of nitrogen discovered in 1911 by STRUTT. If an electric discharge is passed through nitrogen at low pressure, the gas continues to glow after the discharge has stopped. Investigation of the glowing gas showed that it was more active than ordinary nitrogen. If passed into the vapour of mercury, cadmium, zinc, sulphur, etc., the corresponding nitrides are formed, while acetylene and ethylene react vigorously with "active" nitrogen forming cyanogen, C_2N_2, and prussic acid, HCN. It is thought that in this form of nitrogen the molecules are monatomic, but the problem is not yet solved; it is doubtful, even, whether absolutely *pure* nitrogen can be converted into the "active" form, since a trace of oxygen, carbon dioxide, or hydrogen sulphide has to be present in the gas before "activity" can be obtained.

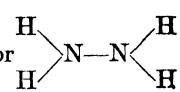
COMPOUNDS OF NITROGEN.

With hydrogen, nitrogen forms three compounds—

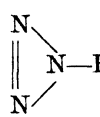
Ammonia, NH_3 or



Hydrazine, N_2H_4 or



Hydrazoic acid, N_3H or



Of these, the first two are important.

Ammonia, NH_3.

In the form of its compound with hydrochloric acid, *ammonium chloride*, NH_4Cl, ammonia has been known for over 2,000 years. This salt occurs naturally in Armenia and in other parts of Asia, and appears to have been called originally *sal armeniac*. The early chemists, however, confused

it with the natural sodium sesquicarbonate or *natron* found in the Libyan desert near the temple of JUPITER AMMON, and the name was changed in the course of time into *sal ammoniac* through this misconception.

PLINY (*Hist. Nat.*, xxxi, chap. 39) ascribes its discovery to KING PTOLEMY—" King Ptolemy discovered it near Pelusium while making a camp. Following his example, men found it by digging in the sand in the waste places from Egypt to Arabia, and also in the dry localities throughout Africa as far as the Oracle of Ammon. It grows by night, according to the phases of the moon. The country near Cyrene is famous for its sal ammoniac, so called because it is found beneath the sand (Greek *ammos*). . . . It grows in long pieces."

" GEBER," in the thirteenth century, describes its purification in the following words—" Grind it first . . . then let it be ſublimed in an high *Body* and *Head*, until it all aſcend pure. Afterward diſſolve it upon a *Porphiry* in the open *Air*, if you would of it make *Water*; or keep the *Sublimate* ſufficiently pure."

PRIESTLEY was the first to prepare ammonia gas (1774). He made it by heating a mixture of lime and sal ammoniac, and collected the gas over mercury. He called it *alkaline air*.

Ammonia occurs in the soil in small quantities, and in larger quantities, as ammonium sulphate $(NH_4)_2SO_4$, in the *soffioni* or *fumaroles* of Tuscany. It is obtained by the destructive distillation of many organic materials, such as horns, hoofs, bones, and coal. The old name for an aqueous solution of ammonia, *spirit of hartshorn*, indicates the method of preparation.

Ammonia is prepared in the laboratory by Priestley's method—

$$Ca(OH)_2 + 2NH_4Cl = CaCl_2 + 2NH_3 + 2H_2O.$$

It cannot be dried by means of sulphuric acid, phosphorus pentoxide, or calcium chloride, as it combines with these substances; it is therefore dried by passing through a glass " tower " containing lumps of quicklime, and is then collected by upward displacement or over mercury.

Technical Preparation.—Ammonia and its compounds are very important commercial products. The chief sources are—

(i) The aqueous liquid obtained in the manufacture of coal-gas.

(ii) A similar liquid obtained in the manufacture of coke.

(iii) The distillation of shale.

(iv) The manufacture of water-gas (p. 301).

(v) Synthetic and electrical methods.

(i), (ii) and (iv).—Coal contains about 1·5 per cent. of nitrogen, and much of this is obtained in the form of ammonia when coal is heated in the absence of air. On passing the gases through water the ammonia dissolves, giving the so-called *ammoniacal liquor*. About 5 lb. of ammonia are obtained from every ton of coal in the manufacture of coal-gas, and the coke left in the retorts still contains much nitrogen which is liberated as ammonia when steam is passed over the red-hot coke in the manufacture of water-gas.

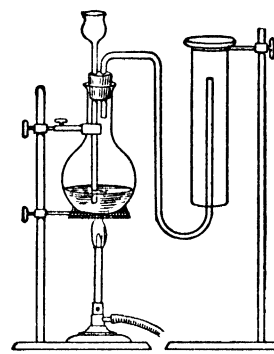


FIG. 71.—Preparation of moist Ammonia.

The ammoniacal liquors are treated with lime and then distilled; the ammonia which comes off is collected in aqueous sulphuric acid and the solution of ammonium sulphate so obtained evaporated to crystallization. The product is an impure ammonium sulphate (95 per cent.). Ammonia may be liberated from it, if desired, by heating with lime; if the gas is then passed into water ammonia solution is obtained. Pure ammonia is sometimes made from the crude ammonium sulphate by heating the latter to about 200° for some time, to decompose organic matter present as impurity, and then raising the temperature to 380°, when pure ammonia is given off and a compound $(NH_4)_2S_2O_7$ left.

(iii) *Shale.*—Shale consists of a hard slate-like clay, often containing a considerable amount of carbonaceous matter (" bituminous shale "). When bituminous shale is destructively distilled, an ammoniacal distillate is obtained, from which the ammonia can be extracted in the form of ammonium sulphate by addition of sulphuric acid followed by evaporation of the solution. About 70,000 tons of ammonium sulphate are prepared annually in this way, chiefly in Scotland.

(v) *Synthetic methods.*—When nitrogen and hydrogen are sparked together, in the proportions by volume in which they occur in ammonia, about 2 per cent. of the mixture is converted into ammonia, heat being evolved in the process. Ammonia is thus an exothermic substance, and we might expect that the reaction

$$2N + 3H_2 \rightarrow 2NH_3$$

would go much more nearly to completion than is represented by the 2 per cent. of ammonia actually obtained. The small yield of ammonia can be explained by supposing that the *rate* of formation of ammonia is very small at ordinary temperatures ; at the temperature of the electric spark the rate would certainly be tremendously increased, but so would the rate of decomposition of the ammonia formed. Hence to synthesize ammonia successfully from nitrogen and hydrogen it seems that a suitable *catalyst* is the first thing necessary.

There are, however, other points to be considered. (i) As ammonia is an exothermic compound, increase of temperature would lead to a diminution of the proportion of ammonia in the equilibrium mixture of this gas with nitrogen and hydrogen. (ii) The equation $N_2 + 3H_2 \rightleftharpoons 2NH_3$ shows us that a decrease in volume takes place when ammonia is formed from nitrogen and hydrogen. We should therefore expect, by Le Chatelier's principle, that increase of pressure would aid the formation of ammonia.

To prepare ammonia synthetically, then, on a scale which will assure commercial success, the following conditions have to be observed—

(*a*) The reaction velocity of the combination of nitrogen and hydrogen must be increased by raising the temperature or by addition of a suitable catalyst, or both.

(*b*) The temperature must not be so high that the proportion of ammonia in the equilibrium mixture is lowered too far for the process to be commercially successful.

(*c*) High pressures should be employed, to increase the proportion of ammonia formed.

(*d*) It is clear that the most effective way of preventing the reverse reaction (decomposition of ammonia) is to remove the ammonia from the sphere of action as soon as it is formed.

In the following table are shown the percentages of ammonia in the equilibrium mixture at various temperatures and pressures—

Pressure in Atmospheres.	Temperature.							
	200°.	400°.	550°.	600°.	650°.	750°.	800°.	1,000°.
1	15	0·4	0·08	0·05	0·03	0·016	0·012	0·0044
100	81	25	6·7	4·5	3	1·5	1·15	0·044
200	86	36	12	8	6	3	2	0·87

The catalyst generally used (HABER process) is a mixture of finely divided iron and molybdenum. The nitrogen and hydrogen must be carefully purified before use ; they are then compressed to about 200 atmospheres and passed over the catalyst at a temperature of 500°. The ammonia so formed is cooled and dissolved in water or else liquefied. This process is a great commercial success, and as nitric acid may be obtained by oxidation of ammonia, this and other methods rendered Germany independent of Chile saltpetre during the European war of 1914–1918.

Cyanamide process.—When calcium cyanamide, $CaCN_2$ (p. 248), is treated with steam, ammonia is formed—

$$CaCN_2 + 3H_2O = CaCO_3 + 2NH_3.$$

As calcium cyanamide is now prepared on a large scale by passing nitrogen over calcium carbide heated in the electric furnace, the preparation of ammonia in this way is used for commercial purposes.

Properties.—Ammonia is a colourless gas with a pungent

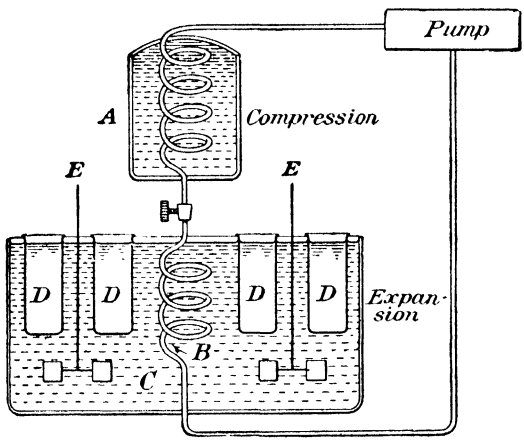


FIG. 72.—Ammonia Ice-making Machine.

A. The compressed ammonia is cooled in *A* (through which cold water circulates) and liquefies. *B*. In coil *B* the liquid ammonia is under reduced pressure and evaporates rapidly, the gas passing back to the pump whence it passes to *A* again, and so on. *C*. Vessel containing calcium chloride solution which does not freeze. *D, D*. Vessels containing water which is frozen. *E, E*. Stirrers.

smell. It is lighter than air and therefore may be collected by upward displacement, especially as it is extremely soluble in water and therefore cannot be collected at the pneumatic trough. Ammonia can easily be liquefied, as was first shown by FARADAY. Liquid ammonia is a colourless liquid boiling at −33·5° and solidifying to a colourless crystalline solid at −78°. It is used in commerce for *refrigerating* or ice-making

since by rapidly evaporating it low temperatures are produced; the gaseous ammonia may then be liquefied again by passing it through a condenser surrounded by cold water and compressing it. (Fig. 72.)

Ammonia is not a base, since it combines directly with acids to form salts *without elimination of water*; it is, in fact, the *anhydride* of a base, the true base being *ammonium hydroxide*, NH_4OH, which is formed when ammonia is dissolved in water. The following equations illustrate the point—

$NH_3 + HCl = NH_4Cl$
basic anhydride + acid = salt *but no water.*

$NH_4OH + HCl = NH_4Cl + H_2O$
base + acid = salt + *water.*

Dry ammonia has no action on litmus, moist ammonia turns red litmus blue.

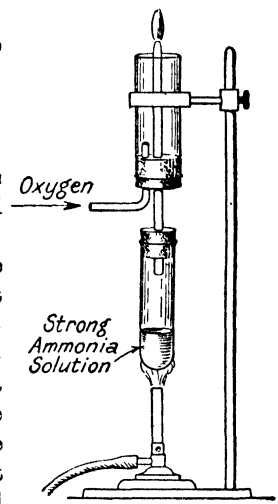


FIG. 73.—Ammonia burning in Oxygen.

Ammonia attempts to burn in the air but cannot quite manage it; it will, however, readily burn in oxygen-forming nitrogen, steam, and ammonium nitrate and nitrite. Ammonia is readily oxidized by oxygen in the presence of a platinum spiral. The heat evolved in the process is sufficient to keep the platinum red hot and often to ignite the mixture of ammonia and oxygen. The ammonia flame is of a characteristic brownish yellow colour.

When ammonia is dissolved in water an evolution of heat occurs. If air is blown through the solution, the ammonia is rapidly driven off and heat therefore absorbed. This reaction was at one time made use of in ice-making (CARRÉ'S process, now superseded by that previously described). The aqueous solution of ammonia contains ammonia and also ammonium hydroxide, NH_4OH. This is a weak base and partially ionizes into $NH_4^{\cdot}$ and OH', ammonium and hydroxyl ions.

If, therefore, ammonia is in contact with its saturated solution, the following equilibria occur—

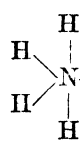
$$\underset{\text{gas}}{NH_3} \rightleftharpoons \underset{\text{dissolved}}{NH_3} + H_2O \rightleftharpoons NH_4OH \rightleftharpoons NH_4^{\cdot} + OH'.$$

Pure ammonium hydroxide, NH_4OH, was not isolated until 1909, when it was prepared by RUPERT, who obtained it as a colourless crystalline solid melting at −79° and rapidly decomposing on rise of temperature.

Ammonium.—The group of atoms NH_4 behaves in many respects like an atom of an alkali metal such as sodium or potassium. The following table shows certain of the resemblances—

	Ammonium.	Sodium.
Chloride . . .	NH_4Cl, white crystals	NaCl, white crystals
Nitrate . . .	NH_4NO_3	$NaNO_3$
Sulphate . .	$(NH_4)_2SO_4$	Na_2SO_4
Hydroxide . .	NH_4OH	NaOH
Carbonate . .	$(NH_4)_2CO_3$	Na_2CO_3

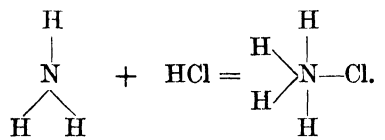
The salts of the NH_4 group are very familiar in appearance and properties to those of sodium, and for this reason the name *ammonium* was given to this group of atoms or *radical*, to indicate its apparent *metallic* nature. The ammonium group is univalent, as the nitrogen atom in it is quinquevalent and only four of these valencies are used to attach the hydrogen atoms—



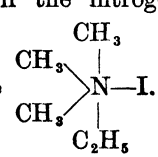
. It is therefore capable of combining directly with a univalent acid residue or of replacing an atom of sodium, etc., in a compound. Up to the present, there is no satisfactory evidence that the ammonium radical has been isolated, though claims to this effect have

been made. It was at one time supposed that if it could be isolated it would present a metallic form. If a concentrated solution of ammonium chloride is poured over some sodium amalgam, the latter swells up and forms a peculiar mass called *ammonium amalgam*, which was considered to be an amalgam of mercury with ammonium, NH_4. On standing, the substance loses ammonia and hydrogen, and mercury is left. The question whether ammonium amalgam is really what it professes to be or not is still unsolved ; there is evidence both ways. In any case, the *ammonium ion*, NH_4, certainly exists in solution. It would be very interesting if " ammonium " itself were isolated and proved to have metallic properties !

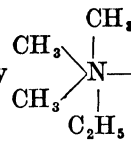
AMMONIUM SALTS.—When ammonia combines directly with acids the nitrogen atom of the ammonia molecule increases in valency from 3 to 5, and ammonium SALTS are formed—



Chemists were at one time inclined to regard these ammonium salts as loose compounds of ammonia with the acid, the ammonia and acid molecules being held together by a sort of residual or weak valency just as, in cases of hydrated salts, the water of crystallization is loosely held. VICTOR MEYER, however, in 1874 showed that in ammonium salts the nitrogen atom was quinquevalent, in the following way. He took trimethylamine, $N(CH_3)_3$, and ethyl iodide, C_2H_5I, and allowed them to react together, thus obtaining ethyltrimethylammonium iodide. If this is a loose " molecular compound " it would have a constitution represented by the formula $N(CH_3)_3.C_2H_5I$, whereas if the nitrogen in it is pentavalent the formula would be



He next took ethyldimethylamine, $N(CH_3)_2C_2H_5$, and allowed it to

react with methyl iodide, CH_3I, obtaining a compound *identical* with the ethyltrimethylammonium iodide previously made. Now if the nitrogen is quinquevalent it is clear that the reaction of $N(CH_3)_3$ with C_2H_5I would yield the same compound as that produced by the reaction of $N(CH_3)_2C_2H_5$ and CH_3I, namely  , whereas if only the loose "molecular" compound were formed the first reaction would give $N(CH_3)_3.C_2H_5I$ and the second $N(CH_3)_2C_2H_5.CH_3I$, which would presumably be different from one another in properties. Hence the quinquevalency of nitrogen in the ammonium compounds may be assumed. Stereochemical work on nitrogen compounds of the type NRR′R″R‴I (where R, R′, R″ and R‴ are four different carbon radicals) has supported this conclusion.

Ammonium hydroxide, NH_4OH, has been described above. It is largely used in qualitative analysis, for the precipitation of metals as hydroxides. It is a weak base, that is, it is only slightly ionized in aqueous solution, and as this ionization may be largely reduced by the addition of ammonium chloride it is possible to cause the precipitation of the hydroxides of iron, chromium, and aluminium from a solution and at the same time to prevent the precipitation of the hydroxides of zinc, manganese, cobalt and nickel even though these metals may be present in the same solution. This is the principle of the separation of Group III metals from those of Group IV (analytical table groups, not periodic system groups) (see p. 135).

Ammonium chloride, NH_4Cl, is a white crystalline solid. It is made by boiling ammonium sulphate with sodium chloride in aqueous solution—

$$(NH_4)_2SO_4 + 2NaCl \rightleftharpoons Na_2SO_4 + 2NH_4Cl.$$

On concentrating the solution the sodium sulphate crystal-

lizes out first and may be removed ; the solution of ammonium chloride may then be evaporated. It is purified by sublimation as described by GEBER. It is used in Leclanché cells and also in dry cells. Its vapour is dissociated (p. 82). Ammonium chloride is used in soldering (as a "flux"), because the hydrochloric acid which is set free on heating cleans the surface of the metal and thus enables the solder to "bite." It is also used in the manufacture of dyes and in calico-printing.

Ammonium sulphate, $(NH_4)_2SO_4$, is obtained from ammoniacal liquor (p. 339). It is a white crystalline solid very largely used as an artificial manure. It is also used in the fermentation industries. It is decomposed on heating, one of the products being ammonia, while the other is *ammonium hydrogen sulphate*, NH_4HSO_4. At a higher temperature further decomposition occurs, yielding steam, sulphur dioxide and nitrogen.

Ammonium nitrate, NH_4NO_3, is a white deliquescent crystalline solid, very soluble in water, the process of solution being accompanied by absorption of heat ; it is therefore used in refrigeration on a small scale, e.g. preparation of ice-cream (though here it has now been largely replaced by solid carbon dioxide ; see p. 305). It is prepared by passing ammonia into fairly concentrated (60 per cent.) nitric acid. If heated, it splits up into nitrous oxide, N_2O, and water—

$$NH_4NO_3 = N_2O + 2H_2O.$$

This decomposition occasionally becomes very violent and an explosion may result. Ammonium nitrate is an endothermic substance, and as it is also a powerful oxidizing agent it is largely used as a constituent of explosives. A mixture of ammonium nitrate and aluminium powder is called "ammonal," and is one of the explosives used in Mills' bombs. "Amatol" is a mixture of 4 parts of ammonium nitrate with 1 part of trinitrotoluene ("T.N.T."). Ammonium nitrate explosives are usually fairly safe to handle.

Ammonium carbonate, $(NH_4)_2CO_3$, is made commercially by heating ammonium sulphate with powdered limestone ;

the sublimate obtained is crude ammonium carbonate. It contains also *ammonium bicarbonate*, NH_4HCO_3; and *ammonium carbamate*, $O=C\begin{<}{NH_2}{ONH_4}$, the ammonium salt of a peculiar acid called *carbamic acid*, $O=C\begin{<}{NH_2}{OH}$. If commercial ammonium carbonate is treated with a concentrated solution of ammonia it is converted into the normal carbonate, a white crystalline solid.

Ammonium sulphide.—Normal ammonium sulphide, $(NH_4)_2S$, is formed when a mixture of two volumes of ammonia and one of sulphuretted hydrogen, H_2S, is cooled to $-18°$. It is a white crystalline solid, readily decomposing even in solution, into ammonia and *ammonium hydrogen sulphide*, NH_4HS—

$$(NH_4)_2S = NH_3 + NH_4HS.$$

The latter compound may also be formed by passing sulphuretted hydrogen into a strong solution of ammonia until no more will dissolve.

The solution of the ammonium hydrogen sulphide so obtained is colourless when freshly prepared, but slowly goes yellow on exposure to air. The same yellow solution may be made by adding sulphur to the warm colourless solution of ammonium hydrosulphide. It contains *ammonium polysulphides*, $(NH_4)_2S_x$, of which the chief is said to be $(NH_4)_2S_4$. The yellow colour assumed by the colourless solution of ammonium hydrogen sulphide on exposure to air is therefore to be explained by (i) oxidation, with liberation of sulphur, followed by (ii) solution of the sulphur in excess of ammonium hydrogen sulphide to form ammonium polysulphides.

"Yellow ammonium sulphide" (as it is called) is used in qualitative analysis and also as a reducing agent in organic chemistry.

Composition of Ammonia.—The vapour density of ammonia is 8·5, hence the molecular weight is 17. As the

atomic weight of nitrogen is 14, the formula must be NH_3. Additional evidence can be obtained in the following ways—

(i) A measured volume of ammonia is placed in a eudiometer tube over mercury and sparked until no further change in volume occurs. The gas is now practically completely (98 per cent.) decomposed into nitrogen and hydrogen. The volume is noted, and a measured excess of oxygen introduced and a spark passed. Explosion occurs, all the hydrogen present being converted into steam, which condenses to liquid water, the volume of which is negligible compared with the volumes of the gases in the experiment. After cooling, the residual volume is noted. From the results, a formula for ammonia may be calculated. *Example*—

Volume of ammonia taken = 15 c.c.
Volume of mixture of nitrogen and hydrogen formed = 30 c.c.
Volume after addition of oxygen = 58 c.c.
Volume after explosion = 24·25 c.c.
∴ Contraction on explosion = 33·75 c.c.

Of this, ¾ will be hydrogen, since 2 volumes of hydrogen combine with 1 volume of oxygen to form water.
i.e. 22·5 c.c.
But volume of nitrogen + hydrogen = 30 c.c.
∴ Volume of nitrogen = 30 − 22·5 = 7·5 c.c.
∴ 15 c.c. of ammonia yield 7·5 c.c. nitrogen and 22·5 c.c. hydrogen.
∴ 2 volumes ,, ,, 1 volume ,, ,, 3 volumes ,,
∴ by Avogadro, 2 molecules of ammonia yield 1 molecule nitrogen and 3 molecules hydrogen.
∴ 2 molecules of ammonia consist of 2 atoms of nitrogen and 6 of hydrogen.
∴ 1 molecule of ammonia contains 1 atom of nitrogen and 3 of hydrogen, and the formula is NH_3.

(ii) HOFMANN'S METHOD.—A long tube (Fig. 74), fitted at each end with a tap and with a funnel attached at one end, is filled with chlorine. In the funnel is placed concentrated ammonia solution. On this entering the tube drop by drop, vigorous reaction occurs and the tube becomes filled with white fumes of ammonium chloride. After the reaction is complete the top tap is turned off, and the tube is placed in a pneumatic trough containing water. The bottom tap is then opened, when water rushes in, and after levelling, the residual gas is found to occupy one-third of the volume of the original chlorine. This residual gas proves to be nitrogen. The

hydrogen which was combined with this nitrogen in ammonia has been removed by the chlorine; now chlorine combines with its own volume of hydrogen, therefore the volume of hydrogen which was combined with the residual nitrogen is three times the volume of the latter. In other words, the ammonia consists of nitrogen and hydrogen combined together in the proportion by volume of 1 to 3. Hence, by Avogadro's Hypothesis, the molecule of ammonia must be $(NH_3)x$; in other words, the *empirical* formula of ammonia is NH_3. The *true* formula cannot be determined by Hofmann's method, which is therefore not so good as that given under (i).



FIG. 74.

x may of course be found by a vapour density determination.

Tests for Ammonia and Ammonium Salts.—All ammonium salts when heated with caustic soda solution evolve ammonia, which may be detected by the smell and by its action on moist red litmus.

NESSLER'S solution gives a yellow precipitate or coloration with an alkaline solution of an ammonium salt. Nessler's solution is a solution of potassium mercuri-iodide, K_2HgI_4, made by adding potassium iodide solution to a solution of mercuric chloride till the first-formed precipitate of mercuric iodide is just redissolved—

$$2KI + HgCl_2 = 2KCl + HgI_2.$$
$$HgI_2 + 2KI = K_2HgI_4.$$

The yellow precipitate given with ammonia is NHg_2I. This test for ammonia is used in water-analysis. Under suitable conditions it will detect 1 part of ammonia in 2,000,000 of water.

Hydrazine, N_2H_4, is prepared by the action of sodium hypochlorite upon ammonia solution in the presence of glue, which acts as a negative catalyst on the decomposition of the hydrazine so formed—

$$NaOCl + NH_3 = NaOH + NH_2Cl.$$
$$NH_2Cl + NH_3 = N_2H_4 + HCl.$$

It is a colourless crystalline solid (M.P. about 1° C.) with a weakly basic reaction in aqueous solution. Its derivatives, especially *phenylhydrazine*, $C_6H_5.NH.NH_2$, are more important than the base itself.

Hydrazoic acid, N_3H, may be obtained as follows. *Sodamide*, $Na.NH_2$, is first made by heating sodium in dry ammonia. This is then heated in nitrous oxide, when sodium hydrazoate is formed—

$$NaNH_2 + N_2O = H_2O + NaN_3.$$

The sodium hydrazoate is now decomposed with dilute sulphuric acid and the liquid distilled, when an aqueous solution of hydrazoic acid collects in the receiver.

Pure hydrazoic acid is a colourless, volatile and very explosive liquid, boiling at 37°. The lead salt, $Pb(N_3)_2$, has been used as a detonator, but is not so useful for this purpose as the more generally employed mercury fulminate.

Hydroxylamine, $NH_2.OH$.—This is a colourless deliquescent crystalline solid, which may be obtained by reducing nitric oxide with tin and hydrochloric acid, by the electrolytic reduction of nitric acid (BOEHRINGER, TAFEL and others), and by the action of sulphur dioxide upon a solution of sodium carbonate and sodium nitrite. It is a powerful reducing agent and is extensively used in organic chemistry, since it gives beautifully crystalline compounds called *oximes* with aldehydes, ketones, and other substances containing the carbonyl group, $>CO$. *Example*—

$$\begin{matrix} CH_3 \\ \diagdown \\ \quad >CO \\ \diagup \\ CH_3 \\ \text{Acetone.} \end{matrix} + H_2N.OH = \begin{matrix} CH_3 \\ \diagdown \\ \quad >C = N.OH \\ \diagup \\ CH_3 \\ \text{Acetone oxime or acetoxime.} \end{matrix} + H_2O.$$

Hydroxylamine is a basic substance and readily forms salts by addition. It is usually kept in the laboratory in the form of its hydrochloride, $NH_2OH.HCl$.

Oxides of Nitrogen.—Nitrogen forms five oxides—

N_2O, nitrous oxide.

NO, nitric oxide.

N_2O_3, nitrogen trioxide or nitrous anhydride.
N_2O_4 or NO_2, nitrogen peroxide or tetroxide.
N_2O_5, nitrogen pentoxide or nitric anhydride.

and four oxyacids—

$H_2N_2O_2$, hyponitrous acid.
$H_2N_2O_3$, nitrohydroxylaminic acid.
HNO_2, nitrous acid.
HNO_3, nitric acid.

Since the starting-point for the preparation of all the rest of these compounds is nitric acid, it is convenient to study this substance first.

Nitric Acid, HNO_3.

Nitric acid was probably known to the Arabian chemists

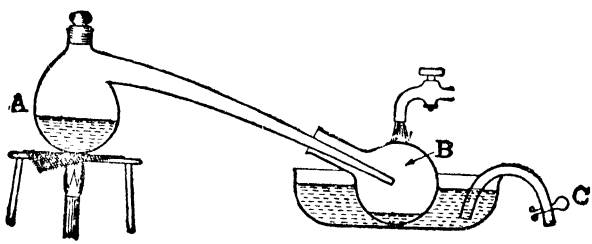


FIG. 75.—Preparation of Nitric Acid.

of the eighth century ; it was certainly prepared by " GEBER " in the thirteenth century, who gives detailed instructions for the operation—

" First ℞ of *vitriol* of *Cyprus*, *lib.* 1. of *Saltpeter*, *lib.* 1½, and of *Jamenous Allom* one fourth part ; extract the *Water* with *Redneſs* of the *Alembeck* (for it is very *Solutive*) and vſe it in the before alleadged *Chapters*. This is alſo made much more acute, if in it you ſhall diſſolve a fourth part of *Salammoniac* ; becauſe that diſſolves *Gold*, *Sulphur*, and *Silver*." (The " more acute " liquid is of course *aqua regia*.) [1]

The first chemist to make nitric acid by the action of sulphuric acid upon potassium nitrate was GLAUBER (1650)

[1] *i.e.*, a mixture of nitric and hydrochloric acids.

LAVOISIER in 1776 showed that it contained oxygen, and CAVENDISH (1784) proved that it contained hydrogen and nitrogen as well.

Preparation.—Nitric acid is prepared in the laboratory, and also commercially, by heating potassium or sodium nitrate with concentrated sulphuric acid—

(i) $KNO_3 + H_2SO_4 = KHSO_4 + HNO_3$,

and, on further heating,

(ii) $KHSO_4 + KNO_3 = K_2SO_4 + HNO_3$.

In practice, the action is never taken beyond the first stage,

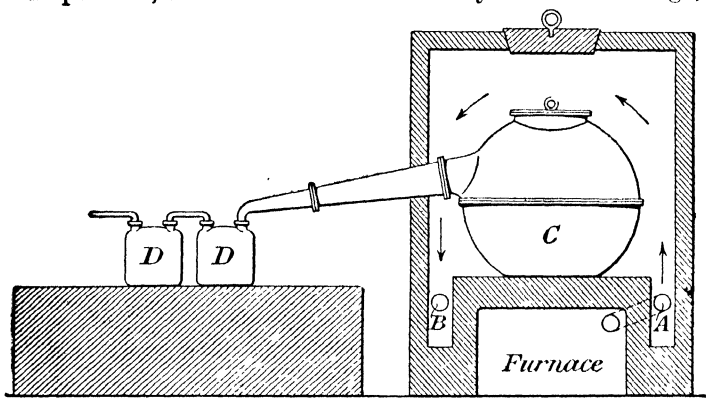


FIG. 76.—Manufacture of Nitric Acid.

A. Entrance for furnace gases. *B*. Exit for furnace gases. *C*. Iron retort. *D*. Receivers.

as the temperature required for the second is so high that much of the nitric acid is decomposed.

The distillate consists of nitric acid mixed with a little water, which may be removed by addition of concentrated sulphuric acid followed by redistillation. The acid so obtained is of a yellow colour; this is due to the presence in it of the yellow gas nitrogen peroxide. If a current of dry air or dry carbon dioxide is blown through the acid the nitrogen peroxide is swept away and the resulting acid is colourless.

Manufacture.—Much nitric acid is made, as already described, by heating sodium nitrate (Chile saltpetre) with concentrated sulphuric acid. However, the supplies of Chilean nitrate will eventually be exhausted, and in view of this fact, attempts were made to convert atmospheric nitrogen into nitric acid. For many years no appreciable advance was made toward the solution of this problem, but it has now been successfully solved. It is, indeed, reported that Germany had decided on war in 1913, but was forced to wait until 1914 because her chemists were not quite satisfied with the methods for converting nitrogen from the air into nitric acid. Once these methods were perfected, Germany became independent of Chilean nitrate, and therefore had no fear of a shortage of explosives or artificial manures.

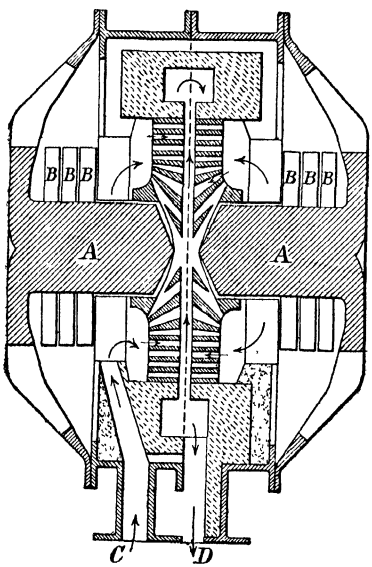


FIG. 77.—Birkeland Eyde Furnace.
A. Core. *B.* Winding. *C.* Gas entrance. *D.* Gas exit.

The methods of manufacture of nitric acid from the air are of two sorts—

(i) Direct combination of nitrogen and oxygen to form oxides of nitrogen at the temperature of the electric arc; nitric acid is then made by dissolving these oxides in water.

(ii) Oxidation of synthetic ammonia (*q.v.*) to oxides of nitrogen and preparation of the nitric acid from these oxides as in (i).

(i) The first successful method of converting the oxygen and nitrogen of the air into oxides of nitrogen on a commercial scale was invented by the Scandinavian scientists BIRKE-

LAND and EYDE in 1903. They pass air through an electric arc which is drawn out into a thin disc of flame by means of a powerful electromagnet. The disc of arc is some 6–8 feet in diameter, and is enclosed in an iron furnace lined with resistant material. The issuing gas contains about 2 per cent. of nitric oxide, NO. The hot gases are cooled by passing through pipes in a boiler, and the steam that is thus produced is used to concentrate the solution of nitrates obtained in the process. During the cooling the nitric oxide present combines with oxygen of the excess of air to form nitrogen peroxide (about 600° C.). The gas is then passed up an iron or granite tower down which water is sprayed, where part of the nitrogen peroxide is converted into nitric acid and part into nitric oxide—

(i) $2NO_2 + H_2O = HNO_3 + HNO_2$.
(ii) $2HNO_2 = H_2O + NO + NO_2$.

The nitric oxide is immediately converted into nitrogen peroxide again by the excess of air present, and thus by having a sufficiently large number of condensing towers practically all the nitrogen peroxide originally present is converted into nitric acid. The solution of nitric acid that collects at the base of the towers is pumped up and sprayed in again until it reaches a concentration of about 35 per cent. It is then neutralized by lime and converted into calcium nitrate, which can be obtained, by evaporation of the solution, as a white solid. As normal calcium nitrate is deliquescent, it is troublesome to transport and handle, so that it is usually converted into a non-deliquescent *basic calcium nitrate* (*Norwegian saltpetre* or *air saltpetre*) by addition of a suitable weight of lime.

"Norwegian saltpetre" is largely used as an artificial manure; for many purposes it is better than sodium nitrate, as the lime it contains very often improves the tilth of the soil.

Sodium nitrite, $NaNO_2$, is obtained as a by-product in the above process, by absorbing the residual oxides of nitrogen in a further tower down which a cool dilute solution of sodium hydroxide or carbonate trickles. The commercial success of Birkeland and Eyde's process depends upon cheap electrical

power such as is supplied by the numerous waterfalls of Norway.

In the *Badische Process*, worked at Ludwigshafen, the arc is drawn out into a thin flame some 30 feet in length. Special forms of apparatus are used to remove the nitric oxide as soon as it is formed and to cool it rapidly.

(ii) That nitric acid may be made by the oxidation of ammonia has been known since 1788, and the French appear to have made it in this way for munition purposes during the Peninsular Wars, but the process had no commercial value until quite recently, after the problem of making synthetic ammonia had been successfully solved (p. 340). The reaction which takes place may be represented by the equation—

$$4NH_3 + 5O_2 = 4NO + 6H_2O,$$

the nitric oxide thus formed being converted into nitric acid as described under (i). The final result may be expressed thus—

$$NH_3 + 2O_2 = HNO_3 + H_2O.$$

For successful oxidation of ammonia by air, the gases must be carefully purified and passed over a suitable catalyst (generally platinum gauze) at a temperature of 500–550° C. The reaction is exothermic, so that after starting it proceeds automatically. An alloy of iron and bismuth or iron and copper has occasionally been substituted for the platinum; different catalysts require different temperatures for maximum efficiency.

Properties.—Nitric acid is a colourless fuming liquid of sp. gr. 1·53 and m.p. −41°. Ordinary "commercial" concentrated nitric acid contains 68 per cent. by weight of pure acid. When nitric acid is boiled it partially dissociates into nitrogen peroxide, oxygen, and water—

$$4HNO_3 \rightleftharpoons 4NO_2 + O_2 + 2H_2O.$$

Nitric acid is the strongest acid known, being equally strong with hydrochloric acid. It is also a powerful oxidizing agent, and these two characteristics often clash. When nitric acid acts upon metals, we may imagine that hydrogen is first

formed, in the usual way, but that the excess of nitric acid then oxidizes the hydrogen and is itself reduced. Reduction of nitric acid may go on in various stages—

(i) $2HNO_3 + 2H = 2H_2O + 2NO_2$, nitrogen peroxide.
(ii) $2HNO_3 + 4H = 3H_2O + N_2O_3$, nitrous anhydride.
(iii) $2HNO_3 + 6H = 4H_2O + 2NO$, nitric oxide.
(iv) $2HNO_3 + 8H = 5H_2O + N_2O$, nitrous oxide.
(v) $2HNO_3 + 10H = 6H_2O + N_2$, nitrogen.
(vi) $2HNO_3 + 12H = 4H_2O + 2NH_2OH$, hydroxylamine.
(vii) $2HNO_3 + 16H = 6H_2O + 2NH_3$, ammonia.

Any or all of these products may therefore be obtained when nitric acid acts upon a metal. Of course, in the cases of the basic substances ammonium and hydroxylamine, the nitrates of these bases would be obtained, and not the free bases. With magnesium, dilute nitric acid reacts so rapidly that some of the hydrogen escapes oxidation and may be detected in the gases evolved.

The stage to which the reduction of nitric acid is carried, in the reaction of this substance with metals, depends upon various factors—

(i) *Concentration of the acid.*—Since solutions of metallic nitrates have very little oxidizing power, we can conclude that the oxidizing powers of nitric acid are due chiefly to the undissociated HNO_3 molecules and not to the NO_3' ions. But nitric acid is a strong acid, i.e. it readily dissociates in solution. We should therefore expect that dilution of the acid would cause a great diminution in oxidizing power, and this is indeed the case.

(ii) *The temperature.*—Reduction as a rule proceeds further with rise of temperature, but this is by no means always true.

(iii) *The nature of the metal.*—Powerful reducing agents, such as zinc, will carry the reduction to a lower stage than will metals like copper.

(iv) *The nature of the products of the reaction,* if these remain in solution.

EXAMPLES OF THE ACTION OF NITRIC ACID.

(i) *Lead.* $Pb + 4HNO_3 = Pb(NO_3)_2 + 2H_2O + 2NO_2$.

(ii) *Copper.* $3Cu + 8HNO_3 = 3Cu(NO_3)_2 + 4H_2O + 2NO.$
(iii) *Zinc.* $4Zn + 10HNO_3 = 4Zn(NO_3)_2 + 3H_2O + NH_4NO_3.$
(iv) *Tin.* $5Sn + 20HNO_3 = H_{10}Sn_5O_{15} + 5H_2O + 20NO_2.$

$H_{10}Sn_5O_{15}$ is a white insoluble substance called *metastannic acid*; on heating it decomposes into *stannic oxide* and water—

$$H_{10}Sn_5O_{15} = 5SnO_2 + 5H_2O.$$

It must be realized that these equations are only approximate, since the actual reactions are much more complicated and vary according to the conditions.

(v) *Sulphur* → sulphuric acid, H_2SO_4.
(vi) *Phosphorus* → phosphoric acid, H_3PO_4.
(vii) *Iodine* → iodic acid, HIO_3.
(viii) *Arsenic* → arsenic acid, $HAsO_3$.

(ix) *Ferrous sulphate* reduces nitric acid to nitric oxide, which combines with excess of ferrous sulphate to form a dark brown compound $(FeSO_4)_2.NO$. This is the principle of the "*brown-ring*" test for nitrates. The suspected nitrate is dissolved in a little water and a few drops of ferrous sulphate solution added. Sulphuric acid is then carefully poured in and sinks to the bottom as a lower layer. Where the two layers meet, a brown ring is formed if a nitrate is present. Nitric acid is first liberated by the sulphuric acid and then reduced by the ferrous sulphate as above—

$$6FeSO_4 + 3H_2SO_4 + 2HNO_3 = \underset{\text{Ferric sulphate.}}{3Fe_2(SO_4)_3} + 2NO + 4H_2O$$

$$4FeSO_4 + 2NO = 2(FeSO_4)_2NO.$$

(x) With *bases*, nitric acid yields *nitrates*, all of which are soluble with the exception of that of an organic base, *diphenylendoanilodihydrotriazole*. This substance is therefore used, under the name of "Nitron," as a test for nitric acid or a nitrate, with a solution of which it gives a white precipitate of "Nitron" nitrate.

Action of heat on the nitrates—

A. *Potassium* and *sodium* nitrates first melt, then evolve oxygen; the *nitrite* of the metal is left—

$$2KNO_3 = 2KNO_2 + O_2.$$

B. *Ammonium* nitrate yields nitrous oxide—

$$NH_4NO_3 = N_2O + 2H_2O.$$

C. Nitrates of *heavy metals*, except silver and mercury, yield the oxide of the metal, nitrogen peroxide, and oxygen—

$$2Pb(NO_3)_2 = 2PbO + 4NO_2 + O_2.$$

D. *Silver* and *mercury* nitrates yield the metal, nitrogen peroxide, and oxygen—

$$Hg(NO_3)_2 = Hg + 2NO_2 + O_2.$$

Solid nitrates are powerful oxidizing agents and are therefore used in the preparation of explosives. Gunpowder, for instance, consists of potassium nitrate (75 per cent.), with sulphur (10 per cent.), and charcoal (15 per cent.).

(xi) With *organic compounds*, nitric acid acts in two ways: (*a*) as an oxidizing agent, or (*b*) as a *nitrating* agent.

(*a*) Dilute nitric acid will readily oxidize compounds of the hydrocarbon benzene, C_6H_6. Thus, toluene, $C_6H_5.CH_3$, is oxidized by dilute nitric acid to *benzoic acid*, $C_6H_5.COOH$. Xylene, $C_6H_4(CH_3)_2$, is converted into *phthalic acid*, $C_6H_4(COOH)_2$.

(β) Upon the "fatty" compounds, of which methane, CH_4, is the parent substance, dilute nitric acid has little action, but when it does react it usually introduces one or more $-NO_2$ groups into the molecule; this action is called *nitration*.

(γ) Concentrated nitric acid *nitrates* benzene compounds. Thus if benzene itself is shaken with a mixture of nitric and sulphuric acids, *nitrobenzene*, $C_6H_5NO_2$, is formed in the cold, and *dinitrobenzene*, $C_6H_4(NO_2)_2$, on heating—

$$C_6H_6 + HNO_3 = C_6H_5.NO_2 + H_2O.$$
$$C_6H_6 + 2HNO_3 = C_6H_4(NO_2)_2 + 2H_2O.$$

These nitrocompounds are often highly explosive, e.g. lyddite or *picric acid*, $C_6H_2(NO_2)_3.OH$, made by acting upon phenol, C_6H_5OH, with nitric and sulphuric acids, and T.N.T. or *trinitro-toluene*, $C_6H_2(NO)_3.CH_3$, were both largely used in the war as high explosives. They burn quietly if

ignited, but explode violently if detonated by the explosion of a " cap " of mercury fulminate or lead hydrazoate, etc.

(δ) Concentrated nitric acid on fatty compounds acts as an oxidizing agent. Thus, if cane-sugar, $C_{12}H_{22}O_{11}$, is warmed with the concentrated acid, volumes of brown fumes (nitrogen peroxide) are given off, and a solution of oxalic acid, $\begin{matrix}COOH\\|\\COOH\end{matrix}$, an oxidation product of sugar, is left.

(ε) With certain organic compounds containing hydroxyl groups (—OH), such as glycerol and cellulose, nitric acid forms true *nitrates*, for instance,

$$\begin{matrix}CH_2.OH\\|\\CH.OH\\|\\CH_2.OH\\\text{Glycerol.}\end{matrix} \quad \begin{matrix}HNO_3\\\\HNO_3\\\\HNO_3\end{matrix} = \begin{matrix}CH_2.NO_3\\|\\CH.NO_3\\|\\CH_2.NO_3\\\text{Glyceryl trinitrate.}\end{matrix} + 3H_2O.$$

Glyceryl trinitrate is a colourless very explosive oil commonly but incorrectly called " nitroglycerine." The above reaction is reversible ; hence sulphuric acid is added to absorb the water as soon as it is formed and thus prevent the reverse action. *Dynamite* is a powder made by absorbing " nitroglycerine " in *kieselguhr*, a siliceous earth composed of the remains of minute sea-organisms. In America, it is usual to replace the kieselguhr by wood-powder.

The action of concentrated nitric acid upon cellulose (cotton-wool) results in the formation of the so-called " nitrocelluloses " or *gun-cottons* and *collodions*. Gun-cotton has the empirical formula $C_{12}H_{14}(NO_3)_6O_4$; it is used as a " *brisant* " explosive, but not as a " propellant." It has to be detonated ; it burns quite quietly if ignited.

Oxides of Nitrogen.

Nitrous oxide, N_2O.—This substance was discovered by Priestley in 1772, but more carefully investigated by Davy (1799). Davy showed that it could be made by heating ammonium nitrate—

$$NH_4NO_3 = N_2O + 2H_2O,$$

and called it nitrous oxide.

Davy's method still remains the best way of preparing nitrous oxide, but as the decomposition of ammonium nitrate occasionally becomes explosively violent, it is safer to use a mixture of sodium nitrate and ammonium sulphate.

Nitrous oxide is also formed when nitric acid is reduced by means of stannous chloride and hydrochloric acid—

$$2HNO_3 + 4SnCl_2 + 8HCl = 4SnCl_4 + 5H_2O + N_2O.$$

The gas may be purified from nitric oxide (which is often present as an impurity in nitrous oxide made from ammonium nitrate) by passing through ferrous sulphate solution, when the nitric oxide is retained as the brown compound $(FeSO_4)_2NO$.

Properties.—Nitrous oxide is a colourless gas with a sweet and not unpleasant smell. It is soluble in cold water and is therefore usually collected over hot water, although, since it has a density of 22 (air = 14·4), it may conveniently be collected by downward displacement when cold. If the gas is required dry, it is passed through strong sulphuric acid and collected over mercury.

Nitrous oxide is used as an anæsthetic in dentistry and minor surgical operations. It is sometimes called "laughing-gas," since the inhalation of a mixture of nitrous oxide and air produces hysterical laughter. "The celebrated Mr. Wedgewood, after breathing the gas for some time, threw the bag from him, and kept breathing on laboriously with an open mouth, holding his nose with his fingers, without power to remove them, though aware of the ludicrousness of his situation; he had a violent inclination to jump over the chairs and tables, and seemed so light, that he thought he was going to fly." Nitrous oxide is an *endothermic compound*, and as it is very readily decomposed on heating into a mixture of nitrogen and oxygen, containing 33·3 per cent. by volume of the latter, substances burn very readily in it—nearly as well as in pure oxygen. The heat given out during the decomposition of the nitrous oxide assists in raising the

temperature and therefore aids the combustion. A glowing splint is re-lit by nitrous oxide, but the latter gas may easily be distinguished from oxygen by the following tests—

(i) Nitrous oxide has a characteristic sweet smell.

(ii) Nitrous oxide is much more soluble in cold water than is oxygen.

(iii) Nitrous oxide when mixed with nitric oxide gives no brown fumes of nitrogen peroxide, such as are given by oxygen with nitric oxide.

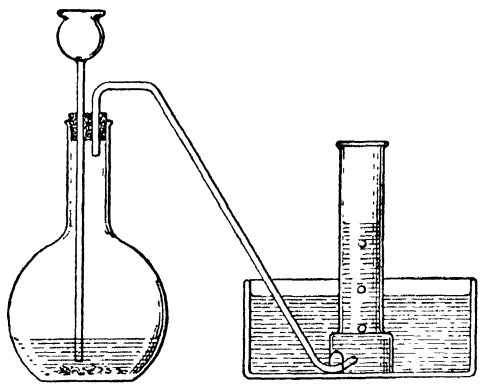


FIG. 78.—Preparation of Nitric Oxide.

(iv) On burning a piece of phosphorus in nitrous oxide, *the residual gas on cooling has the same volume as that of the nitrous oxide started with*—

$$5N_2 + 2P = \underset{\text{Solid.}}{P_2O_5} + 5N_2.$$

The last experiment shows us that 1 volume of nitrous oxide contains 1 volume of nitrogen,

$\therefore$ by Avogadro's Hypothesis,

1 molecule of nitrous oxide contains 1 molecule of nitrogen.

$\therefore$ formula is N_2O_x.

x is found by a vapour density determination,

V.D. = 22 $\therefore$ M.W. = 44.

Of these 44 parts, 28 are nitrogen, ∴ 16 are oxygen. But 16 is the A.W. of oxygen ∴ $x = 1$ and the formula is N_2O.

Nitric oxide, NO.—This oxide of nitrogen must of course have been obtained by the alchemists, two of the commonest of whose chemicals were nitric acid and copper, but it was first isolated and investigated by PRIESTLEY in 1772. Priestley obtained it by acting upon mercury or copper with nitric acid, and called it *nitrous air*. It is still usually prepared by Priestley's method—

$$3Cu + 8HNO_3 = 3Cu(NO_3)_2 + 4H_2O + 2NO.$$

The gas obtained in this way, however, is impure. It may be purified by absorption in ferrous sulphate solution with formation of the brown compound $(FeSO_4)_2NO$, followed by heat, when the brown compound splits up, yielding pure nitric oxide.

A pure gas may be obtained directly (i) by heating potassium nitrate and ferrous sulphate with dilute sulphuric acid, or (ii) by warming mercury with a solution of sodium nitrate in strong sulphuric acid—

(i) $2KNO_3 + 5H_2SO_4 + 6FeSO_4 = 3Fe_2(SO_4)_3 + 2NO + 4H_2O + 2KHSO_4$.

(ii) $6Hg + 2HNO_3 + 3H_2SO_4 = 3Hg_2SO_4 + 4H_2O + 2NO$.

Properties.—Nitric oxide is a colourless gas, which immediately combines with free oxygen when the two are brought into contact; it is therefore impossible to say whether it has any taste or smell. It is an endothermic substance, but more stable than nitrous oxide; it therefore does not support combustion unless the temperature of the burning substance introduced is sufficiently high to bring about rapid decomposition of the surrounding nitric oxide. If this decomposition occurs, the burning substance goes on burning in the oxygen liberated. Feebly burning phosphorus is extinguished if plunged into nitric oxide, but if strongly burning it continues to burn in the gas.

The composition of nitric oxide is determined by enclosing a measured volume in a eudiometer tube over mercury. The eudiometer contains a spiral of thick iron wire which may be

raised to a red heat by means of an electric current. On heating, the wire reacts with the nitric oxide, forming solid oxide of iron (whose volume is practically equal to that of the iron from which it came, and may therefore be neglected) and nitrogen. After cooling, it will be found that the volume of the residual nitrogen is half that of the nitric oxide taken.

1 volume of nitric oxide contains $\frac{1}{2}$ volume of nitrogen,

$\therefore$ by Avogadro's Hypothesis,

1 molecule of nitric oxide contains $\frac{1}{2}$ molecule of nitrogen,

$\therefore$ formula is NO_x.

x is found as for nitrous oxide.

Note that the composition of nitric oxide cannot conveniently be determined by explosion with hydrogen, as these two gases do not form an explosive mixture, unless a trace of nitrous oxide is present.

Nitric oxide is practically insoluble in water and may therefore be collected at the pneumatic trough; it is soluble in ferrous sulphate solution, nitric acid, acidified potassium permanganate and other substances. A mixture of carbon disulphide vapour and nitric oxide burns with a bright bluish flame, formerly used by photographers for taking flashlight photographs.

Nitrogen trioxide, N_2O_3, or nitrous anhydride, is formed by the action of nitric acid upon arsenious oxide—

$$2H_2O + As_2O_3 + 2HNO_3 = 2H_3AsO_4 + N_2O_3.$$
(Arsenic acid.)

The gas is dried by means of phosphorus pentoxide and then passed through a U-tube surrounded by a freezing-mixture, when a deep blue liquid is obtained. If this is further dried by standing over phosphorus pentoxide for some weeks, it may be boiled without decomposition, and the vapour density shows that the molecules are N_4O_6. In the presence of even a trace of moisture, decomposition begins, first into the monomolecular form, N_2O_3, and then into $NO_2 + NO$.

Ordinary gaseous "N_2O_3" is almost completely dissociated into nitrogen peroxide and nitric oxide. This mix-

ture is sometimes called " nitrous fumes " ; on solution in ice-cold water it yields *nitrous acid*—

$$N_2O_3 + H_2O = 2HNO_2,$$

and in an alkali, a nitrite—

$$N_2O_3 + 2NaOH = 2NaNO_2 + H_2O.$$

Nitrogen trioxide is therefore *nitrous anhydride*, the anhydride of nitrous acid.

Nitrogen peroxide, NO_2 or N_2O_4, or nitrogen dioxide, or nitrogen tetroxide.—This is the commonest oxide of nitrogen.

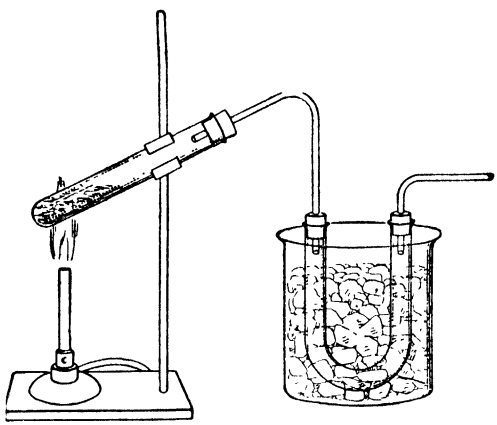


FIG. 79.—Preparation of Nitrogen Peroxide.

It is formed when nitric oxide comes into contact with free oxygen, when nitric acid acts upon certain metals and various organic compounds, and when the nitrates of heavy metals are heated. It is generally prepared in small quantity by the action of heat upon lead nitrate—

$$2Pb(NO_3)_2 = 2PbO + 4NO_2 + O_2.$$

The mixture of gases is passed through a U-tube surrounded by a freezing-mixture ; the oxygen passes on while the nitrogen peroxide condenses to a yellowish liquid.

A better method of obtaining nitrogen peroxide on a larger

scale is to pass sulphur dioxide into fuming nitric acid, keeping the liquid cold, until no more will dissolve. On heating the product, *nitrososulphuric acid*, with sodium nitrate a steady stream of fairly pure nitrogen peroxide is evolved—

(i) $SO_2 + HNO_3 = HSO_4.NO$.
(ii) $HSO_4.NO + NaNO_3 = N_2O_4 + NaHSO_4$.

Properties.—Nitrogen peroxide is at ordinary temperatures a reddish brown gas, consisting of a mixture of NO_2 and N_2O_4 molecules. It is convenient to give the name "nitrogen dioxide" to the gas consisting entirely of NO_2 molecules, "nitrogen tetroxide" to the liquid and solid forms consisting entirely of N_2O_4 molecules, and to call the ordinary gas "nitrogen peroxide." The dissociation of this substance has already been discussed (p. 83).

Nitrogen tetroxide is a pale yellow crystalline solid melting at −11° to a yellow liquid. This liquid boils under atmospheric pressure at 22°. At −11° it consists practically completely of N_2O_4 molecules, but as the temperature rises the liquid darkens and partially dissociates into NO_2 molecules. At the boiling point it consists of about 86 per cent. N_2N_4 molecules and 14 per cent. NO_2 molecules. At 150°, the gas consists entirely of nitrogen dioxide molecules, NO_2. Further heating causes dissociation into nitric oxide and oxygen—

$$\underset{\text{Pale yellow solid.}}{N_2O_4} \rightleftharpoons \underset{\text{Pale yellow liquid.}}{N_2O_4} \rightleftharpoons \underset{\text{Red gas.}}{2NO_2} \rightleftharpoons \underset{\text{Colourless gas.}}{2NO + O_2}.$$

Nitrogen peroxide dissolves in water to give a mixture of nitrous and nitric acids—

$$N_2O_4 + H_2O = HNO_2 + HNO_3,$$

and in alkalis to give a mixture of nitrate and nitrite—

$$N_2O_4 + 2NaOH = NaNO_3 + NaNO_2 + H_2O.$$

It is therefore a "mixed anhydride," being half-way between nitrous anhydride, N_2O_3, and nitric anhydride, N_2O_5.

It is a very strong oxidizing agent. It does not support combustion unless the temperature of the burning substance

is high enough to decompose the gas into nitrogen and oxygen. Thus a splint or taper is extinguished, but strongly burning phosphorus continues to burn. A mixture of hydrogen and nitrogen peroxide if passed over platinum black yields ammonia and steam. Carbon monoxide is oxidized to carbon dioxide by nitrogen peroxide, even at ordinary temperatures.

Interesting compounds called *nitroxyls* have been obtained by SABATIER and SENDERENS by the action of nitrogen peroxide on finely divided metals in the cold. They have the formula $M(NO_2)_x$, where M is an atom of the metal. (Cf. the *carbonyls*, p. 301.)

Nitrogen peroxide converts moist sulphur dioxide into sulphuric acid—

$$SO_2 + H_2O + NO_2 = H_2SO_4 + NO,$$

and is used for this purpose in the manufacture of sulphuric acid by the lead chamber process (p. 469).

Nitrogen pentoxide, N_2O_5, or nitric anhydride, was discovered by DEVILLE in 1849, who passed a stream of dry chlorine over dry silver nitrate in the cold—

$$4AgNO_3 + 2Cl_2 = 4AgCl + 2N_2O_5 + O_2.$$

It may also be obtained by mixing phosphorus pentoxide with concentrated nitric acid, and distilling off the nitrogen pentoxide formed—

$$2HNO_3 + P_2O_5 = \underset{\text{Metaphosphoric acid.}}{2HPO_3} + N_2O_5.$$

Properties.—It is a white deliquescent substance which explodes on heating and will dissolve in water with evolution of heat, forming nitric acid—

$$N_2O_5 + H_2O = 2HNO_3.$$

It is therefore nitric anhydride. Nitrogen pentoxide is a strong oxidizing agent.

Nitrous acid, HNO_2.—When nitrogen trioxide is dissolved in ice-cold water nitrous acid is formed—

$$N_2O_3 + H_2O = 2HNO_2.$$

Salts of this acid with the alkali metals may be obtained by heating the corresponding nitrates—

$$2NaNO_3 = 2NaNO_2 + O_2$$

or by passing nitrous fumes (p. 365) into a solution of the metallic hydroxide. The acid itself has never been isolated, as it very readily decomposes into nitric oxide, nitrogen peroxide and water, or into nitric oxide, nitric acid and water—

(i) $3HNO_2 = HNO_3 + 2NO + H_2O$.
(ii) $2HNO_2 \rightleftharpoons NO + NO_2 + H_2O$.

Potassium and sodium nitrites are the most important compounds of nitrous acid. They are pale yellow crystalline solids, readily soluble in water. When acted upon by a dilute acid they yield nitrous acid, which immediately begins to decompose according to the equations given above. The acid and its salts may act either as reducing agents or as oxidizing agents.

(*a*) *Oxidizing Reactions.*—In these reactions the nitrous acid may be considered to split up as follows—

$$4HNO_2 = 4NO + O_2 + 2H_2O.$$

Thus, with potassium iodide free iodine is obtained—

$$2KI + 2HNO_2 = 2KOH + I_2 + 2NO;$$

sulphur dioxide is oxidized to sulphuric acid—

$$SO_2 + 2HNO_2 = H_2SO_4 + 2NO;$$

and stannous chloride in the presence of hydrochloric acid is oxidized to stannic chloride—

$$SnCl_2 + 2HCl + 2HNO_2 = SnCl_4 + 2H_2O + 2NO.$$

(*b*) *Reducing Reactions.*—In these changes, the nitrous acid is oxidized to nitric acid and can therefore bring about reduction—

$$2HNO_2 + O_2 = 2HNO_3.$$

Thus nitrous acid reduces potassium permanganate solution acidified with sulphuric acid, especially on warming—

$$2KMnO_4 + 3H_2SO_4 + 5HNO_2 = 5HNO_3 + K_2SO_4 + 2MnSO_4 + 3H_2O.$$

This reaction is used as a means of estimating the strength of a solution of nitrous acid or a nitrite. It is best to add a measured volume of the solution of the nitrite to a measured volume, in excess, of standard permanganate, acidified as usual; the liquid is then warmed and the excess of permanganate estimated by titration with standard ferrous ammonium sulphate or oxalic acid.

Nitrites occasionally occur in drinking-water, where their presence probably indicates contamination of the water by sewage or other organic matter. They are tested for in water analysis by means of a solution of *m*-phenylenediamine, $C_6H_4(NH_2)_2$, in excess of hydrochloric acid. This reagent gives a brown colour with a nitrite.

Sodium nitrite is largely used in the aniline dye industry.

Hyponitrous acid, $H_2N_2O_2$, is obtained as a white flaky crystalline solid by evaporating the ethereal solution made by adding silver hyponitrite to a dry solution of hydrogen chloride in ether. The silver chloride precipitated in the action is filtered off before the solution is evaporated.

$$Ag_2N_2O_2 + 2HCl = 2AgCl + H_2N_2O_2.$$

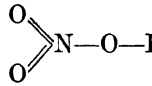
Hyponitrous acid is an explosive substance. The sodium salt is prepared by reducing sodium nitrite with sodium amalgam and water; the silver salt may be obtained as a yellow precipitate by double decomposition of the sodium salt and silver nitrate.

Nitrohydroxylaminic acid, $H_2N_2O_3$.—When methyl nitrate, CH_3NO_3, is added to a solution of hydroxylamine and caustic soda in methyl alcohol, a white precipitate of the sodium salt of nitrohydroxylaminic acid, $Na_2N_2O_3$, is obtained. The free acid itself is unknown. Addition of dilute hydrochloric acid to the sodium salt causes a vigorous effervescence with liberation of nitric oxide. Nitric oxide may perhaps be regarded as the anhydride of nitrohydroxylaminic acid, though the reaction—

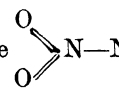
$$2NO + H_2O = H_2N_2O_3$$

has never been observed.

Constitution of Nitric and Nitrous Acids.—Nitric acid

is considered to have the structure represented by the formula  . Nitrous acid could then be either

 or $O = N—O—H$.

In practice, it is found that sodium nitrite behaves in two different ways, as if it had both the structure  , and also that expressed by the formula $O = N — ONa$. It is an example of a tautomeric substance. (Cf. sulphurous acid, p. 466.)

The Nitrogen Cycle.—Nitrogen is an essential constituent of living matter. Plants require it to be presented to them in the form of *nitrates*, which they take up in solution through their roots, from the soil. In the course of the life-process of the plant, the nitrogen of the nitrates becomes converted into complex nitrogenous organic compounds called *proteins*. The fate of these proteins is twofold. The plant may die, in which case the proteins it contains are returned to the soil; or it may be eaten by an animal, when the protein is digested and becomes a part of the animal organism. During the life of the animal, proteins are continually being used up and the nitrogen excreted in the form of a less complicated organic substance such as *urea* (man) or *hippuric acid* (horses, etc.). If, therefore, dead plants and the excreta and dead bodies of animals are returned to the soil, the latter will not become impoverished of nitrogen, but the nitrogen returned in this way will be of no direct use to plants, which must have it in the form of nitrates. Luckily there is an agency at work which converts organic nitrogenous compounds in the soil into nitrates. This agency is the *bacterial flora*. The soil swarms with bacteria, which cause "decay" of nitrogenous organic matter. The first product is ammonia; by the aid of the oxygen of the air one class of bacteria (the nitrite-forming

bacteria) converts the nitrogen of this ammonia into *nitrites*, and a second kind converts the nitrites into nitrates. (These two classes of bacteria are called the *nitrifying bacteria*.) In this way the cycle of changes undergone by the nitrogen in nature is complete (Fig. 80).

There are, however, several factors that modify this simple "nitrogen cycle." In the first place, there are certain species of soil bacteria that convert nitrates into *nitrogen*, which escapes into the air and is therefore lost; these are the

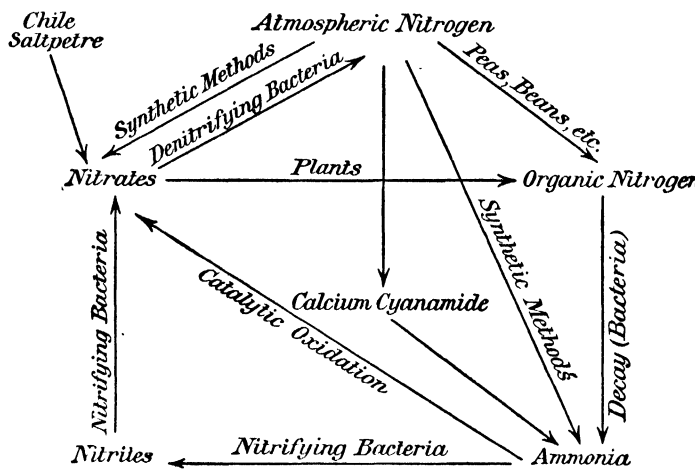


FIG. 80.

denitrifying bacteria. Secondly, a great deal of nitrogen is taken from the soil and never replaced, owing to our wasteful system of turning sewage into the sea whenever possible. Thirdly, in order to get sufficiently large crops to feed the population of the world, large quantities of nitrates or ammonium salts have to be added to soil, as artificial manures. Fourthly, certain plants, such as peas beans, and clover, have the power of making direct use of atmospheric nitrogen, by means of peculiar bacteria which live in nodules on their roots; but the enrichment of the soil brought about in this way and by the production of nitric acid in the air during thunder-

storms is not sufficient to make up for the annual drain on nitrogen content of the soil caused by growing and removing a crop.

In other words, for the establishment of a true equilibrium in the nitrogen cycle, at present much nitrogen has to be added to the soil, by man, in the form of nitrates or ammonium salts. The production of ammonium salts in the manufacture of coal-gas is far too little to supply the need, and the beds of Chile saltpetre are being rapidly exhausted. Hence the great importance of the recently-perfected methods of synthesizing nitric acid and ammonia, a problem to which the attention of chemists was fortunately directed in good time by the foresight of the late SIR WILLIAM CROOKES.

The complete *Nitrogen Cycle* may be represented by Fig. 80 on the previous page.

QUESTIONS

1. Describe the synthetic production of ammonia.
2. What are the chief properties of ammonia? What evidence have we that in ammonium compounds the nitrogen is pentavalent?
3. Compare the properties of ammonium salts with those of the alkali metals.
4. Describe the preparation and properties of hydroxylamine, hydrazine, and hydrazoic acid.
5. What oxides does nitrogen form? How are they made and what are their chief properties?
6. What do you understand by the Nitrogen Cycle?
7. Write an account of the various methods employed for the fixation of atmospheric nitrogen.
8. Discuss the action of nitric acid upon (*a*) metals, (*b*) organic compounds.
9. Are nitrites oxidizing agents or reducing agents? Illustrate your answer with examples. How would you estimate the strength of a solution of sodium nitrite?

PHOSPHORUS

Group in Periodic System: V; *Symbol:* P; *Valency:* 3 and 5; *Atomicity of Vapour:* 4; *Atomic Weight:* 31·02; *Melting Point:* 44°; *Specific Gravity:* 1·83.

History.—During the course of his chemical researches, BRAND of Hamburg discovered phosphorus. He made it, in

1669, by evaporating large quantities of urine to a thick syrup, mixing this with sand, and distilling. Brand sold the secret of his discovery to KRAFFT, who made a grand tour of Europe exhibiting the marvel at various Courts, including that of Charles II. The striking properties of the new substance excited the curiosity of chemists, and KUNCKEL (1678) and BOYLE (1680) independently discovered the way to prepare it. It was for long called *English phosphorus*, apparently on account of its preparation by Boyle.

In 1771 GAHN showed that phosphorus is present in bones, and SCHEELE devised a means of extracting it from bone-ash.[1] In 1772 LAVOISIER concluded that phosphorus was an element.

Occurrence.—Phosphorus is too reactive an element to exist naturally in the uncombined state. It is widely distributed, though in comparatively small quantity, in the form of *phosphates* or salts of phosphoric acid, H_3PO_4. The chief naturally occurring phosphates are *phosphorite* and *sombrerite*, impure $Ca_3(PO_4)_2$; *apatite*, $3Ca_3(PO_4)_2.CaF_2$; *chlorapatite*, $3Ca_3(PO_4)_2.CaCl_2$; *vivianite*, $Fe_3(PO_4)_2.8H_2O$; *wavellite*, $[Al_2(PO_4)_2]_2.Al_2(OH)_6.9H_2O$; *Redonda phosphate* (impure calcium phosphate); and *coprolites* (fossilized excreta containing calcium phosphate). It is an essential constituent of all living matter, and its presence in soil is therefore of the greatest importance. Soils poor in phosphorus have to be treated with phosphatic manures, such as *basic slag* (p. 549), or *calcium superphosphate* (p. 248). Calcium phosphate is the chief constituent of bones.

Preparation.—The actual details of modern manufacturing processes for the preparation of phosphorus are jealously guarded trade secrets, but the general principles are known.

(i) *Extraction from Bones.*—The bones are first treated with organic solvents such as benzene, carbon disulphide, ether, or acetylene tetrachloride (which has the great advantage of being non-inflammable) to remove fats; the residue is then heated with water under pressure, when a solution of glue is obtained. The solid left is then destructively distilled in iron

[1] A boy once told me in reply to a question on phosphorus, that "phosphorus was made by Scheele from Beau Nash"!

retorts in absence of air, when a distillate called bone-oil or DIPPEL'S oil comes over, and a mixture of finely divided carbon and calcium phosphate is left. This mixture is called *animal charcoal*, or *bone black*. It is employed as a decolourizing agent in the refinement of sugar, and after use in this way is burnt in the air, the residue consisting of bone-ash (about 80–85 per cent. calcium phosphate).

The bone-ash is treated with an equivalent weight of concentrated sulphuric acid, when calcium sulphate and a solution of phosphoric acid are formed—

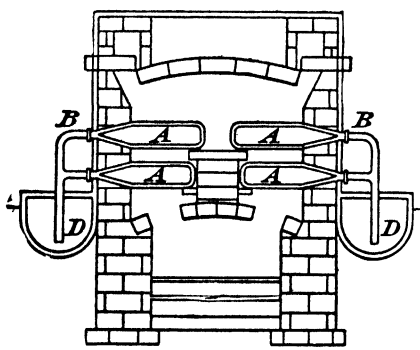


FIG. 81.—Bone Ash Phosphorus Furnace.
A. Retorts. *B*. Distilling pipe. *D*. Collecting pots

$$Ca_3(PO_4)_2 + 3H_2SO_4 = 3CaSO_4 + 2H_3PO_4$$

Orthophosphoric acid.

The calcium sulphate, which is insoluble, is allowed to settle and the clear solution of phosphoric acid run off and evaporated till it is of a syrupy consistency. The syrup consists of *meta*phosphoric acid, HPO_3—

$$H_3PO_4 = H_2O + HPO_3.$$

It is mixed with about one quarter of its weight of crushed and powdered coke and the mixture strongly heated in retorts of Stourbridge clay—

$$2HPO_3 + 6C = H_2 + 6CO + 2P.$$

Phosphorus vapour distils off and is condensed under water to a yellow liquid, which is purified by filtration through chamois leather and in other ways not known to the public. On cooling, the liquid phosphorus sets to a yellow crystalline solid. It is usually cast in sticks.

The extraction of phosphorus from bones is now obsolescent,

and will doubtless soon be replaced entirely by the modern process described in the next paragraph.

(ii) *Extraction from Mineral Phosphates.*—Nearly 100 years ago the German chemist WÖHLER suggested that phosphorus could be made by heating mineral phosphates with sand and coke to a very high temperature. This method was not used until 1898 owing to the difficulty of procuring at a reasonable cost the high temperature necessary for the reaction to occur, but in 1898 READMAN, ROBINSON, and PARKER solved the problem by using an electric furnace. Since that date, most of the phosphorus of commerce has been made by the electrical process, by the firm above-mentioned, by ALBRIGHT and WILSON (Niagara Falls), and by VIOLET (Paris and Lyons).

The phosphates are mixed with sand, SiO_2, and coke in the proportion (determined by analysis of the ore) to correspond with the equation—

$$Ca_3(PO_4)_2 + 5C + 3SiO_2 = \underset{\text{Calcium silicate.}}{3CaSiO_3} + 2P + 5CO.$$

The mixture is then heated to a high temperature by means of the electric arc struck between two stout carbon rods in a strong brickwork furnace. The calcium silicate melts and sinks to the bottom, whence it is run off as required; phosphorus vapour and carbon monoxide escape through a pipe at the top, and fresh mixture is added continuously by means of a hopper and screw arrangement, as shown in the figure. The process is thus continuous.

The phosphorus vapour is condensed under water in copper vessels and is purified as described in (i), or by melting under a solution of potassium dichromate and dilute sulphuric acid, which oxidizes the impurities and removes them from the phosphorus, or by redistillation, etc.

Properties.—When freshly prepared, phosphorus is a translucent pale yellow waxy crystalline solid, which can easily be cut with a knife. It gradually darkens on exposure to light, becoming finally very dark brown.

Its specific gravity is 1·8. It melts at 44° and boils at 290°.

The liquid and vapour are colourless, and vapour density determinations show that the molecule of the vapour is P_4. At high temperatures partial dissociation occurs—

$$P_4 \rightleftharpoons P_2 + P_2.$$

Phosphorus is practically insoluble in water but readily dissolves in many organic solvents, such as carbon disulphide, and also in phosphorus trichloride. It ignites in moist air at 30° C.

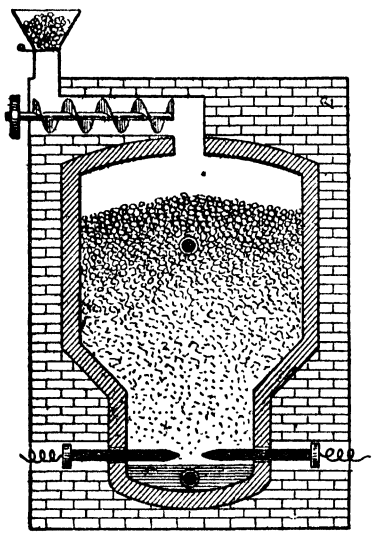


FIG. 82.—Electric Furnace for manufacture of Phosphorus.

The name "phosphorus" (*light-bearer*) was given to the element on account of its peculiar property of glowing in the dark. NICOLAS LEMERY, in his *Cours de Chimie* (1694), mentions certain practical jokes which had been carried out by means of the phosphorescence and ready ignition of phosphorus. He says that a piece of phosphorus was placed in the bed of a visitor to Boyle; a servant had to extinguish the conflagration by throwing buckets of water over both bed and visitor.

The glow is due to slow oxidation of the phosphorus, chiefly to *phosphorous oxide*, P_4O_6. When phosphorus is burnt in air or oxygen the main product is *phosphoric oxide* or phosphorus pentoxide, P_2O_5. Phosphorus will not burn in absolutely dry oxygen. The glow of phosphorus may be shown in an elegant manner by the following experiment. A few pieces of phosphorus are placed in a round-bottom flask with a little water. On boiling the water, phosphorus vapour passes up with the steam and oxidizes at the mouth of the flask with a greenish

flame, which is so cold that it will not burn paper or even set fire to a match.

Phosphorus is very chemically active. It will combine directly with halogens, oxygen and many metals. It is very poisonous, the vapour causing a disease called " phossy-jaw," or decay of the bones of the jaw (and of other parts of the body as well).

Red Phosphorus.—Phosphorus exists in many allotropic modifications; the form already described is called yellow, white, or *α*-phosphorus. If this form is heated in an inert atmosphere to 250° (especially in the presence of a trace of iodine as catalyst) it is converted into a red modification, ***red phosphorus***. This was discovered by SCHRÖTTER in 1845 and was considered to be amorphous until 1890, when RETGERS showed that it was minutely crystalline. Red phosphorus is important commercially, and is manufactured by heating the yellow form in a cast-iron pot to a temperature of 230–250°. It is important that the temperature should not rise above 250°, as at higher temperatures the reaction may become explosive. Thermometers are therefore placed in the pot and have to be encased in iron tubes, since hot phosphorus attacks glass.

Red phosphorus is not so chemically active as the yellow variety. It is so insoluble in water that it is non-poisonous when introduced into the alimentary canal; if, however, it is injected into the blood, the characteristic symptoms of phosphorus poisoning make their appearance. It will not dissolve in carbon disulphide, and has a high ignition point (260°). Its specific gravity is 2·25. It does not glow in moist air, and will not take fire spontaneously in chlorine, as the yellow form does.

Transformation of red phosphorus into yellow, and of yellow into red.

(i) *Yellow to red.* Heat to 240° in an inert atmosphere, with trace of iodine as catalyst.

(ii) *Red to yellow.* Heat in an inert atmosphere until the vapour is produced (above 550°). On rapidly cooling the vapour yellow phosphorus is formed.

There is no point at which yellow and red phosphorus can exist in equilibrium together; the yellow form is always unstable with regard to the red. Phosphorus is therefore a *monotropic* substance. (Cf. sulphur, p. 458.) The velocity of transformation of yellow into red at ordinary temperatures is so small that the yellow form *appears* to be stable. The vapour pressure of yellow phosphorus is greater than that of the red form at the same temperature, and the change of the yellow into the red is accompanied by evolution of 3,700 calories per gram-atom.

Other allotropic forms of phosphorus are known. SCHENCK'S *scarlet phosphorus* is important on account of its use in the match industry. It is prepared by boiling a solution of yellow phosphorus in phosphorus tribromide, PBr_3, until no further precipitation of the scarlet form occurs. It is more active than red phosphorus, but is non-poisonous and does not spontaneously oxidize in the air.

Matches.—Matches were invented by CHANCEL in 1805. The earliest forms consisted of wooden splints tipped with a mixture of potassium chlorate and sugar. To ignite these it was necessary to carry a bottle of sulphuric acid into which the match could be dipped. In spite of the inconvenience of this procedure, Chancel's matches were widely used for nearly half a century. Matches which ignite by friction were invented about 1840 by the Frenchman SAURIA and others, including GENERAL CONGREVE, an English officer. They consisted of strips of wood headed with a mixture of antimony sulphide, potassium chlorate and gum, and were ignited by rubbing vigorously on sandpaper. About the same time, a mixture of yellow phosphorus, sulphur and potassium chlorate was employed in match-making, but the disadvantage of these matches was that they often ignited at inconvenient moments. Nevertheless, yellow phosphorus matches were popular for many years until the effects on the workmen ("phossy-jaw") became so marked that laws were passed forbidding the use of such a poisonous and dangerous chemical.

"Strike anywhere" matches are now tipped with a mixture of Schenck's scarlet phosphorus, potassium chlorate, red lead,

gum and a colouring matter. "Safety" matches are made from a mixture of potassium chlorate, antimony sulphide, red lead, potassium dichromate and gum. They must be ignited by rubbing on a specially prepared surface (on the side of the box) containing red phosphorus, powdered sand or glass, antimony sulphide and gum. Most of the processes in the modern manufacture of matches are carried out by machinery.

COMPOUNDS OF PHOSPHORUS.—Phosphorus forms four hydrides—

PH_3, phosphine or "phosphoretted hydrogen."
P_2H_4, liquid hydrogen phosphide.
$P_{12}H_6$ and P_2H_2, solid hydrogen phosphides.

The true nature of these solids is still doubtful.

Phosphine, PH_3.—Phosphine was first prepared by GENGEMBRE in 1783, by heating yellow phosphorus with caustic potash solution. This method is still employed for laboratory preparation of the gas—

$$4P + 3KOH + 3H_2O = 3KH_2PO_2 + PH_3.$$

KH_2PO_2 is called potassium hypophosphite. To conduct the experiment caustic potash solution and some pieces of yellow phosphorus are placed in a round-bottomed flask fitted with a cork carrying a delivery tube and another tube which admits coal-gas. All air is first swept from the apparatus by a stream of coal-gas and the flask is then heated. Phosphine comes off, and as each bubble rises from the water of the trough into the air it ignites spontaneously and forms a vortex ring of white phosphorus pentoxide.

Phosphine may also be prepared by the action of water upon calcium phosphide, Ca_3P_2—

$$Ca_3P_2 + 6H_2O = 3Ca(OH)_2 + 2PH_3;$$

or by heating phosphorous acid—

$$4H_3PO_3 = 3HPO_3 + 3H_2O + PH_3;$$

or by the action of dilute caustic soda solution upon phosphonium iodide—

$$PH_4I + NaOH = NaI + H_2O + PH_3.$$

The gas prepared in the last two ways is much purer than that prepared by the first two, and is not spontaneously inflammable. The spontaneous ignition of phosphine is caused by the presence in the gas of traces of the liquid hydrogen phosphide, P_2H_4, which is itself spontaneously inflammable and thus sets fire to the phosphine. The liquid hydride may be removed by passing the gas through a U-tube surrounded by a freezing-mixture, which retains the P_2H_4 but allows the phosphine (no longer spontaneously inflammable)

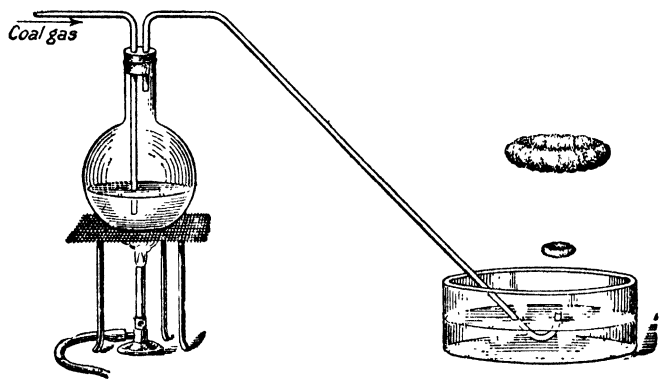


FIG. 83.—Preparation of Phosphine.

to pass on. Decomposition of phosphonium iodide is the best way of getting pure phosphine.

Phosphine is a colourless gas, only slightly soluble in water (*contrast ammonia*, p. 342). It has an unpleasant smell, reminiscent of decayed fish, and is extremely poisonous. The presence of traces of calcium phosphide in calcium carbide causes phosphine to be present as an impurity in ordinary acetylene, hence the bad smell of the gas. Pure acetylene has a sweetish and not at all unpleasant odour. Phosphine is a *basic anhydride*, like ammonia, for it will combine directly with acids to form *phosphonium salts*. The base, however, phosphonium hydroxide, PH_4OH, is unknown, and a solution of phosphine in water has no action on litmus. The chief

phosphonium compound is *phosphonium iodide*, PH_4I. It is prepared by mixing phosphorus and iodine in a current of carbon dioxide and then dropping water slowly on to the mixture—

$$9P + 5I + 16H_2O = 4H_3PO_4 + 5PH_4I.$$

The phosphonium iodide may then be sublimed off by gentle heat, and is obtained in the form of beautiful colourless crystals; it is decomposed if added to water or solutions of caustic alkalis, with evolution of phosphine. Phosphonium iodide and the chloride both dissociate on heating, as does ammonium chloride.

Phosphides of Metals.—These substances may be prepared by the action of phosphorus or phosphine upon solutions of certain metallic salts, such as silver nitrate and copper sulphate, which yield black precipitates of Ag_3P and Cu_3P_2 respectively. They may also be made by passing phosphorus vapour over the strongly heated metallic oxide, or by heating the phosphate of the metal with carbon in the electric furnace. The last method is used in the preparation of calcium phosphide. Commercial calcium phosphide is a reddish brown solid that yields spontaneously inflammable phosphine on treatment with water. Mixed with calcium carbide it is therefore used in *Holmes' signals*, which consist of tins containing the mixture, attached to a buoy. When required for use, the tins are pierced at each end and thrown into the sea. The acetylene evolved is ignited by the ignition of the phosphine it contains, and the sea is lit up.

Halogen Compounds of Phosphorus.—Phosphorus combines with the halogens to form two series of compounds, PX_3 and PX_5, where X = F, Cl, Br, or I. The chief of these compounds are *phosphorus trichloride*, PCl_3, *phosphorus pentachloride*, PCl_5, and *phosphorus tribromide*, PBr_3. In PX_3 the phosphorus atom is tervalent, in PX_5 it is quinquevalent.

Chlorides.—*Phosphorus trichloride* is prepared by passing chlorine through molten phosphorus in a retort from which all air has previously been removed by a stream of carbon dioxide. The phosphorus takes fire and burns in the chlorine.

and the phosphorus trichloride distils over as a colourless oily liquid. It fumes in the air and is decomposed by water with formation of phosphorous acid and hydrochloric acid—

$$PCl_3 + 3H_2O = H_3PO_3 + 3HCl.$$

It is extensively employed in organic chemistry for replacement of hydroxyl groups by chlorine atoms.

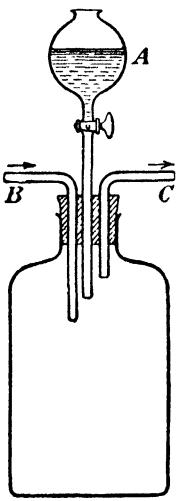


FIG. 84.—Preparation of Phosphorus Pentachloride.

A. Phosphorus trichloride. *B*. Chlorine in. *C*. Excess chlorine out.

Phosphorus pentachloride is made by allowing phosphorus trichloride to react with excess of chlorine. A convenient apparatus for the purpose is shown in the figure. It consists of a wide-necked jar fitted with a cork carrying a dropping-funnel and two delivery tubes. A current of dry chlorine is slowly passed through the jar, and the trichloride run in drop by drop from the funnel. Solid phosphorus pentachloride collects in the jar. It is a yellowish crystalline substance with a peculiar smell. It sublimes on heating and the vapour is dissociated into PCl_3 and Cl_2 (pp. 83, 124). It fumes in the air and is vigorously attacked by water; the first change results in the formation of a colourless oily liquid, *phosphorus oxychloride*, $POCl_3$, and this is then acted upon by more water, yielding *orthophosphoric acid*, H_3PO_4.

(i) $PCl_5 + H_2O = POCl_3 + 2HCl.$

(ii) $POCl_3 + 3H_2O = H_3PO_4 + 3HCl.$

Like the trichloride, phosphorus pentachloride is used in organic chemistry for replacing hydroxyl groups by chlorine atoms. Thus, if it is added to ethyl alcohol, a violent reaction occurs and ethyl chloride is formed—

$$C_2H_5OH + PCl_5 = C_2H_5Cl + POCl_3 + HCl,$$

while if benzoic acid and phosphorus pentachloride are ground together in a mortar the mass soon liquefies and volumes of

hydrochloric acid gas come off, benzoyl chloride being left—

$$C_6H_5.CO.OH + PCl_5 = C_6H_5.CO.Cl + POCl_3 + HCl.$$

Phosphorus tribromide is a colourless liquid, very similar to phosphorus trichloride, made by dropping bromine on to red phosphorus. The tribromide and tri-iodide are used in many organic and inorganic reactions, but are usually made *in situ* when required, by direct action of halogen upon phosphorus.

Oxides.—Phosphorus forms three oxides [1] and a doubtful fourth—[P_4O ? *phosphorus suboxide*], *phosphorous oxide*, P_2O_3, *phosphorus tetroxide*, P_2O_4, and *phosphoric oxide* (or *phosphorus pentoxide*), P_2O_5.

Phosphorous oxide, or *phosphorus trioxide*, P_2O_3, is formed, together with the pentoxide, when phosphorus is burnt in a limited supply of air. The phosphorus is burnt in a long hard glass tube, and the products of combustion passed through a plug of glass wool. This stops the pentoxide, which is a solid, but the more volatile trioxide, being still in the gaseous state, passes through and is condensed in a cooled U-tube. It is a white crystalline solid rather waxy in appearance. It melts at 23° and boils at 173°; it rapidly oxidizes in the air to the pentoxide, and dissolves in water, slowly in the cold but much more rapidly on heating, with formation of *phosphorous acid*, H_3PO_3. It may therefore be called phosphorous anhydride—

$$P_2O_3 + 3H_2O = 2H_3PO_3.$$

The vapour density of the trioxide is 110, corresponding to the double formula P_4O_6. As, however, all the chemical reactions in which the substance takes part can be satisfactorily expressed by using the formula P_2O_3, it is customary to use this formula, and not the double one which is no doubt more accurate. Phosphorus trioxide is a poisonous substance and smells of garlic.

Phosphorus tetroxide, P_2O_4, is formed when the trioxide is heated under pressure, $4P_2O_3 = 3P_2O_4 + 2P$.

It is a white crystalline solid, and resembles nitrogen

[1] Besson claims to have obtained P_2O as well, but this may be merely impure red phosphorus.

peroxide in dissolving in water to give a mixture of acids; in this case phosphorous and phosphoric acids. It is therefore a "mixed anhydride"—

$$P_2O_4 + 3H_2O = H_3PO_3 + H_3PO_4.$$

Phosphorus pentoxide, P_2O_5, is made by burning phosphorus in excess of air or oxygen. The commercial product always contains a little trioxide as impurity. The vapour density shows that the vapour consists chiefly of P_4O_{10} molecules, but the simple formula P_2O_5 is generally used as it satisfactorily expresses the chemical behaviour of the compound.

It is a white crystalline solid with a great affinity for water; it is, indeed, the most effective *drying-agent* known. It is very quickly turned to a semi-liquid mass, *metaphosphoric acid*, HPO_3, on exposure to air, and dissolves in water with a hissing noise forming metaphosphoric acid in the cold but orthophosphoric acid if the water is hot—

(i) $P_2O_5 + H_2O = 2HPO_3$.
(ii) $P_2O_5 + 3H_2O = 2H_3PO_4$.

In addition to its drying powers it possesses the property of taking the elements of water out of many substances which contain them. Thus it yields nitrogen pentoxide with nitric acid, sulphur trioxide with sulphuric acid, acetonitrile with acetamide, and carbon sub-oxide with malonic acid—

(i) $2HNO_3 - H_2O = N_2O_5$.
(ii) $H_2SO_4 - H_2O = SO_3$.
(iii) $CH_3.CO.NH_2 - H_2O = CH_3.CN$.
Acetamide. Acetonitrile.

(iv) $CH_2(COOH)_2 - 2H_2O = C_3O_2$.
Malonic acid. Carbon sub-oxide.

Phosphorus pentoxide is the anhydride of the phosphoric acids, *orthophosphoric acid*, *metaphosphoric acid*, and *pyrophosphoric acid*.

Oxyacids of Phosphorus.—Many oxyacids of phosphorus

are known, and some of them are of importance. We shall consider the following only—

Hypophosphorous acid, H_3PO_2.
Orthophosphorous acid, H_3PO_3.
Hypophosphoric acid, H_2PO_3.
Orthophosphoric acid, H_3PO_4.
Pyrophosphoric acid, $H_4P_2O_7$.
Metaphosphoric acid, HPO_3.

Hypophosphorous acid, H_3PO_2.—A sodium salt of this acid is formed when yellow phosphorus is boiled with caustic soda solution, as in the preparation of phosphine. Baryta-water instead of caustic soda yields the corresponding barium salt—

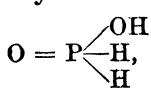
$$3Ba(OH)_2 + 8P + 6H_2O = 3Ba(H_2PO_2)_2 + 2PH_3.$$
Barium hypophosphite.

If the solution of the barium hypophosphite is first treated with carbon dioxide, to remove excess of baryta as carbonate, and the filtered solution then evaporated, colourless crystals of the salt separate out.

The free acid may be obtained by addition of the calculated weight of sulphuric acid to a solution of the barium salt. The precipitated barium sulphate is filtered off and the filtrate evaporated.

$$Ba(H_2PO_2)_2 + H_2SO_4 = BaSO_4 = 2H_3PO_2.$$

As obtained in this way hypophosphorous acid is a colourless syrup which can be frozen to white crystals melting at 17°. It is a weak monobasic acid, and probably has the constitution represented by the formula—



the replaceable hydrogen being that in the hydroxyl group. Hypophosphorous acid and its salts decompose on heating, with evolution of phosphine—

$$4H_3PO_2 = 2HPO_3 + 2H_2O + 2PH_3.$$

The hypophosphites of sodium, potassium and calcium are used in medicine, e.g. in "*Parrish's Chemical Food*." If

sodium hypophosphite is added to copper sulphate solution a precipitate of copper hydride, CuH, is formed.

Orthophosphorous acid, H_3PO_3, is formed by dissolving phosphorus trioxide in water—

$$P_2O_3 + 3H_2O = 2H_3PO_3,$$

or by the action of a phosphorus trihalide on water,

$$\text{e.g. } PCl_3 + 3H_2O = H_3PO_3 + 3HCl.$$

On evaporating the solution until the temperature has risen to 180°, and then cooling, crystals of orthophosphorous acid separate.

Phosphorous acid is a white crystalline solid melting at 72°. It is a dibasic acid, and a powerful reducing agent since it readily takes up oxygen to go to orthophosphoric acid, H_3PO_4. Thus it reduces silver, copper and gold salts, in solution, to the metals. Its constitution is probably $O=P(H)(OH)(OH)$, although from its formation from phosphorus trichloride and water we should expect it to be $P(OH)_3$

$$P(Cl)_3 + 3HOH = 3HCl + P(OH)_3$$

Compare nitrous and sulphurous acids (pp. 370 and 466).

Organic derivatives of both forms of phosphorous acid represented by the above formulæ are known.

On heating, phosphorous acid splits up into phosphine and metaphosphoric acid—

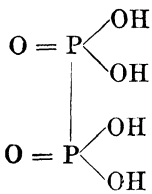
$$4H_3PO_3 = 3HPO_3 + 3H_2O + PH_3.$$

Hypophosphoric acid, H_2PO_3, may be prepared by adding yellow phosphorus to silver nitrate solution and decomposing the precipitated silver hypophosphate with hydrochloric acid—

$$Ag_2PO_3 + 2HCl = 2AgCl + H_2PO_3.$$

It is a white crystalline solid which on heating splits up

into phosphine and phosphoric acid. It is not a reducing agent, and probably has the composition $O=P\begin{matrix}OH\\OH\end{matrix}$ in which the phosphorus is quadrivalent, or the double molecule



may be formed.

Orthophosphoric acid, H_3PO_4, is the most important acid of phosphorus. It may be obtained by decomposing calcium phosphate with sulphuric acid—

$$Ca_3(PO_4)_2 + 3H_2SO_4 = 3CaSO_4 + 2H_3PO_4,$$

and evaporating the solution after filtration from the calcium sulphate. It is also formed when phosphorus pentoxide is added to boiling water—

$$P_2O_5 + 3H_2O = 2H_3PO_4,$$

and when a solution of metaphosphoric acid, HPO_3, is boiled—

$$HPO_3 + H_2O = H_3PO_4.$$

The pure acid may be most conveniently prepared by boiling yellow or red phosphorus (preferably the latter) with concentrated nitric acid. The mixture is placed in a round-bottom flask fitted with a reflux condenser.

The aqueous solution of the acid obtained in any of the above ways is concentrated until the temperature rises to 140°. The syrupy liquid is then allowed to cool in a desiccator, and the acid separates out as colourless rhombic crystals, melting at 41·7°.

Orthophosphoric acid is soluble in water, forming a feebly acid solution. It ionizes chiefly into $H^{\cdot}$ and H_2PO_4', although even this dissociation is small. The further dissociation

$$H^{\cdot} + H_2PO_4' \rightleftharpoons H^{\cdot} + H^{\cdot}PO_4''$$

is practically negligible. Nevertheless, phosphoric acid is a tribasic acid and forms three sodium salts,

NaH_2PO_4, sodium dihydrogen orthophosphate,
Na_2HPO_4, disodium hydrogen orthophosphate,
Na_3PO_4, trisodium orthophosphate, or normal sodium orthophosphate.

Normal sodium phosphate gives a strongly *alkaline* solution. This is easily explained on the ionic theory. Sodium phosphate, like all sodium salts, ionizes very largely in solution—

$$Na_3PO_4 \rightleftharpoons 3Na^{\cdot} + PO_4'''.$$

But orthophosphoric acid is a very weak acid, and the PO_4''' ions immediately react with the hydrogen ions present in water to form the H_2PO_4' ion—

$$H_2O \rightleftharpoons H^{\cdot} + OH'$$
$$2H^{\cdot} + PO_4''' \rightleftharpoons H_2PO_4'.$$

The equilibrium between the water molecules and the hydrogen and hydroxyl ions is thus upset, and more water ionizes, thus furnishing more hydrogen ions to the PO_4''' ions. This process goes on until practically all of the PO_4''' ions have been converted into H_2PO_4' ions. The hydroxyl ions corresponding to the hydrogen ions which have been taken up are left over and thus the solution has an alkaline reaction.

The disodium salt, Na_2HPO_4, is ordinary laboratory "sodium phosphate." It has a *slightly* alkaline reaction in solution.

The monosodium salt, NaH_2PO_4, has a very slightly acid reaction in solution.

The constitution of orthophosphoric acid is probably represented by the following formula—



Titration with caustic soda using litmus or phenolphthalein as indicator gives the disodium salt; with methyl orange the colour change occurs at the stage corresponding to NaH_2PO_4.

Pyrophosphoric acid, $H_4P_2O_7$, is formed when orthophosphoric acid is cautiously heated at a temperature of

about 215–220°. Two molecules of the orthophosphoric acid lose one molecule of water—

$$2H_3PO_4 = H_4P_2O_7 + H_2O.$$

Pyrophosphoric acid is a white crystalline solid melting at 61°. It is a tetrabasic acid, but salts of the types $NaH_3P_2O_7$ and $Na_3HP_2O_7$ are not known—only the normal and diacid salts of the types $Na_4P_2O_7$ and $Na_2H_2P_2O_7$ have hitherto been prepared. If dissolved in water, pyrophosphoric acid changes slowly in the cold, but more rapidly on warming, into orthophosphoric acid.

Pyrophosphates may often be made by heating the corresponding orthophosphates; thus "sodium phosphate," Na_2HPO_4, on heating yields sodium pyrophosphate—

$$2Na_2HPO_4 = H_2O + Na_4P_2O_7.$$

Pyrophosphates in solution gradually revert to ordinary sodium phosphate; the change is accelerated by the addition of a little mineral acid.

The estimation of "P_2O_5" in a solution is often carried out by addition of ammonia, ammonium chloride and magnesium sulphate, when a precipitate of *magnesium ammonium orthophosphate* is obtained. This is collected and heated to redness, when it loses ammonia and water and leaves a residue of *magnesium pyrophosphate*, which is weighed.

$$2MgNH_4PO_4 = H_2O + 2NH_3 + Mg_2P_2O_7.$$

Metaphosphoric acid, HPO_3, may be made by heating the ortho or the pyro acid to redness—

$$H_3PO_4 = H_2O + HPO_3$$
$$H_4P_2O_7 = 2HPO_3 + H_2O,$$

or by adding phosphorus pentoxide slowly to cold water—

$$P_2O_5 + H_2O = 2HPO_3.$$

It is a glassy transparent solid and is put on the market as "glacial phosphoric acid." It is a monobasic acid and the chief salt is *sodium metaphosphate*, $NaPO_3$. This is formed when sodium ammonium hydrogen orthophosphate or

microcosmic salt (so-called because it is found in the urine of the "microcosm," i.e. man), is strongly heated—

$$NaNH_4HPO_4 = NaPO_3 + H_2O + NH_3.$$

Fused sodium metaphosphate dissolves many metallic oxides to form coloured orthophosphates; microcosmic salt is therefore sometimes used instead of borax for the "bead" test in analysis.

Tests for Phosphates.—All phosphorus oxyacids and their salts when heated with ammonium molybdate solution, $(NH_4)_2MoO_4$, and excess of concentrated nitric acid, give a yellow precipitate of variable composition called *ammonium phosphomolybdate*. If the precipitation is carried out under certain specified conditions, the precipitate has a definite composition, and this reaction may then be used for the estimation of phosphates or "P_2O_5."

With *silver nitrate* solution, orthophosphates give a yellow precipitate,
pyrophosphates give a white precipitate,
metaphosphates also give a white precipitate.

With a solution of white of egg, *metaphosphates* cause coagulation,
ortho and pyro phosphates have no action.

For further tests, see FENTON'S *Notes on Qualitative Analysis.*

ARSENIC

Group in Periodic System: V; *Symbol:* As; *Valency:* 3 and 5; *Atomicity of Vapour:* 2–4; *Atomic Weight:* 74·96; *Melting Point*, under pressure: about 817°; *Specific Gravity:* 5·727.

History.—In the form of its sulphides, *realgar* and *orpiment*, arsenic has long been known. The Greek alchemists employed it in their operations, and further investigations on it were carried out by the chemists of Islam in the early

middle ages. They called the arsenic sulphides *zarnīkh*, and some of them regarded the element (which they knew how to extract from its sulphides) as a kind of mercury—"Eastern Mercury." They supposed it to be a constituent of certain metals. It is interesting to note that the famous Muslim chemist ABU'L-QĀSIM AL-'IRĀQĪ (thirteenth century A.D.) pointed out the close resemblance between *zarnīkh* (As_2S_3) and *kuhl* (Sb_2S_3). ALBERTUS MAGNUS (1193–1282) prepared metallic arsenic by heating orpiment with soap; while arsenious oxide, As_2O_3, or "white arsenic," was made by roasting the sulphides and collecting the sublimate. "GEBER" (thirteenth century) gives the following instructions for the preparation of white arsenic—

"*Arſnick* [sulphide] is beaten to *Powder* and muſt then be boyled in *Vinegar*, and all its combuſtible *Fatneſs* extracted, and it then dryed. Then ℞ of *Copper*, calcined, *lib.* 1. Of *Allom* calcined ½ a pound, and of *Common-Salt* prepared as much as of the *Allom*. Mix theſe with your *Arſnick* prepared, and having ground all well together, moyſten the *Mixture* with diſtilled *Vinegar* (that it may be liquid) and boyl the ſame, as you did in *Sulphur*; and then ſublime it in an *Aludel* (without an *Alembeck*) of the height of one *Foot*. Gather what aſcends white, denſe, clear, and lucid, and keep it; becauſe it is ſufficiently prepared for the Work."

Occurrence.—Small quantities of arsenic are found free in nature, but it occurs chiefly as *realgar*, As_2S_2, the red sulphide, *orpiment*, As_2S_3, the yellow sulphide, *arsenical pyrites* or *mispickel*, FeAsS, and *cobalt glance*, CoAsS.

Preparation.—When arsenical pyrites is heated out of contact with air the arsenic volatilizes and may be condensed and collected. Arsenic may be obtained from white arsenic, arsenious oxide, by heating with powdered charcoal. The mixture of white arsenic and charcoal is heated in a fireclay crucible, and the sublimate of arsenic collected in a conical iron receiver placed over the crucible—

$$As_2O_3 + 3C = 2As + 3CO.$$

Properties.—Arsenic resembles phosphorus in the fact that it exists in several allotropic forms.

(i) Ordinary "*metallic*" arsenic or γ-arsenic is a hard, brittle, greyish, crystalline substance which conducts heat and electricity well. It has a specific gravity of 5·73, is insoluble in carbon disulphide, and, in fact, in general physical properties is distinctly metallic. On heating it begins to volatilize at the temperature of boiling water; at a higher temperature it rapidly changes it into a yellow vapour of density 150 (H = 1) at 860° and 75 at 1,800°. These figures show that at 860° the vapour consists of As_4 molecules (As = 75) and at 1,800° of As_2 molecules. At intermediate temperatures some of each kind of molecule would be present.

Metallic arsenic is used in the manufacture of shot, since an alloy of lead with about 0·5 per cent. arsenic is harder than pure lead and forms better shot.

It is insoluble in water, but is oxidized by nitric acid to *arsenic acid*, H_3AsO_4. With sulphuric acid it yields arsenious oxide. It takes fire spontaneously in chlorine, if finely powdered, forming *arsenic trichloride*, $AsCl_3$. If heated in air or oxygen it burns with a characteristic bluish flame, forming arsenious oxide.

(ii) "*Amorphous*" arsenic (β-arsenic) is obtained by vaporizing "metallic" arsenic in a current of hydrogen and allowing the vapour to condense on the cold parts of the tube. It probably consists of very minute crystals of the ordinary form.

(iii) *Yellow* arsenic (α-arsenic) (corresponding to yellow phosphorus) is made by cooling arsenic vapour in liquid air in absence of light. It is a yellow crystalline solid, soluble in carbon disulphide and readily oxidizing in the air. During the oxidation the arsenic *glows*, as does yellow phosphorus. It quickly changes into "metallic" arsenic on exposure to light.

Compounds of Arsenic.

Arseniuretted hydrogen, arsenic hydride, or **arsine,** AsH_3.—Arsine is formed by the reduction of a solution of any soluble arsenic compound with nascent hydrogen. Under these conditions, however, it is mixed with excess of hydrogen, so that to obtain the pure gas other methods are used—

(i) Action of water on aluminium arsenide, on heating—

$$AlAs + 3H_2O = Al(OH)_3 + AsH_3.$$

(ii) Action of dilute hydrochloric acid on zinc arsenide—

$$Zn_3As_2 + 6HCl = 3ZnCl_2 + 2AsH_3.$$

The gas may be collected by downward displacement. It is colourless and poisonous and has an offensive smell. It is practically insoluble in water (cf. ammonia and phosphine). It burns with a bluish flame, forming water and arsenious oxide—

$$2AsH_3 + 3O_2 = As_2O_3 + 3H_2O.$$

When arsine is passed through a hot tube it is split up into arsenic and hydrogen, and the former element condenses as a black mirror on the cool parts of the tube farther on. (See *tests for arsenic*, p. 397.)

Arsine is a reducing agent, and precipitates silver from a dilute solution of silver nitrate—

$$AsH_3 + 6AgNO_3 + 3H_2O = 6Ag + 6HNO_3 + \underset{\text{Arsenious acid.}}{H_3AsO_3}.$$

Other hydrides of arsenic have been described, but they are ill-defined and unimportant.

Arsenic trichloride, $AsCl_3$, is a colourless fuming oily liquid (B.P. 130°) formed by synthesis from its elements or by distilling a mixture of arsenious oxide, salt, and sulphuric acid—

$$As_2O_3 + 6HCl \rightleftharpoons 2AsCl_3 + 3H_2O.$$

Salt and sulphuric acid are used instead of concentrated hydrochloric acid since arsenic trichloride is partially decomposed by water, first into a basic chloride and then into arsenious acid, hydrochloric acid being liberated—

(i) $$AsCl_3 + 2H_2O \rightleftharpoons As\begin{matrix}Cl\\OH\\OH\end{matrix} + 2HCl.$$

(ii) $$As\begin{matrix}Cl\\OH\\OH\end{matrix} + H_2O \rightleftharpoons H_3AsO_3 + HCl.$$

Compare the hydrolysis of phosphorus trichloride, which is practically complete.

A better method of obtaining arsenic chloride was described

by PARTINGTON (1929). He heated a mixture of arsenious oxide and sulphur chloride under a reflux condenser, and passed chlorine through it. Arsenic chloride was formed, and could be distilled off.

If chlorine is passed into strongly cooled arsenic trichloride, it has been stated that the *pentachloride* is formed, $AsCl_5$, though the observation has not been confirmed.

Arsenious oxide, As_2O_3, "*white arsenic*," is obtained by roasting the element itself, or its sulphides, in a current of air or oxygen. It occurs in three modifications—

(i) *Amorphous* or *vitreous* arsenious oxide, formed by carefully and slowly condensing the vapour. In damp air it gradually passes into the crystalline octahedral form. It is the most soluble of the three forms.

(ii) *Octahedral* arsenious oxide, the ordinary form, produced when the vapour is condensed without special precaution. It is only slightly soluble in water.

(iii) *Rhombic* arsenious oxide, formed by heating (i) or (ii) to about 200° for some hours. It is unstable.

The aqueous solution of arsenious oxide has a slight acid reaction, owing to the formation of arsenious acid—

$$As_2O_3 + 3H_2O \rightleftharpoons 2H_3AsO_3 \rightleftharpoons 2H^{\cdot} + 2H_2AsO_3'.$$

This is a very weak acid and has never been isolated, although *arsenites* are known, e.g. Ag_3AsO_3, silver arsenite.

Arsenious oxide and the arsenites are good reducing agents, since they readily take up oxygen to form arsenic pentoxide and arsenates respectively. Sodium arsenite solution is often used for the estimation of iodine—

$$2Na_3AsO_3 + 2I_2 + 2H_2O = \underset{\text{Sodium arsenate.}}{2Na_3AsO_4} + 4HI.$$

For this purpose, an excess of sodium bicarbonate is added to the sodium arsenite solution, to take up the hydriodic acid as formed. Alkali cannot be used, as it would react with the iodine—

$$2NaOH + I_2 = NaI + NaIO + H_2O.$$

Scheele's green is copper hydrogen arsenite, $CuHAsO_3$. This and similar arsenical colouring matters were, and still are

to some extent, used in wall-papers—a dangerous habit, for if the walls are damp and the paper gets attacked by moulds, arsine (or an organic derivative of arsine) is set free. Cases of poisoning have often occurred from arsenical wall-papers.

Arsenious oxide vapour at comparatively low temperatures (500–800°) has a density corresponding to the formula As_4O_6, but as the temperature rises the vapour density gradually falls until it reaches a minimum value, corresponding to the formula As_2O_3, at about 1,800°.

Arsenious oxide and indeed all soluble arsenic compounds are extremely poisonous, 0·2 of a gram of white arsenic being a fatal dose. However, the system may become accustomed to this poison, which is often used to beautify the skin and improve the wind.

Arsenic pentoxide, As_2O_5, is formed by acting upon arsenious oxide with concentrated nitric acid and igniting the arsenic acid so obtained—

$$2H_3AsO_4 = 3H_2O + As_2O_5.$$

It is a white deliquescent crystalline solid, which dissolves in water to form arsenic acid. At a high temperature it splits up into oxygen and arsenious oxide.

Arsenic acid, H_3AsO_4, prepared as above, is a white crystalline solid containing water of crystallization. Its salts are the *arsenates*; the only one of importance is disodium hydrogen arsenate, Na_2HAsO_4, which is used in calico-printing. Arsenic acid or arsenic pentoxide is sometimes used in organic chemistry as an oxidizing agent, e.g., in the preparation of quinoline. H_3AsO_4 is *ortho*arsenic acid; the corresponding *pyro* and *meta* acids are known, $H_4As_2O_7$ and $HAsO_3$.

Pyroarsenic acid is made by heating the ortho acid to 160°; it dissolves in water with evolution of heat, reforming ortho-arsenic acid—

$$2H_3AsO_4 \rightleftharpoons H_4As_2O_7 + H_2O.$$

Meta-arsenic acid is formed when the ortho acid is heated to 200°. It is a white substance that dissolves in water with evolution of heat, reforming orthoarsenic acid—

$$H_3AsO_4 \rightleftharpoons H_2O + HAsO_3.$$

Magnesium ammonium arsenate, $MgNH_4AsO_4$, insoluble in water, yields the pyroarsenate on heating—

$$2MgNH_4AsO_4 = Mg_2As_2O_7 + 2NH_3 + H_2O.$$

Arsenites and arsenates give a yellow precipitate with ammonium molybdate and excess of boiling nitric acid. (Cf. *phosphates*, p. 390.)

Arsenic trisulphide, As_2S_3, or **orpiment**, is found naturally occurring. It was formerly used as a pigment, called *auri pigmentum*, whence the name "orpiment." It is obtained as a yellow precipitate by passing sulphuretted hydrogen through a solution of arsenious oxide in dilute hydrochloric acid—

$$2AsCl_3 + 3H_2S \rightleftharpoons As_2S_3 + 6HCl.$$

It may be obtained in the colloidal state by passing sulphuretted hydrogen through a hot solution of arsenious oxide in water.

Arsenic pentasulphide, As_2S_5, is formed as a red precipitate by addition of hydrochloric acid to a solution of sodium thioarsenate—

$$2Na_3AsS_4 + 6HCl = 6NaCl + 3H_2S + As_2S_5$$

Arsenic disulphide, As_2S_2, or *realgar* (the Arabic name of the substance), is a red mineral found in many parts of the world. It is used in making fireworks and in tanning.

Thioarsenites and thioarsenates.—Arsenic trisulphide will dissolve in solutions of caustic alkalis, to form a mixture of an arsenite and *thioarsenite*—

$$As_2S_2 + 4NaOH = Na_2HAsO_3 + Na_2HAsS_3 + H_2O.$$

Thioarsenites are also formed by dissolving arsenic trisulphide in a solution of an alkali sulphide, as in Group II of the analysis tables—

$$As_2S_3 + 3(NH_4)_2S = 2(NH_4)_3AsS_3.$$

Addition of dilute acid to a solution of a thioarsenite precipitates the arsenic as arsenic trisulphide.

Solutions of thioarsenites will dissolve sulphur, giving

thioarsenates, e.g., Na_3AsS_4, which are also formed by dissolving arsenic trisulphide in solutions of alkali polysulphides, such as yellow ammonium sulphides. The thioarsenite is first formed and is then oxidized by excess of sulphur to the thioarsenate. The final product in Group II in analysis (see above) is therefore the thioarsen*ate*.

Tests for Arsenic.—Since the days of Paracelsus, arsenic compounds have been favourite tools of the poisoner, and as such a small dose is fatal the detection of arsenic becomes a matter of importance. Fortunately, there is no poison easier to detect, and the need for a systematic study of chemistry on the part of poisoners is becoming more and more evident! The symptoms of arsenical poisoning have been prominent so many times in the newspapers of late years that there is no need for their description to be given here.

The test usually employed for arsenic in criminal investigations is called MARSH'S test. All the apparatus and chemicals used must obviously be free from arsenic. Hydrogen is liberated from zinc and dilute sulphuric acid in a small flask, and a weighed quantity of the material to be tested is introduced. All the arsenic present, if any, is converted into arsine, and the mixture of arsine and hydrogen evolved is passed through a heated tube, where the arsine is decomposed and arsenic deposited as a mirror on the cold parts of the tube beyond the flame. By comparing the mirror formed with those made under similar circumstances with known weights of arsenic, the weight of arsenic present in the material under investigation may be estimated. This method is susceptible of very great accuracy.

Arsenic in very small quantity is normally present in the human body.

The arsenic mirror may be distinguished from a similar mirror of antimony (p. 400) by treatment with bleaching-powder solution, in which the arsenic is soluble and the antimony insoluble.

For other tests for arsenic, see FENTON'S *Notes on Qualitative Analysis*.

ANTIMONY

Group in Periodic System : V ; *Symbol :* Sb ; *Valency :* 3, 4, and 5 ; *Atomicity of Vapour :* 1–3 ; *Atomic Weight :* 121·8 ; *Melting Point :* 630·6° ; *Specific Gravity :* 6·71–6·86.

History.—Antimony and many of its compounds have been known from the most remote times. The naturally occurring sulphide was called by the Greek alchemists στίμμι (*stimmi*), *stibi*, *larbason*, or *chalcedony*. The modern names *stibnite* for antimony sulphide, Sb_2S_3, is derived from *stibi*, as is also the pseudo-Latin name for the element, *stibium*. DIOSCORIDES describes stibi as a shiny, brittle mineral, containing no earthy impurities ; if it is heated with red-hot charcoal it becomes like lead [that is, the sulphide is reduced to the metal].

Stibi was, and still is, used by the ladies of the East to darken the eyebrows. The Arabs called it *kuhl* ; thus the poet MUTANABBI (915–965) says :

> " *How pale and dull the deepest black of kuhl*
> *Against the lustrous blackness of thine eyes !* "

The name *antimony* is alleged to have arisen from the pseudonymous BASIL VALENTINE'S unfortunate experiment, about A.D. 1400, on the effect of the powdered metal as a tonic for monks ; the results were so disastrous that the substance was called *anti-moine* ! It is a pity that this story must be rejected as apocryphal, since the name was in use at least 300 years earlier. The chemist who wrote, about 1600, under the assumed name of Basil Valentine made, however, a thorough investigation of antimony and its compounds, and published his results in a wonderful book called the *Triumphal Chariot of Antimony*, which is, I think, the first monograph on a chemical element. All that was known of antimony until the end of the eighteenth century is clearly described in the *Triumphal Chariot*—a masterpiece of chemical literature and obviously the work of a first-rate chemist.

Occurrence.—Small quantities of antimony occur naturally, but the element is generally found as *stibnite*, Sb_2S_3.

Preparation.—The crushed stibnite is heated with scrap iron in graphite crucibles—

$$Sb_2S_3 + 3Fe = 2Sb + 3FeS,$$

and the metal purified by fusion with potassium nitrate. It is also extracted by burning the sulphide to the oxide and reducing this with charcoal and sodium carbonate.

$$\text{(i)}\quad 2Sb_2S_3 + 9O_2 = 2Sb_2O_3 + 6SO_2.$$
$$\text{(ii)}\quad Sb_2O_3 + 3C = 3CO + 2Sb.$$

Properties.—Antimony is a lustrous silvery metal, brittle and crystalline. Its specific gravity is 6·7 ; it melts at 630·6° and boils at about 1,400°. Antimony is stable in the air at ordinary temperatures, but will burn if heated, forming white fumes of antimony trioxide, Sb_2O_3, mixed with the tetroxide, Sb_2O_4.

Dilute acids have no action on antimony, but it dissolves in the hot concentrated acids to give the *chloride* (with hydrochloric acid), the *sulphate* (with sulphuric acid), or the *hydrated oxide*, " antimonic acid " (with nitric acid).

Antimony is commercially important, since it will take a high polish and expands on solidification ; the latter property enables it to be cast in moulds. It is largely used in the form of alloys, such as *Britannia metal* (antimony 12 per cent., tin 86 per cent., copper 2 per cent.), *pewter* (rather less antimony than in Britannia metal), and *type-metal* (lead 65 per cent., antimony 25 per cent., tin 10 per cent.). Type-metal and linotype metal are used for the type for printing. They are hard and can take very fine impressions, on casting. The best type (such as that made for ALDUS in Italy in the fifteenth century) is made from silver.

Antimony, like phosphorus and arsenic, can be obtained in several allotropic forms. *Yellow* antimony is made by passing ozonized oxygen into liquid antimoniuretted hydrogen or stibine, SbH_3, at −90°. It resembles yellow phosphorus and yellow arsenic in being soluble in carbon disulphide, but differs from them in being, apparently, amorphous.

Black antimony is obtained by the action of oxygen on liquid stibine at −40°. It is amorphous.

Explosive antimony was first obtained by GORE in 1858, by electrolysis of a strong solution of antimony trichloride in hydrochloric acid between a platinum cathode and antimony anode. A black shining deposit of antimony is formed on the cathode. It explodes violently when scratched with a hot glass rod. Gore showed that explosive antimony always contains about 6 per cent. of the trichloride together with traces of hydrochloric acid. It may be a solid solution of the trichloride in black antimony.

Antimony hydride, antimoniuretted hydrogen, or stibine, SbH_3, is prepared by the action of hydrochloric acid upon an alloy of magnesium and antimony containing 33 per cent. of the latter metal. The alloy may contain magnesium antimonide, Mg_3Sb_2, in which case the equation for the reaction would be

$$Mg_3Sb_2 + 6HCl = 3MgCl_2 + 2SbH_3.$$

Mixed with hydrogen, it is obtained by the action of nascent hydrogen upon a solution of any soluble antimony salt. If the gas is passed through a hot tube, a deposit of antimony is obtained. (Cf. Marsh's test for arsenic, p. 397.)

If pure stibine, obtained by the first method, is cooled by liquid air it forms a colourless liquid boiling at $-17°$ and freezing to a white solid at $-88°$. It is very soluble in certain organic solvents such as ether and petrol and especially carbon disulphide.

With air or oxygen it reacts to give water and antimony and is a strong reducing agent. Thus it reduces nitric oxide to a mixture of nitrous oxide, nitrogen and ammonia, and gives a black precipitate of silver with silver nitrate solution. It has no basic properties, thus resembling arsine but differing from phosphine and ammonia.

Antimony trichloride, $SbCl_3$, is formed when antimony burns in chlorine or when antimony trisulphide is heated with concentrated hydrochloric acid—

(i) $2Sb + 3Cl_2 = 2SbCl_3$.

(ii) $Sb_2S_3 + 6HCl \rightleftharpoons 2SbCl_3 + 3H_2S$.

On evaporating the solution, crystals of the trichloride can

be obtained. These are deliquescent and colourless and melt at 73°. Antimony trichloride boils, without decomposition, at 223°. It is decomposed by water, with formation of insoluble basic chlorides—

$$SbCl_3 + H_2O = SbOCl + 2HCl.$$

SbOCl is antimony oxychloride or *powder of Algaroth*; it is insoluble in water and is white in colour. The reaction $SbCl_3 + H_2O \rightleftharpoons SbOCl + 2HCl$ is reversible; thus antimony trichloride will dissolve completely in a little water, but on dilution the equilibrium is shifted very largely to the right and a white precipitate of the oxychloride is obtained. This, as would be expected, redissolves on addition of sufficient hydrochloric acid. A great excess of water carries the hydrolysis a stage further—

$$SbOCl + 2H_2O = Sb(OH)_3 + HCl,$$

forming a hydrated antimonious oxide $Sb(OH)_3$ or $Sb_2O_3.3H_2O$.

Antimony pentachloride, $SbCl_5$, is obtained as a colourless or slightly yellow fuming liquid, B.P. 140°, by passing a stream of dry chlorine through the trichloride. Although it may be boiled without decomposition, its vapour dissociates at higher temperatures into the trichloride and chlorine—

$$SbCl_5 \rightleftharpoons SbCl_3 + Cl_2.$$

Water at ordinary temperatures decomposes it, yielding antimonic acid and hydrochloric acid. (Cf. phosphorus pentachloride, p. 382.)

$$SbCl_5 + 4H_2O = H_3SbO_4 + 5HCl.$$

Compounds of antimony with bromine, iodine, and fluorine are also known.

Antimony trioxide, Sb_2O_3, is made by hydrolysing the trichloride with hot water, and washing the precipitate with sodium carbonate solution until all hydrochloric acid is removed—

$$2SbCl_3 + 3H_2O = Sb_2O_3 + 6HCl.$$

It may also be prepared by strongly heating antimony in a current of steam. It is purified by sublimation.

Antimony trioxide is a white powder which can be vaporized unchanged. Vapour-density determinations show that the vapour consists of Sb_4O_6 molecules. It is almost insoluble in water, but dissolves in alkalis forming *antimonites*. It also dissolves in hydrochloric acid, yielding the chloride, but is insoluble in nitric and sulphuric acids. If boiled with a solution of potassium hydrogen tartrate it dissolves, forming *potassium antimonyl tartrate* or *tartar emetic*, often represented as

$$2K(SbO)C_4H_4O_6.H_2O.$$

This compound is of great importance in medicine, and is also used in the dye industry as a mordant.

Antimony tetroxide, Sb_2O_4.—When the trioxide is heated in the air it burns, forming the tetroxide. This is a white solid which will dissolve in alkalis to form salts called *hypoantimoniates*.

Antimony pentoxide, Sb_2O_5, is made by acting upon antimony with strong nitric acid and carefully igniting the residue. It is a yellow powder, and on treatment with alkalis under suitable conditions can be made to yield *antimoniates*, e.g., *sodium meta-antimoniate*, $NaSbO_3$. The acids corresponding to the pentoxide, viz., *orthoantimonic acid*, *pyroantimonic acid*, and *meta-antimonic acid*, have all been prepared but are unimportant except that they form a further point of resemblance between antimony, arsenic and phosphorus.

Antimony trisulphide, Sb_2S_3, occurs naturally as the grey mineral *stibnite*. It may be obtained as an orange red precipitate by passing sulphuretted hydrogen through a solution of antimony chloride acidified with hydrochloric acid—

$$2SbCl_3 + 3H_2S \rightleftharpoons Sb_2S_3 + 6HCl.$$

The red form passes into the grey form if heated to 230° in an inert atmosphere.

Thioantimonites and *thioantimonates*, corresponding to the thioarsenites and thioarsenates (p. 396), are known, and may be made in an analogous way. *Ammonium thioantimonate*, $(NH_4)_3SbS_4$, is made by dissolving antimony trisulphide in yellow ammonium sulphide.

Antimony pentasulphide, Sb_2S_5, is obtained as an orange precipitate by adding hydrochloric acid to a solution of a thioantimonate—

$$2(NH_4)_3SbS_4 + 6HCl = 6NH_4Cl + 3H_2S + Sb_2S_5.$$

It is unstable, readily splitting up into the trisulphide and sulphur.

BISMUTH

Group in Periodic System: V; *Symbol:* Bi; *Valency:* 2, 3, and 5; *Atomicity of Vapour:* 1–2; *Atomic Weight:* 209·0; *Melting Point:* 269°; *Specific Gravity:* 9·823.

History.—Bismuth was unknown to the ancient chemists or, if known, was considered to be a kind of lead. The name *wismath* was given by RULANDUS (*Lexicon Alchemiæ Rulandi*, Frankfort, 1612) to a certain metallic sulphide, but the name was afterwards applied to a new element, bismuth. "Wismath" is derived from *wis mât* or *wiesse Masse*, white mass or metal; the *w* was changed into *b* for the purpose of writing the name in Latin, from the alphabet of which language the letter *w* is missing. Bismuth and its compounds were studied by PARACELSUS and AGRICOLA and more especially by BASIL VALENTINE, but BERGMANN (eighteenth century) first carefully distinguished between it and antimony, tin, and lead. The French chemist LEMERY, 1694, made a large fortune by selling "*le seul Magistère de Bismut*" (bismuth oxynitrate or *pearl white*) as a cosmetic to the ladies of the Court.

Occurrence.—Bismuth occurs chiefly as the native metal, but *bismuth ochre* (Bi_2O_3) and *bismuthite* or *bismuth glance* (Bi_2S_3) are also found in small quantities.

Preparation.—The native metal is melted and the molten bismuth allowed to run off from the earthy residue. If it is required to extract the metal from the ores, these are first roasted and then reduced by smelting with coke, scrap iron, and a flux. The metal is then purified by fusion with saltpetre, which oxidizes the impurities. A convenient method of obtaining the pure metal is to reduce the carefully purified oxide, e.g. with potassium cyanide.

Properties.—Bismuth looks very much like antimony; it is a lustrous white metal with a red reflex. It is crystalline and brittle and is readily powdered. Its specific gravity is 9·8; it melts at 269°, and boils at 1,450–1,500°. It is a poor conductor of electricity (metals as a rule conduct well, while non-metals do not).

Bismuth is stable in air at ordinary temperatures, but if heated strongly will burn with a bluish flame, forming the trioxide Bi_2O_3. It is dissolved by dilute nitric acid, yielding bismuth nitrate, $Bi(NO_3)_3$. Other dilute acids have no action on it. Concentrated sulphuric acid acts upon it on heating, forming a basic sulphate or the normal sulphate according to the conditions.

Bismuth is commercially important on account of the valuable alloys it forms. As a rule, these alloys are very hard, expand on solidification, and easily melt. The commonest is *Wood's metal*, which consists of bismuth 4, lead 2, cadmium 2, and tin 1, and melts at 60°–68°. Others are *Rose's metal* (79°), 9 bismuth, 5 lead, 4 tin; *Newton's metal* (94°), 8 bismuth, 5 lead, 3 tin; *Lipowitz's Alloy* (70°), 15 bismuth, 8 lead, 8 tin, 3 cadmium. These easily fusible alloys are used for fuse wires, safety-valves for boilers, automatic fire-sprinklers, and so on. For the latter purpose it is advisable not to have the melting-point of the alloy too low. In the hot summer of 1921 there were many reports of automatic sprinklers suddenly starting work unnecessarily; the heat of the sun had been sufficient to melt the alloy which controlled them. The "magic spoons" that disappear when used to stir a cup of tea are made of a low melting-point bismuth alloy.

Compounds of Bismuth

Bismuth hydride, BiH_3, has not yet been isolated. It is probably formed in small quantity by the action of concentrated hydrochloric acid upon bismuth magnesium alloy.

Bismuth trioxide, Bi_2O_3, is a yellow powder obtained by heating bismuth nitrate—

$$4Bi(NO_3)_3 = 2Bi_2O_3 + 12NO_2 + 3O_2.$$

It is used in the pottery trade for making glazes.

It has no acidic properties, but is, on the contrary, basic, and dissolves in acids, forming bismuth salts—

$$Bi_2O_3 + 6HCl = 2BiCl_3 + 3H_2O.$$

Bismuth pentoxide, tetroxide, and **dioxide,** Bi_2O_5, Bi_2O_4, and Bi_2O_2, are also known. The pentoxide will dissolve in fused caustic alkalis to form *bismuthates*, e.g., $NaBiO_3$, which are used as oxidizing agents.

Bismuth trichloride, $BiCl_3$, is made by heating bismuth in a stream of chlorine. It is a white crystalline solid melting at 227° and boiling at 447°. It is hydrolysed by water, forming bismuth oxychloride, a white insoluble powder—

$$BiCl_3 + H_2O \rightleftharpoons BiOCl + 2HCl.$$

The oxychloride will dissolve in hydrochloric acid.

Bismuth pentachloride is unknown.

Bismuth nitrate, $Bi(NO_3)_3$.—In the form of its pentahydrate, $Bi(NO_3)_3.5H_2O$, this salt is obtained by dissolving bismuth in dilute nitric acid and evaporating the solution to crystallization. It will dissolve in a *small quantity* of water or in dilute nitric acid, unchanged, but is hydrolysed to a white insoluble basic or subnitrate by excess of water—

$$Bi(NO_3)_3 + 2H_2O \rightleftharpoons Bi\begin{<}{OH}{OH}{NO_3}\end{} + 2HNO_3.$$

Large excess of water hydrolyses the subnitrate further, to the hydroxide—

$$Bi\begin{<}{OH}{OH}{NO_3}\end{} + H_2O \rightleftharpoons Bi(OH)_3 + HNO_3.$$

"Bismuth subnitrate" is used in medicine, in cases of diarrhœa, etc., and is still employed, as in Lemery's time, as a cosmetic. It has, however, the disadvantage from the latter point of view of going yellow on exposure to air and thus giving the fair user a somewhat jaundiced appearance.

Bismuth sulphide, Bi_2S_3, is insoluble in alkali sulphides and does not yield thiobismuthites or thiobismuthates.

Bismuth carbonate.—The white precipitate obtained on adding ammonium carbonate to bismuth nitrate solution is a *basic* bismuth carbonate.

QUESTIONS

1. Show that the elements nitrogen, phosphorus, arsenic, antimony, and bismuth are properly classified together.
2. Describe the preparation of phosphine, phosphorus pentachloride and phosphorous oxide.
3. How is phosphorus manufactured? Give an account of the history of this element.
4. Discuss the allotropy of phosphorus.
5. Write a short account of the evolution of the match.
6. What is the basicity of orthophosphoric acid? Explain the behaviour towards indicators of aqueous solutions of orthophosphates.
7. What do you know of the history of arsenic and antimony?
8. Compare and contrast the properties of arsenic with those of (*a*) phosphorus, (*b*) antimony.
9. Show the stupidity of poisoners who use arsenic.
10. How is stibine prepared? What are its properties?
11. Give an account of the history and uses of bismuth.
12. Is bismuth a metal? Give your reasons.

CHAPTER XXVI

GROUP VI

TYPICAL ELEMENTS: **Oxygen, Sulphur.**

Sub-group A: **Chromium,** Molybdenum, **Tungsten,** Uranium.

Sub-group B (similar to typical elements): Selenium, Tellurium.

OXYGEN, SULPHUR

Oxygen and sulphur, both non-metals, have many resemblances to one another, as will appear from the descriptions of these elements and their compounds. Close similarities between oxygen and chromium simply do not exist; diligent search will enable us to find certain points in which sulphur and chromium are related—thus, they both form acidic oxides MO_3 (sulphur trioxide, SO_3, and chromium trioxide, CrO_3), while the *sulphates*, M'_2SO_4, are isomorphous with the *chromates*, M'_2CrO_4. It cannot be denied, however, that from the point of view of chemical relationship, the Periodic System has many failures.

Oxygen, sulphur, selenium and tellurium are much more closely related to one another in properties than they are to the other elements of the group; in fact, sulphur, selenium and tellurium form a triad of elements the members of which really do resemble one another very closely. The study of selenium and tellurium, however, lies beyond the scope of this book.

Oxygen

Group in Periodic System: VI; *Symbol:* O; *Valency:* **2**; *Atomicity:* 2; *Atomic Weight:* 16·00.

History.—Oxygen is said to have been known to the Chinese of the eighth century A.D. It is fashionable to attribute the discovery of any important substance or process to the Chinese, since it is difficult to disprove such a theory. Up to the present no one has suggested that the Chinese were acquainted with the existence of istopes.[1] Oxygen was discovered before 1773 by Scheele and in 1774 by Priestley. Scheele's results were, however, not published until 1777, so

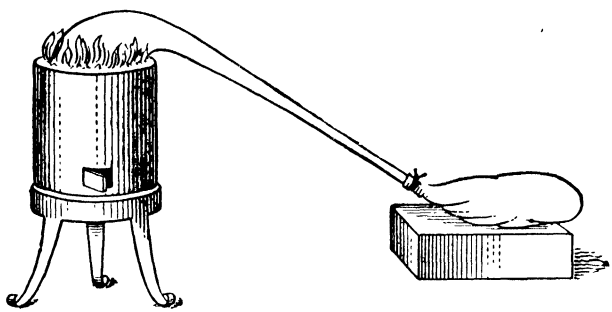
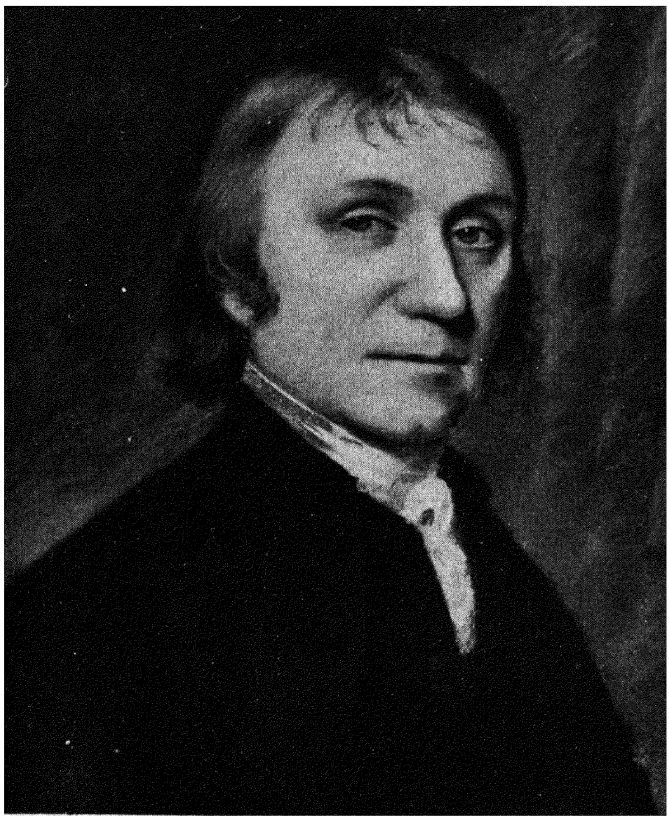


Fig. 85.—Scheele's Apparatus for the Preparation of Oxygen.

that the credit of the discovery is usually given to Priestley. Scheele obtained the gas by heating a mixture of nitre (potassium nitrate) and oil of vitriol (sulphuric acid), and called it *fire-air*. He also made it by heating red oxide of mercury. It was from the latter substance that Priestley obtained oxygen. He heated the mercuric oxide by means of a burning-glass, or double convex lens, which brought the sun's rays to a focus upon it. Priestley and Scheele both interpreted their results in the light of the current theory of combustion,

[1] The Greek alchemists were in the habit of talking about the *two leads*. What remarkable prescience! Seriously, though, the habit of reading modern theories into the ideas of antiquity is a vicious tendency that requires severe treatment.



Nat. Portrait Gallery.

JOSEPH PRIESTLEY

the **Theory of Phlogiston.** In his *Physica Subterranea* (1669), BECHER said, "[Combustible] metals contain an inflammable principle which by the action of fire goes off into the air; a metal *calx* is left." According to the phlogiston theory, then, metals consist of two things—a *calx*, different in different metals, and an inflammable principle common to all metals. This inflammable principle was called *phlogiston* by STAHL (1723), and combustion was considered to consist in the liberation of phlogiston from the burning body. A metallic calx could be reconverted into the metal by heating it with a substance rich in phlogiston, such as carbon. Cavendish's discovery of inflammable air proved of great assistance to the phlogiston theory, for it enabled the theory to explain satisfactorily another set of facts. When a metal such as zinc is dissolved in dilute sulphuric acid, inflammable air (considered by Cavendish to be nearly pure phlogiston) is evolved and a solution left which on evaporation yields crystals of white vitriol. Chemists argued that if zinc calx were taken and dissolved in dilute sulphuric acid, the solution of white vitriol should be obtained *without evolution of inflammable air*, since this has already been got rid of in converting the zinc into zinc calx. Experiment showed that this deduction was borne out in practice.

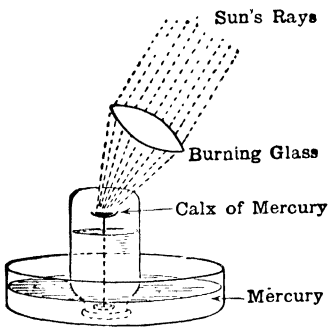
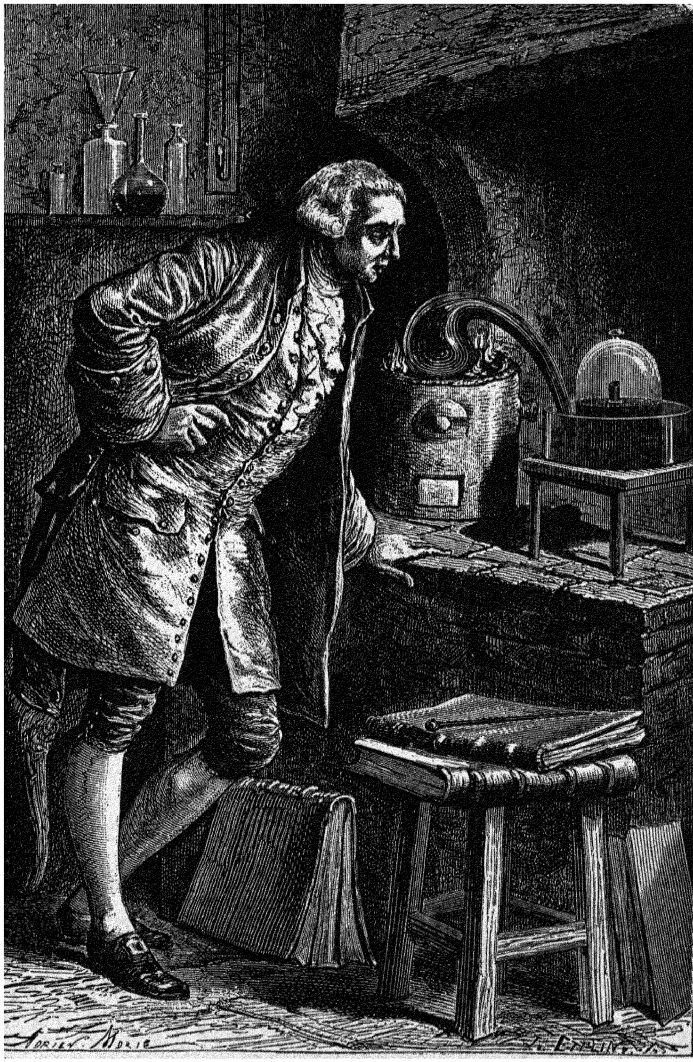


FIG. 86.—Priestley's Apparatus for the Preparation of Oxygen.

An inconvenient observation for the theory of phlogiston was that when a given weight of metal is converted into its calx, an *increase* in weight occurs, whereas a *decrease* would be expected since phlogiston has been lost. Phlogistian chemist overcame this difficulty by assuming that phlogiston is lighter than air, and that therefore when it combines with a sub-



ANTOINE LAURENT LAVOISIER IN HIS LABORATORY

stance tries to lift it as a balloon lifts a weight. Hence when a substance loses phlogiston it becomes heavier. This theory received support from the extreme lightness of Cavendish's inflammable air.

These facts are sufficient to show us that the phlogiston theory was a remarkably good one, correlating facts which were otherwise apparently disconnected, and predicting results that were afterwards verified by experiment. Let us imagine ourselves to be chemists of the eighteenth century, and attempt to explain Priestley's experiment on "red calx of mercury" in the light of the phlogiston theory.

Calx of mercury we assume to be mercury *minus* phlogiston. We have heated this in a glass cylinder containing air, and have obtained mercury. This means that phlogiston must have been taken up by the calx; where can this phlogiston have come from? Obviously from the air in the cylinder. But the air in the cylinder is ordinary atmospheric air—does this contain phlogiston? Certainly, for fires all over the world are constantly liberating phlogiston and turning it into the air. Admitting this, what should be the properties of the residual air in the cylinder? Clearly this air has lost phlogiston, and is therefore "de-phlogisticated"; it should therefore be able to take up more phlogiston than the same volume of ordinary air—in other words, (*a*) things should burn in it more brightly, since they can give up their phlogiston more readily, and (*b*) it should support life longer. Both of these results were actually obtained by Priestley, who therefore gave the name *dephlogisticated air* to his new gas, though the arguments he employed were not quite the same as those we ourselves have made above.

However, the fact that an increase of weight occurs on calcination was felt by many chemists to be a serious objection to the phlogiston theory, in spite of the ingenious explanation mentioned above. Antoine Laurent Lavoisier in 1774 heated tin in a closed flask containing air, and found that the flask as a whole did not increase in weight. The tin, however, was converted into tin calx, and on opening the flask air rushed in. Lavoisier now weighed the flask and

contents again, and made the important observation that the difference of weight between the tin and tin calx was equal to the weight of the air that rushed in when the flask was opened. Further experiments convinced Lavoisier that only a part of the air is concerned in calcination, and he therefore concluded that the air contains at least two different gases, only one of which is absorbed by the metal during calcination.

In the autumn of 1774 Priestley dined in Paris with Lavoisier at the house of a mutual friend, Lord Shelburne, and described his discovery of dephlogisticated air. Lavoisier at once realized that Priestley's gas was probably that constituent of the air which combined with metals during combustion, and devised an experiment to test this idea.

He confined mercury in a glass retort provided with a long neck communicating with air in a bell-jar placed in a trough of mercury. The level of the mercury in the bell-jar was noted by means of a strip of gummed paper. The mercury in the retort was heated for several days to a temperature just below its boiling-point. Lavoisier found that the mercury in the retort became covered with a red powder and that the level of the mercury in the bell-jar rose. After some time, no more red powder seemed to be forming and the mercury in the bell-jar stopped rising. At this stage Lavoisier noted the decrease in volume of the air in the bell-jar and found that it was approximately one-fifth. The residual air would not support combustion or life, so he called it *azote*. On heating the red calx or powder formed in the retort, he obtained a volume of gas *equal to the diminution in volume of the air in the bell-jar*; this gas was of course Priestley's dephlogisticated air, and supported combustion extremely well. Lavoisier showed further that the increase in weight of the mercury in the retort during the above experiment was exactly equal to the loss in weight of the air in the bell-jar, and that a gas exactly like ordinary air could be produced artificially by mixing 1 volume of " dephlogisticated air " with 4 volumes of azote.

His first conclusion was that *air consists of two gases, azote and dephlogisticated air, in the proportion by volume of* 4 *to* 1;

in combustion, only the latter gas is concerned, and this combines with the burning substance, hence the increase in weight. The difference between the two theories of combustion is therefore as follows—

Phlogiston Theory: Metal = Calx + Phlogiston.
Lavoisier's Theory: Metal + dephlogisticated Air = Calx.

To mark the difference, Lavoisier re-named dephlogisticated air, calling it at first *eminently breathable air*, but afterwards *oxygen* (acid-producer) since he found that when non-metals were burnt in the gas and the products of combustion dissolved in water the resulting solutions were *acid.* He concluded further that oxygen was an essential constituent of all acids, in which he was not quite right.

Lavoisier's work forms the foundation of modern chemistry. On it Dalton was able to build his atomic theory, and from that time chemistry has never looked back. In 1869 WURTZ expressed the feeling of many chemists when he said, "*La Chimie est une science française; elle fut constituée par Lavoisier d'immortelle mémoire.*" Lavoisier, however, was not appreciated by the Revolutionists, who in 1794 guillotined him, with the comment, "*La République n'a pas besoin de savants.*"

Occurrence.—Oxygen forms 21 per cent. by volume and 23 per cent. by weight of the air. In water it is combined with hydrogen in the proportion by weight of 88·9 per cent. oxygen to 11·1 per cent. hydrogen. About 50 per cent. of the earth's crust is composed of oxygen, and it is an essential constituent of all living matter. It is probably present in the sun and in other stars.

Preparation.—Oxygen may be made by heating mercuric oxide, manganese dioxide, nitre, barium peroxide, and many other substances. Potassium chlorate is usually employed. If this salt is heated to about 360° it melts and oxygen is evolved (Fig. 87); after a time the gas stops coming off and the liquid thickens, owing to the formation of potassium perchlorate, $KClO_4$.

$$8KClO_3 = 5KClO_4 + 3KCl + 2O_2.$$

If at this stage the temperature be raised to about 630°, the potassium perchlorate is split up into potassium chloride and oxygen—

$$KClO_4 = KCl + 2O_2.$$

Omitting the intermediate stage, we can therefore represent the action of heat on potassium chlorate as

$$2KClO_3 = 2KCl + 3O_2.$$

In the laboratory, it is usual to add a catalyst to increase the speed of the reaction. Manganese dioxide is generally

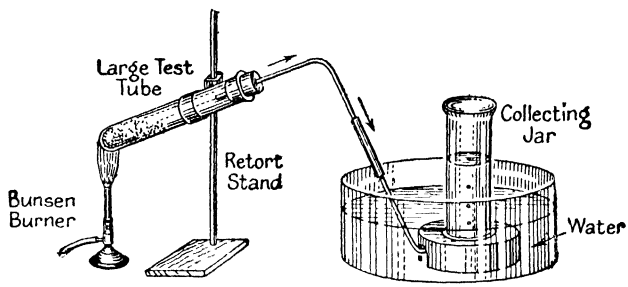


Fig. 87.

used, although many other substances will do equally well. The oxygen is then evolved in a steady stream at a temperature lower than the melting-point of the potassium chlorate (340° C.).

Oxygen may be conveniently prepared in the laboratory by allowing water from a dropping-funnel to drop on to sodium peroxide in a flask fitted with a cork carrying a delivery-tube (Fig. 88)—

$$2Na_2O_2 + 2H_2O = 4NaOH + O_2.$$

The trade name for sodium peroxide is *oxone*.

Pure oxygen is prepared by Baker's method—electrolysis of a dilute solution of barium hydroxide, oxygen coming off from the anode.

Commercially, oxygen is prepared by the fractional distilla-

tion of liquid air. Since oxygen boils at −182° and nitrogen at −196°, when liquid air is allowed to boil a partial separation can be effected.

Oxygen is put on the market compressed in steel cylinders at a pressure of about 120 atmospheres.

Properties.—Oxygen is a colourless gas with no taste or smell. It is slightly heavier than air. It dissolves sparingly

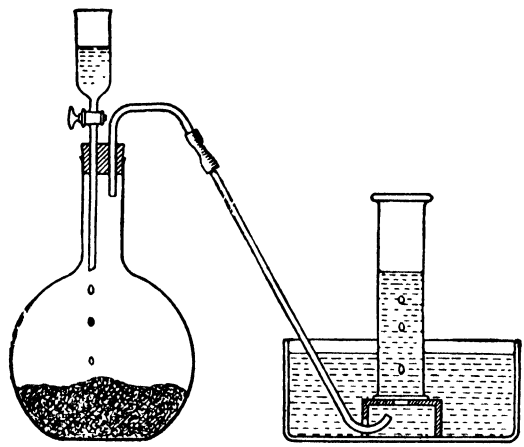


FIG. 88.

in water, 1 litre of water dissolving about 50 c.c. of oxygen at 0° C. It is, of course, the dissolved oxygen, and not the combined oxygen, in water that fish breathe. Oxygen readily supports combustion, the products being called *oxides*.

Oxides are classified as follows—

(i) Acidic oxides. (ii) Basic oxides. (iii) Peroxides and Suboxides. (iv) Neutral Oxides.

(i) *Acidic Oxides.*—When non-metals are burnt in oxygen, the oxides obtained will generally unite with water to form acids, e.g.,

$P_2O_5 + H_2O = 2HPO_3$, meta-phosphoric acid.

$N_2O_5 + H_2O = 2HNO_3$, nitric acid.

$SO_3 + H_2O = H_2SO_4$, sulphuric acid.
$SO_2 + H_2O = H_2SO_3$, sulphurous acid.

They are therefore called *acidic oxides*. Note that they are *not acids*—they form acids when they unite with water. They may therefore be called acid *anhydrides*; thus SO_3 is sulphur trioxide or sulphuric anhydride.

Certain metallic oxides are acidic, e.g., Mn_2O_7, manganese heptoxide, and CrO_3, chromium trioxide.

(ii) Metallic oxides are, however, usually *basic oxides*, and are true bases (contrast acidic oxides and acids), since they will react with acids to form salts + water. Some of them are capable of combining with water to form *hydroxides*, which are still bases—

$CaO + H_2O = Ca(OH)_2$, calcium hydroxide or slaked lime.

Note that hydroxides are not the same as *hydrates*. A hydroxide contains the hydroxyl group —OH, while a hydrate is merely a loose compound of a substance with water, e.g., copper sulphate crystals, $CuSO_4.5H_2O$, are copper sulphate *penta-hydrate*; $BaCl_2.2H_2O$ is barium chloride *dihydrate*. In a solid hydrate, the water is generally present as water of crystallization.

Some basic oxides are soluble in water, giving alkaline solutions owing to the formation of the hydroxides, which yield —OH′ ions—

$$Na_2O + H_2O = 2NaOH \rightleftharpoons 2Na^{\cdot} + 2OH'.$$

The solution of a basic oxide, insoluble in water, by a dilute acid is easily explained in terms of the ionic theory:

Suppose we have some zinc oxide in contact with water. We assume that, although the zinc oxide is apparently insoluble, it is in reality slightly soluble as the hydroxide, which ionizes into $Zn^{\cdot\cdot}$ and 2OH′—

$$ZnO + H_2O \rightleftharpoons Zn(OH)_2 \rightleftharpoons Zn^{\cdot\cdot} + OH' + OH'.$$

We should have then two equilibria, that between zinc hydroxide and zinc oxide and water on the one hand and that between un-ionized zinc hydroxide and zinc and hydroxyl

ions on the other. When an acid, HX, is added, the new ions $H^{\cdot}$ and X' are introduced, the former of which immediately combine with the —OH' ions to form un-ionized water. In this way the equilibrium $Zn^{\cdot\cdot} + 2OH' \rightleftharpoons Zn(OH)_2$ is upset, and more zinc hydroxide ionizes, and this in turn causes more $ZnO + H_2O$ to form zinc hydroxide. In this way the whole of the zinc oxide will be at last dissolved, if sufficient acid be added.

Basic oxides may be prepared—

(*a*) By heating the metal in air or in oxygen.

(*b*) By strongly heating the carbonate of the metal—

$$ZnCO_3 = ZnO + CO_2.$$

(*c*) By heating the hydroxide of the metal—

$$Cu(OH)_2 = CuO + H_2O.$$

(*d*) By heating the nitrate of the metal—

$$Pb(NO_3)_2 = PbO + 2NO_2 + \text{oxygen}.$$

(*e*) By heating a peroxide of the metal, when the excess of oxygen is sometimes lost—

$$Pb_3O_4 = 3PbO + \text{oxygen}.$$

Not all these methods are applicable in every case; sometimes one method is more convenient and sometimes another.

(iii) *Peroxides and Sub-oxides* contain respectively more and less oxygen than would be expected from the normal valency of the other element present. Peroxides are formed by both metals and non-metals. The commonest are—

	Normal oxide.
Sodium peroxide, Na_2O_2. . .	Na_2O.
Hydrogen peroxide, H_2O_2 . . .	H_2O.
Manganese dioxide, MnO_2 . . .	MnO.
Lead peroxide, PbO_2	PbO.
Barium peroxide, BaO_2	BaO.
Nitrogen peroxide, N_2O_4. . . .	N_2O_3.
Chlorine peroxide, ClO_2	Cl_2O.

Peroxides often yield oxygen on heating alone or when heated with strong sulphuric acid. With hydrochloric acid, they sometimes give hydrogen peroxide in the cold (e.g. Na_2O_2,

BaO_2), and on heating give oxygen (e.g. H_2O_2) or chlorine (e.g. $PbO_2 + 4HCl = PbCl_2 + 2H_2O + Cl_2$). A distinction has sometimes been drawn between peroxides and dioxides, but it is artificial and it is better to neglect it.

Suboxides contain less oxygen than the normal oxide, e.g. carbon sub-oxide, C_3O_2. They are as a rule unstable.

It often happens that an element has two or more normal valencies, in which case it may form two or more normal oxides, e.g FeO and Fe_2O_3, both normal basic oxides. In this case, the oxide containing a higher percentage of the element other than oxygen is called the *-ous* (from the Latin *osus*, richness) oxide, and the other the *-ic* oxide ; thus FeO is ferr*ous* oxide and Fe_2O_3 ferr*ic* oxide. Some peroxides behave as normal *-ic* oxides, e.g. when manganese dioxide, MnO_2, is treated with concentrated hydrochloric acid in the cold, it forms a salt + water—

$$MnO_2 + 4HCl = MnCl_4 + 2H_2O.$$

It may therefore be called manganic oxide. On heating, however, it yields chlorine and manganous chloride—

$$MnO_2 + 4HCl = MnCl_2 + 2H_2O + Cl_2,$$

and therefore is a peroxide. These facts serve to show that the classification of oxides given above is convenient only and not rigorous.

(iv) *Neutral Oxides.*—Certain oxides cannot be placed in any of the above classes—they are neither acidic nor basic nor peroxides nor sub-oxides (in the usual sense that sub-oxides are unstable). Such are nitric oxide, NO, carbon monoxide, CO, and water, H_2O. These are called neutral oxides.

A fifth class of oxides might be made of those that show both acidic and basic properties. A common example is aluminium oxide, Al_2O_3. This will dissolve in acids to give a salt of aluminium—

$$Al_2O_3 + 6HCl = 2AlCl_3 + 3H_2O,$$

and also in caustic soda solution to give sodium aluminate—

$$Al_2O_3 + 6NaOH = 2Na_3AlO_3 + 3H_2O.$$

It is therefore both basic and acidic. Such an oxide may be

called *amphoteric* (not " anthropomorphic " as a Clifton boy recently wrote !). Other examples are zinc oxide, stannic oxide (SnO_2), and lead peroxide (PbO_2). In terms of the ionic theory, the phenomenon is explained in the following way. Aluminium oxide in the presence of water dissolves slightly, yielding aluminium hydroxide, $Al(OH)_3$. This in solution ionizes in two ways—

(i) $Al(OH)_3 \rightleftharpoons Al''' + 3OH'$.
(ii) $Al(OH)_3 \rightleftharpoons 3H^{\cdot} + AlO_3'''$.

Both reactions occur simultaneously, the limiting factor being that the hydrogen and hydroxyl ions present are never in greater concentration than they are in pure water. It is clear that if an acid be added, the equilibria will be upset in such a way that the ionization (i) will be increased, while (ii) will be decreased ; whereas if a base be added, the reverse is true.

Further Properties of Oxygen.—Oxygen boils at —182° C. Liquid oxygen is a pale blue liquid, which is attracted by the magnet. Solid oxygen was first prepared in 1911 by Sir James Dewar by evaporating the liquid at extremely low pressures. Oxygen proved very difficult to solidify, and it was only by making use of the low pressures obtainable by the absorptive powers of charcoal cooled in liquid air that success was finally attained. The freezing-point of oxygen is —219° C. Oxygen is used commercially in welding by the oxy-acetylene flame, and medicinally in cases of difficult respiration.

Ozone, O_3

If the Chinese discovered oxygen, we may say that Homer discovered ozone, although he is not usually considered the discoverer. It is, however, interesting to note that Homer mentions in the *Iliad* [1] the peculiar smell that occurs in the vicinity of a flash of lightning (or a " thunderbolt "), and to remember that in all the text-books van Marum (1785) is called the discoverer of ozone because he noticed the same smell near an electrical machine in action. van Marum, ignoring the cat-skins on the machine, ascribed the smell to

[1] Bk. viii. 135.

a new substance. Further researches by SCHÖNBEIN (1839) showed that this new substance was indeed the cause of the smell, and to it Schönbein gave the name of ozone, from the Greek ὄζω, I smell.

Occurrence.—Ozone is said to occur in the air, and many thousands of people who smell the rotting seaweed on our shores remark on the health-giving properties of the ozone in sea-air. In point of fact, it is very difficult to prove that ozone is present in the lower atmosphere in any appreciable quantity: an argument seriously advanced was (*a*) the sky is blue; (*b*) ozone is a blue gas, ∴ (*c*) the air contains ozone. Ozone may be present in the atmosphere—it probably is. Most things are.

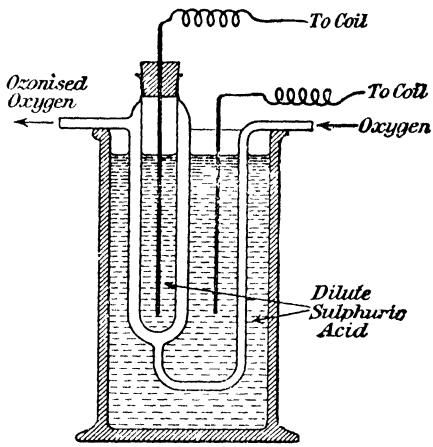


FIG. 89.—Brodie's Ozone Apparatus.

It is certainly true that ozone occurs in the air at a height of some 50 kilometres above sea-level, the amount changing with latitude and also with the weather conditions. The ozone shields the earth from intense ultra-violet radiation from the sun, which would otherwise cause serious effects. "It further causes the upper atmosphere at a height of 40–50 kilometres to be at a temperature in the neighbourhood of the normal boiling-point of water. This, in its turn, gives rise to the zones of abnormal audibility of sound from large explosions at a distance of some hundreds of miles from the explosion itself." (*Nature*, March, 1931.)

Preparation.—Ozone is usually prepared by passing the silent electric discharge through oxygen. It was for long supposed that the oxygen must be moist, and hence some chemists

were of opinion that ozone was an oxide of hydrogen, but SHENSTONE (1907) in the laboratory at Clifton College showed that perfectly dry pure oxygen could be converted into ozone, which therefore must be an allotropic form of oxygen and not an oxide of hydrogen. This had long been suspected, of course.

Various forms of ozonizer are used in the laboratory, one of the most convenient being that known as BERTHELOT'S, although it was invented by BRODIE in 1872. This is shown in Fig. 89. It consists of two coaxial tubes, in the inner of which sulphuric acid is placed. Oxygen may be passed

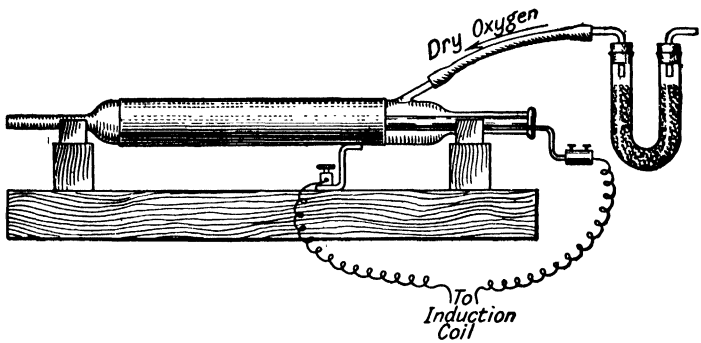


FIG. 90.—Siemens' Ozone Apparatus.

through the annular space between the two tubes, and the outer tube is surrounded by sulphuric acid in a wide gas-jar.

The two terminals of an induction coil are connected to two stout copper wires, one of which is placed in the inner tube of sulphuric acid and one in the sulphuric acid in the gas-jar. When the coil is working, a discharge passes from one lot of sulphuric acid through the oxygen to the other, and some of the oxygen is converted into ozone.

SIEMENS' ozonizer consists of two coaxial glass tubes, the outside of the outer one and the inside of the inner one being coated with tinfoil The oxygen is passed through the space between the tubes, and the two coats of tinfoil are connected one to one terminal of an induction coil and the other to the

other terminal. The principle is thus exactly the same as that of Brodie's apparatus.

The *ozonair* apparatus used in the Tube railways in London consists of a box containing plates of mica covered on each side with a coating of metal. Air is blown through the box and a discharge of electricity made to pass continuously between the plates. Another form of ozonizer used on a commercial scale is that invented by Siemens and Halske. This consists of an iron box containing water into which dip several porcelain tubes. Inside each of these tubes is another tube of aluminium. The iron box is connected to earth and

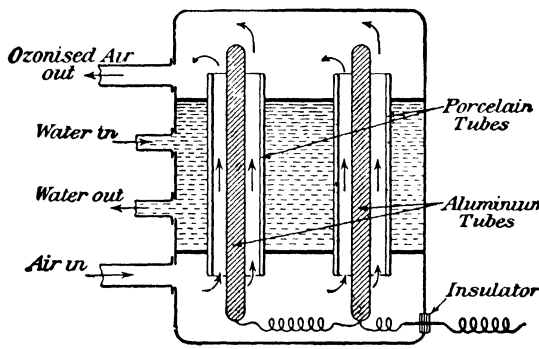


FIG. 91.—Siemens-Halske Ozonizer.

the aluminium tubes are now charged to a high potential. Air is passed over the aluminium tubes and through the porcelain tubes and is ozonized.

Chemically, ozonized oxygen may be prepared by the action of nitric acid on ammonium persulphate, but all the methods hitherto described in this chapter convert at most 10–12 per cent. of the oxygen into ozone. Practically pure ozone (95 per cent.) can be obtained by the electrolysis of acidulated water, using a high current density and a platinum anode the surface of which is scarcely as big as that of a pin's head. Under these conditions, ozone is evolved from the anode

Properties.—Ozone is a poisonous pale blue gas which can be condensed to an ultramarine liquid boiling at about

—112°C. and freezing at —250° to a violet-black solid. Liquid ozone is fairly stable if pure, but readily explodes if organic matter is present. Ozone in the gaseous state is more stable, but is catalytically decomposed by finely divided metals. Silver, however, is converted into silver oxide. (Cf. hydrogen peroxide on silver oxide.) Ozone is a strong oxidizing agent, and readily attacks rubber and other organic compounds. It bleaches indigo, and converts black lead sulphide into lead sulphate, which is white—

$$PbS + 4O_3 = PbSO_4 + 4O_2.$$

Ozone liberates iodine from a solution of potassium iodide,

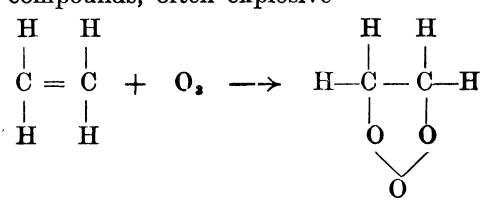
$$2KI + H_2O + O_3 = 2KOH + I_2 + O_2,$$

but as many other oxidizing agents do the same, this cannot be used as a conclusive test for ozone.

When ozone is passed over sulphur, a blue luminescence is shown, and sulphur dioxide and trioxide are obtained; but the action is slow.

One of the most characteristic properties of ozone is that it makes mercury "tail" or stick to glass, probably owing to the formation of a film of an oxide of mercury. The mercury can easily be cleaned afterwards by shaking with water.

Ozone will not react directly with nitrogen, but moist ammonia is at once converted into ammonium nitrite and nitrate. This represents an oxidation of some of the ammonia to nitrous and nitric acids, which then combine with the excess of ammonia to form the corresponding ammonium salts. Ferrous salts are oxidized by ozone to ferric salts. Many organic compounds such as turpentine, ethylene, and benzene, combine directly with ozone to form *ozonides*, which are unstable compounds, often explosive—



Ethylene. Ethylene ozonide.

It will have been noticed from the above account of the properties of ozone that this gas can enter into reaction in three ways—

(i) Catalytic decomposition, $2O_3 \longrightarrow 3O_2$.

(ii) In such a way that from one molecule of ozone one molecule of oxygen is liberated, e.g.—

$$2KI + H_2O + O_3 = 2KOH + I_2 + O_2.$$

(iii) In such a way that no oxygen is liberated, e.g. formation of ozonides.

Tests.—(i) The smell. (ii) Liberation of iodine from potassium iodide solution (not characteristic). (iii) "Tailing" of mercury. (iv) Ozone will turn a piece of filter paper soaked in a solution of *tetrabase* (tetramethyl-p-p′-diaminodiphenylmethane) a purple colour; hydrogen peroxide has no action on tetrabase, chlorine turns it blue, and oxides of nitrogen yellow. (v) Filter paper soaked in a solution of benzidine (another organic compound) is turned brown by ozone, red by chlorine and blue by oxides of nitrogen, while hydrogen peroxide has no action. (vi) Tincture of guaiacum is turned blue by ozone.

Composition.—Ozone consists of atoms of oxygen combined together in groups of three, that is, the molecules of ozone are triatomic (O_3) while those of oxygen are diatomic (O_2). Ozone is said to be an *allotropic* form of oxygen. *When an element exists in more than one form, those forms being physically and often chemically distinct, it is said to exhibit allotropy, and the different forms are called allotropes or allotropic forms.* Since in this case allotropy is shown to be accompanied by a different molecular structure, it is possible that allotropy is to be accounted for (*a*) by variations in the atomicity of the molecules of the allotropes, or (*b*) by variations in the arrangement of the atoms in the molecules, whether the atomicity is the same or different. Allotropy is a common phenomenon. (See under *sulphur* and *phosphorus*.)

The proof of the formula of ozone was carried out in a very elegant manner by SORET. Soret enclosed two equal volumes of the same specimen of ozonized oxygen over water

in two graduated tubes (Fig. 92). Into one tube he introduced a little turpentine, which absorbed the ozone without liberation of oxygen; the decrease in volume therefore is equal to the volume of ozone originally present. As an equal volume of the same specimen of ozonized oxygen was used in the second tube, this must contain the same volume of ozone as the first tube, and this volume is now known. The second tube was heated and then allowed to regain its original temperature, when it was found that an

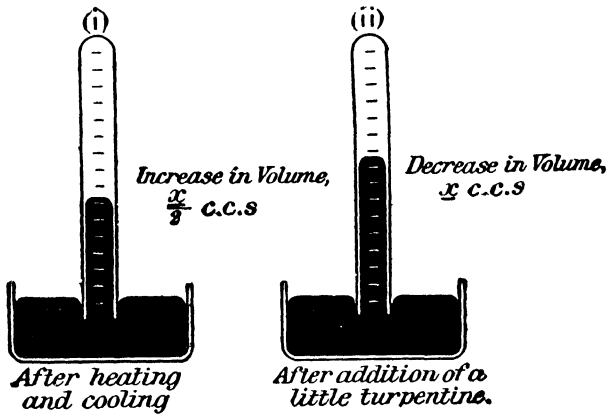


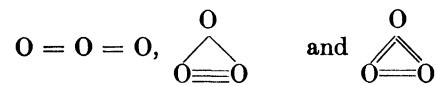
FIG. 92.

increase in volume had occurred, and all the ozone was decomposed into oxygen. The volume of oxygen formed must be equal to the volume of ozone decomposed *plus* the increase in volume.

Soret found that the decrease in volume in the first tube was exactly twice the increase in volume in the other. Hence, 1 volume of ozone gives $1\frac{1}{2}$ volumes of oxygen, $\therefore$ by Avogadro's Hypothesis, one molecule of ozone gives $1\frac{1}{2}$ molecules of oxygen. But the molecule of oxygen is O_2 $\therefore$ that of ozone is O_3.

The further question remains, what is the structural for

mula for ozone? If oxygen is uniformly bivalent, the structure of the ozone molecule must be  . From analogy with other substances, however, we might expect such a substance to be stable—more stable indeed than oxygen itself—but the reverse is true. Since one atom of oxygen is easily lost by the molecule of ozone, it is possible that this atom has a special position in the molecule. Such arrangements can be conceived of, if we assume that oxygen may act as a quadrivalent element in ozone. Many compounds are known in which oxygen is quadrivalent, so that there is no difficulty in assuming its quadrivalence in ozone. We could then construct such formulæ as



Of these, the second would seem to be that most likely to lose an atom of oxygen, but at present there is no conclusive evidence on the point.

Endothermic Nature of Ozone.—When ozone is transformed into oxygen, a considerable amount of heat is evolved; conversely, when ozone is formed from oxygen heat is absorbed, therefore ozone is an *endothermic* substance—in fact, when one gram-molecule of ozone is formed from oxygen, 34,100 calories are absorbed. By the principle of Le Chatelier, therefore, we should expect ozone to be formed when oxygen is heated. However, if we pass a stream of ozonized oxygen through a hot tube, no ozone can be detected in the issuing gas. These facts seem to be contradictory to one another; how are we to reconcile them?

In the first place, the reaction $2O_3 = 3O_2$ is a reversible one, $2O_3 \rightleftharpoons 3O_2$. Hence at any given temperature and pressure there will be a certain definite equilibrium mixture of ozone and oxygen. At ordinary room temperature and atmospheric pressure, the percentage of ozone in the equilibrium mixture is quite inappreciable, and even at 1,300° C. it is only 0·15. But the ozonized oxygen from the ozonizer probably contains

about 8 per cent. of ozone; this is far too high a proportion for equilibrium, and the ozone will therefore decompose into oxygen until equilibrium is set up. This it does comparatively slowly, so that ozonized oxygen *appears* to be in equilibrium; it is not really so. Now we know that a rise in temperature of 10° approximately doubles the rate of a chemical change. If therefore we heat the ozonized oxygen to say 420°, the room temperature being 20° C., we shall increase the rate of decomposition of the ozone by 2^{40}, and the ozone will reach its equilibrium concentration very quickly. But even at 420°, the percentage of ozone in the equilibrium mixture is too minute to be detected; and hence the paradox.

Uses.—Ozone is an excellent germicide; it is therefore used for sterilizing drinking-water (e.g. at Paris and Lille) and for the purification of air. The statement that it is beneficial to breathe ozone is untrue; the gas has an irritating effect upon the mucous membrane.

Oxidation and Reduction.—When a substance combines with oxygen it is said to be oxidized; reduction takes place when oxygen is removed from a substance. Thus—

$$2Cu + O_2 = 2CuO$$

represents an *oxidation* of copper to copper oxide, while

$$PbO + C = Pb + CO$$

represents the *reduction* of lead oxide to lead, carbon monoxide being evolved as well.

Hydrogen is often used for effecting reduction, and the term was soon extended to cases in which the hydrogen merely added itself on to the substance concerned, and did not actually remove oxygen; thus, acetaldehyde, $CH_3.C\begin{matrix}H\\ \diagdown\!\!\!\!\diagup\\ O\end{matrix}$, if treated with hydrogen under suitable conditions, is converted into ethyl alcohol—

$$CH_3.C\begin{matrix}H\\ \diagdown\!\!\!\!\diagup\\ O\end{matrix} + H_2 = CH_3.CH_2.OH$$

or $C_2H_4O + H_2 = C_2H_6O$.

Here the acetaldehyde is said to have been *reduced*; the reverse process, namely, the conversion of ethyl alcohol into acetaldehyde, is called *oxidation*, although no oxygen has been added to the alcohol—hydrogen has been removed—

$$C_2H_6O - H_2 = C_2H_4O.$$

We may now define (i) *oxidation*, as the removal of hydrogen from a substance, or addition of oxygen to a substance; (ii) *reduction*, as the opposite of oxidation. The conversion of sulphuretted hydrogen into sulphur is therefore an oxidation—

$$H_2S = H_2 + S.$$

Hydrogen is a typical electropositive element and oxygen a typical electronegative element. The terms oxidation and reduction have therefore been still further extended in meaning, to include *an increase in proportion of electronegative constituent in a substance* (OXIDATION), *and an increase in proportion of electropositive constituent* (REDUCTION).

Examples—

(*a*) $FeCl_2 + Cl_2 = 2FeCl_3$ (*oxidation* of ferrous chloride to ferric chloride).

(*b*) K_2MnO_4 + chlorine = $KCl + KMnO_4$ (*oxidation* of potassium manganate to potassium permanganate).

(*c*) $Cu + S = CuS$ (*oxidation* of copper to copper sulphide).

(*d*) $S + H_2 = H_2S$ (*reduction* of sulphur to sulphuretted hydrogen).

(*e*) $MnCl_4 = MnCl_2 + Cl_2$ (*reduction* of manganic chloride to manganous chloride).

Oxidation and reduction may therefore take place although no oxygen or hydrogen is present. Note that every oxidation is necessarily accompanied by a corresponding reduction, and *vice versâ*. Thus, in (*c*) above the sulphur is reduced by the copper, and in (*d*) the hydrogen is oxidized by the sulphur.

In a great many cases, oxidation is accompanied by an increase in valency of the element or group oxidized, and reduction by a decrease. In (*a*) above, the valency of the iron is increased from 2 to 3 during the oxidation. In the case of

electrolytes, it is true to say that oxidation involves increase of charge on the positive ion or decrease in charge on the negative ion, but to *define* oxidation in this way is unsuitable, since non-electrolytes would not be included.

Oxidizing and Reducing Agents.—A substance that will bring about oxidation is an oxidizing agent, while one that causes reduction is a reducing agent. Common oxidizing agents are oxygen, ozone, hydrogen peroxide, chlorine, bromine, sulphur, nitric acid, chlorates, nitrates, peroxides, permanganates, dichromates. Common reducing agents are hydrogen, sulphuretted hydrogen, mixtures producing "nascent" hydrogen, hydrogen iodide, sulphur dioxide, carbon, zinc dust, stannous chloride, and many organic substances.

QUESTIONS

1. Write an essay on "chemistry without oxygen."

2. What do you understand by *oxidation* and *reduction*? Mention the chief oxidizing agents and reducing agents. How would you test a given substance for (*a*) oxidizing powers, (*b*) reducing powers?

3. Write an account of the phlogiston theory of combustion, and estimate its value in the development of chemistry.

4. Do you agree with the Public Prosecutor's statement that "La République n'a pas besoin de savants"?

5. What justification had Wurtz for saying that chemistry is a French science?

6. How does oxygen occur in nature?

7. Describe a laboratory method for the preparation of oxygen. What volume of oxygen, measured over water at 18° C. 740 mm., could be obtained from 30·0 grams of potassium chlorate?

8. Describe, with examples, the classification of oxides.

9. How is ozone prepared (*a*) in the laboratory; (*b*) commercially? What are its commercial uses?

10. What is the formula for ozone, and how has it been ascertained?

11. Ozone is an endothermic substance; how do you account for the fact that if ozonized air is passed through a hot tube, no ozone can be detected in the issuing gas?

12. A specimen of ozonized oxygen was found to diffuse 0·91 times as fast as pure oxygen under the same conditions of temperature and pressure. What is the percentage by volume of ozone in the specimen?

13. 1,000 c.c. of ozonized air were bubbled through potassium iodide solution. To react with the liberated iodine, 9·3 c.c. of N/50 sodium thiosulphate were required. Find the percentage by volume of ozone in the original gas.

14. Mention some characteristic tests for ozone. What is the action of ozone upon (*a*) mercury ; (*b*) lead sulphide ; (*c*) silver ; (*d*) ethylene ?

Hydrogen Peroxide, H_2O_2

History.—Hydrogen peroxide was discovered by Thénard in 1818. He prepared it by the action of dilute acids upon barium peroxide, and showed that it contains twice the proportion of oxygen to hydrogen that is found in water. He therefore called it *eau oxygenée*. Its molecular weight was determined in 1893 by Carrara, using the cryoscopic method ; he obtained the number 34, which corresponds to the formula H_2O_2. Pure hydrogen peroxide was first made by Wolffenstein in 1894.

Occurrence.—Hydrogen peroxide occurs in minute quantities in the atmosphere. It is said that snow may contain as much as 0·0001 per cent. Traces of hydrogen peroxide have been found in plants.

Preparation.—Hydrogen peroxide is formed in small quantity (*a*) when ultraviolet light is passed through water, especially in the presence of oxygen ; (*b*) during electrolysis of acidulated water (probably as a result of the interaction of water and persulphuric acid) ; (*c*) by heating steam to an exceedingly high temperature ; (*d*) during the combustion of hydrogen and many organic compounds such as alcohol and ether.

It is frequently prepared from barium peroxide, BaO_2, or preferably barium peroxide dihydrate, $BaO_2.2H_2O$, by the action of an acid—sulphuric or carbonic is generally used. The barium peroxide is made up into a thin paste with cold water, and this paste is then poured slowly into ice-cold water containing the calculated quantity of sulphuric acid to react completely with the barium peroxide, when

$$BaO_2 + H_2SO_4 = BaSO_4 + H_2O_2.$$

The barium sulphate is precipitated and may be filtered off.

If carbonic acid is to be used, the paste of barium peroxide in ice-cold water is made rather thinner, and a stream of carbon dioxide is blown through. In this way the formation

of an insoluble *barium percarbonate*, $BaCO_4$, is avoided, whereas if the paste is added slowly to water through which carbon dioxide is blown (so that the latter is in excess) much of the percarbonate is precipitated and the yield of hydrogen peroxide is lowered.

The aqueous solution of hydrogen peroxide prepared in this way may be evaporated on the water-bath until it reaches a concentration of about 50 per cent. It is then repeatedly fractionated under reduced pressure until a 99 per cent. solution of hydrogen peroxide is obtained. By cooling a little of this solution in a freezing-mixture of solid carbon dioxide and ether, crystals are obtained; and if the bulk of the 99 per cent. solution is then cooled to −10° C. and inoculated with one of these crystals, a mass of transparent crystals of pure solid hydrogen peroxide separates, melting at −2° C.

If the presence of salt is not deleterious, a solution of hydrogen peroxide may be conveniently prepared by adding sodium peroxide gradually to ice-cold dilute hydrochloric acid—

$$Na_2O_2 + 2HCl = 2NaCl + H_2O_2.$$

The sodium peroxide may also be added to cold dilute sulphuric acid, most of the sodium sulphate crystallizing out. The residual liquid is fractionally distilled, the higher boiling-point fraction containing up to 30 per cent. of hydrogen peroxide.

JAUBERT'S method for obtaining a solution of hydrogen peroxide is to add citric acid to a solution of sodium perborate.

Properties.—Pure hydrogen peroxide at ordinary temperatures is a colourless syrupy liquid with an astringent taste and a strongly acid reaction to litmus. It is comparatively stable, but explodes if brought into contact with platinum black or manganese dioxide. It sets fire to powdered carbon or magnesium and to cotton wool, but is said to have no action on reduced iron. Its specific gravity is 1·46 and its boiling-point 85° at 68 mm. pressure.

Hydrogen peroxide is an exothermic substance, but less so

than water, therefore when it decomposes into water and oxygen heat is evolved—

$$2H_2O_2 = 2H_2O + O_2 + 44{,}800 \text{ calories.}$$

Aqueous solutions of hydrogen peroxide are usually kept in bottles lined with paraffin-wax, since they decompose in contact with glass. They are also readily decomposed, with evolution of oxygen, by finely divided or colloidal metals; thus a colloidal solution of manganese containing 55 grams of manganese in 10,000,000 litres of water exercises a marked catalytic effect on the decomposition of hydrogen peroxide in aqueous solution. Colloidal platinum, copper, etc., have a similar action.

$$2H_2O_2 = 2H_2O + O_2.$$

Certain "organic catalysts" or *enzymes* act in the same way. The presence of traces of hydrocyanic acid, arsenic, etc., retards the action of the above catalysts, which are then said to be "poisoned." The decomposition of aqueous solutions of hydrogen peroxide is also retarded by the addition of alcohol, glycerol, calcium chloride, pyrogallol, or barbituric acid. These substances are therefore often added to commercial hydrogen peroxide solution to make it more stable; they are good examples of *negative catalysts*.

Hydrogen peroxide solutions are put on the market as "10 volume," "20 volume," and "100 volume"; these names refer to the volume of oxygen obtained by the decomposition of the hydrogen peroxide in 1 volume of the solution. The 30 per cent. solution is sold under the name of "perhydrol."

Hydrogen peroxide is a powerful oxidizing agent; it liberates iodine from potassium iodide solution,

$$2KI + H_2O_2 = 2KOH + I_2,$$

and converts lead sulphide into lead sulphate—

$$PbS + 4H_2O_2 = PbSO_4 + 4H_2O,$$

just as ozone does.

It will bleach many coloured substances, and as it is mild in action and leaves no injurious residue it is employed for

bleaching silk, wool, and straw, as well as teeth and hair. It is unfortunate that the bright yellow colour given to hair by hydrogen peroxide is so easily recognizable.

Owing to the readiness with which it loses oxygen it forms a good bactericide, and this property is made use of in hydrogen peroxide mouth-washes and gargles. "*Sanitas*" and other disinfecting solutions also contain hydrogen peroxide.

Action on Silver Oxide.—Although hydrogen peroxide is an oxidizing agent, when it is added to silver oxide the latter is *reduced* to silver, and the hydrogen peroxide decomposed into water and oxygen—

$$Ag_2O + H_2O_2 = 2Ag + H_2O + O_2.$$

This can be explained by the fact that when a molecule of hydrogen peroxide decomposes into water and oxygen, the heat evolved is greater than the heat of formation of silver oxide, which can therefore be split up into silver and oxygen. It is sometimes suggested that the "attraction" of the silver atoms for the one atom of oxygen and of the "water" in hydrogen peroxide for the other ($H_2O.O$) is less than that of the two atoms of oxygen for one another to form a molecule of oxygen. This, however, is nothing more than an expression of the fact of the reaction in other words; it is not an explanation. Besides, if such attraction exists, why does not ozone reduce silver oxide to silver?

Potassium permanganate is readily decolourized by hydrogen peroxide in acid solution, both substances being reduced—

$$K_2Mn_2O_8 + 3H_2SO_4 + 5H_2O_2 = K_2SO_4 + 2MnSO_4 + 8H_2O + 5O_2$$

This reaction may be used to estimate the strength of a hydrogen peroxide solution, but errors are likely to arise if the solution contains glycerol or other organic preservative, as many of these substances are themselves oxidized by potassium permanganate.

Structure of the Hydrogen Peroxide Molecule.

(i) On decomposition, 34 parts by weight of hydrogen peroxide give 18 parts by weight of water and 16 of oxygen.

$\therefore$ empirical formula = HO.

(ii) Cryoscopic determination of molecular weight gives 34

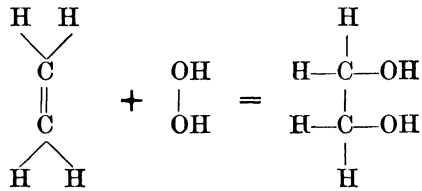
$\therefore$ the formula = H_2O_2.

(iii) The atoms in the molecule may be arranged in two ways—

a. H—O—O—H, or *b*. $\begin{matrix} H \\ H \end{matrix}\!\!>\!O = O$

assuming in *b* that one oxygen is quadrivalent.

In favour of the formula H—O—O—H is the fact that ethylene combines with hydrogen peroxide to form ethylene glycol, which reaction is most easily expressed by the equation—



Ethylene. Ethylene glycol.

Similarly, when treated with diethyl sulphate $(C_2H_5)_2SO_4$, hydrogen peroxide yields ethyl peroxide $(C_2H_5)_2O_2$. Now if this has the formula $\begin{matrix} C_2H_5 \\ C_2H_5 \end{matrix}\!\!>\!O = O$ (corresponding to $\begin{matrix} H \\ H \end{matrix}\!\!>\!O = O$ for hydrogen peroxide) we should expect that on reduction it would give ethyl ether and water—

$$\begin{matrix} C_2H_5 \\ C_2H_5 \end{matrix}\!\!>\!O = O + H_2 = \underset{\text{Ethyl ether.}}{\begin{matrix} C_2H_5 \\ C_2H_5 \end{matrix}\!\!>\!O} + H_2O$$

Experiment shows that it actually gives ethyl alcohol, which indicates that it has the formula, $\begin{matrix} C_2H_5—O \\ | \\ C_2H_5—O \end{matrix}$

$$\begin{matrix} C_2H_5.O \\ | \\ C_2H_5.O \end{matrix} + H_2 = \underset{\text{Ethyl alcohol.}}{2C_2H_5.OH}$$

and therefore hydrogen peroxide would be $\begin{matrix} H—O \\ | \\ H—O \end{matrix}$.

However, the formula $\begin{matrix} H \\ H \end{matrix}\!\!\rangle O = O$ agrees better with the ready decomposition of hydrogen peroxide into water and oxygen, and also with certain physical properties. It is possible that ordinary hydrogen peroxide is an equilibrium mixture of H—O—O—H and $\begin{matrix} H \\ H \end{matrix}\!\!\rangle O = O$

$$H—O—O—H \rightleftharpoons \begin{matrix} H \\ H \end{matrix}\!\!\rangle O = O.$$

Similar cases of compounds reacting as though they had two different structures are common in organic chemistry, where the phenomenon is called *tautomerism*, and it has been shown that such compounds are generally equilibrium mixtures of their two " tautomeric " forms ; hence it is reasonable to advance the same explanation in the case of hydrogen peroxide.

Tests for Hydrogen Peroxide.

(i) The liberation of iodine from potassium iodide is not a conclusive test, since other oxidizing agents produce the same result ; it is, however, alleged that only hydrogen peroxide will liberate iodine from potassium iodide in the presence of ferrous sulphate.

(ii) A dilute solution of potassium dichromate acidified with sulphuric acid gives a deep blue colour with hydrogen peroxide, owing to the formation of a perchromic acid ($HCrO_5$ according to Moissan). This quickly decomposes with evolution of oxygen, but if ether is added it dissolves the perchromic acid to a blue solution in which it is much more stable.

(iii) Tincture of guaiacum mixed with malt extract gives a blue colour with hydrogen peroxide.

(iv) " Tetrabase " (p. 425) is not affected.

(v) Benzidine dissolved in alcohol is not affected.

(vi) Titanium dioxide (TiO_2) dissolves in sulphuric acid to a colourless solution. This is turned an orange colour by hydrogen peroxide, owing to the formation of TiO_3, pertitanic anhydride or titanium trioxide.

QUESTIONS

1. Describe the preparation and properties of pure anhydrous hydrogen peroxide.

2. Mention three characteristic tests for hydrogen peroxide. How would you distinguish between a solution of this substance and (*a*) a solution of ozone ; (*b*) a solution of nitrous acid ; (*c*) a dilute solution of chlorine ?

3. What is the formula for hydrogen peroxide, and how has it been arrived at ? What evidence have we as to the way in which the atoms are arranged in the molecule of hydrogen peroxide ?

4. For what purposes is hydrogen peroxide used (*a*) in the laboratory ; (*b*) commercially ?

5. Hydrogen peroxide is an oxidizing agent. Mention facts in support of this statement, and explain the action of hydrogen peroxide on silver oxide.

6. Calculate the strength of a solution of hydrogen peroxide which is exactly " 10-volume " at 15° C. 760 mm.

7. 20 c.c. of a solution of hydrogen peroxide decolourized 18·5 c.c. of N/10 potassium permanganate. Calculate the strength of the solution.

8. 23·6 c.c. of a hydrogen peroxide solution were treated with excess of potassium iodide and dilute sulphuric acid. The resulting solution was made up to 250 c.c. 20 c.c. of this solution required 15·4 c.c. of N/10 sodium thiosulphate. Find the strength of the original solution of hydrogen peroxide.

9. How would you estimate the weights per litre of hydrogen peroxide and oxalic acid in a solution containing both these substances ?

WATER

Occurrence.—Pure water is never found in nature, but in a more or less impure state is widely distributed in enormous quantities.

NATURAL WATERS.

(i) *Rain-water* is the purest form of natural water. In country districts it contains only gaseous impurities, such as

carbon dioxide, oxygen and nitrogen, which it has absorbed from the atmosphere, together with a little salt from the sea. Near towns, however, rain-water is much less pure, and always contains soot and compounds of sulphur, such as sulphuric acid.

(ii) *River and spring water* contains varying amounts of solid matter in solution, according to the ground in which it occurs. Salts of calcium render the water *hard* (p. 445).

(iii) *Mineral waters* are waters containing unusual impurities known or alleged to have certain curative properties. "Chalybeate" waters, for example, contain iron as ferrous bicarbonate, while the water of a certain spring at Epsom contains magnesium sulphate or "Epsom salt." Probably the most popular "mineral spring" in the world is the Well Zemzem at Mecca, the water of which is drunk by hundreds of thousands of pilgrims annually, and exported in bottles to all parts of the Muhammadan world. It is said to contain magnesium sulphate, and, says SIR RICHARD BURTON, "It is apt to cause diarrhœa and boils, and I never saw a stranger drink it without a wry face."

(iv) *Sea-water* contains about 3·6 per cent. by weight of solid matter in solution, chiefly the chlorides, sulphates and carbonates of sodium, potassium, calcium and magnesium. Salt forms about two-thirds of the total solid matter present.

Composition.—That water is a compound of hydrogen and oxygen was first shown by CAVENDISH in 1781. The *volumetric* composition may be determined by explosion of a mixture of hydrogen and oxygen in a eudiometer tube over mercury (Fig. 93); it is found that 2 volumes of hydrogen require exactly 1 volume of oxygen, and, if the whole experiment is carried out at a temperature above the boiling-point of water, 2 volumes of steam are produced.

Hence, by Avogadro's hypothesis,

2 molecules of hydrogen + 1 molecule of oxygen give 2 molecules of steam.

∴ 1 molecule of hydrogen + ½ molecule of oxygen give 1 molecule of steam.

Therefore the molecule of steam must be H_2O.

Very accurate experiments on the *gravimetric* composition of water were carried out by MORLEY in 1895. A tube through which passed two platinum wires, for sparking, was fitted with two drying tubes containing phosphorus pentoxide, to prevent any loss of the water formed in the reaction. The whole was then evacuated and weighed. Pure *dry* hydrogen and pure *dry* oxygen were next admitted

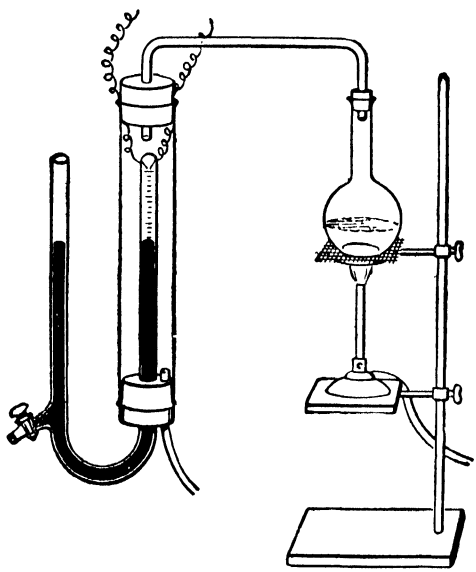


FIG. 93.

(from weighed reservoirs) to the reaction tube through the drying-tubes, and the mixture ignited by a spark, the whole apparatus being kept cold by means of a freezing-mixture. After a suitable weight of the gases had been burnt the residual gas was pumped out and analysed and the tube and water weighed. The weights of the oxygen and hydrogen used were then known, and also the weight of water formed. Morley obtained as a mean of many results the ratio

by weight of oxygen to hydrogen in water 7·9396 : 1. BURT and EDGAR (1915) obtained the ratio 7·9387 : 1.

The gravimetric composition of water is of additional importance since it gives at the same time *the equivalent of oxygen*.

Previous determinations of the composition of water by weight had been carried out by DUMAS and others, from 1820 onwards. These determinations practically all depended on passing hydrogen over heated copper oxide previously weighed, and measuring the weight of the water formed and the loss in weight of the copper oxide (Fig. 95)—

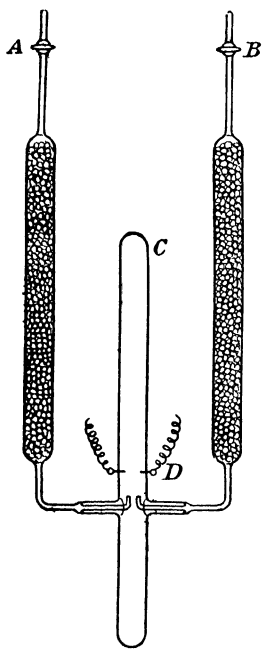


FIG. 94.—Morley's Apparatus for the Composition of Water.

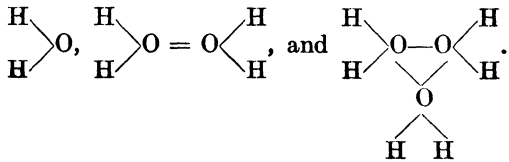
Copper oxide + hydrogen = water + copper.

The results so obtained were all more or less inaccurate owing to the experimental difficulties inherent in this method and to the fact that methods of obtaining absolutely pure hydrogen had not then been elaborated.

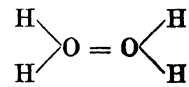
Morley's hydrogen was prepared by electrolysis, dried by phosphorus pentoxide, and absorbed by palladium (p. 183). On heating the "palladium hydride," pure hydrogen was evolved. The oxygen was made by the action of heat upon potassium chlorate.

The *molecular composition* of liquid water is often assumed to be the same as that of steam, namely H_2O, but as a matter of fact liquid water is a very complex substance and probably consists of an equilibrium mixture of H_2O, "hydrol" $(H_2O)_2$, "dihydrol," and $(H_2O)_3$ "trihydrol."

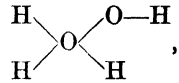
These may have the constitutions represented by the graphic formulæ—



According to ARMSTRONG, the last two of these "hydrols" may exist each in more than one form, e.g.



and



, but the matter is highly speculative and cannot be discussed here.

Ice is solid water, and melts at 0° C. It exists in five or six

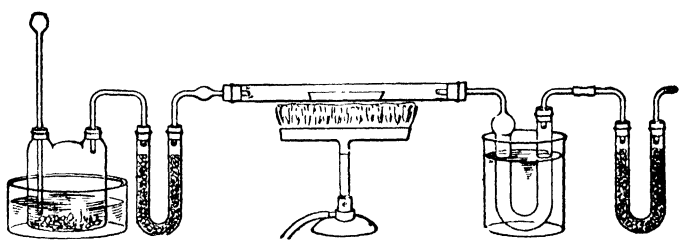


FIG. 95.

different forms of varying density. Ordinary ice is called Ice I and has a density of 0·92.

Properties.—Water is a practically colourless liquid, although it is said that in a layer of considerable thickness it has a bluish green colour. The difficulty of obtaining absolutely pure water in sufficient quantity makes any statement as to its colour open to question; the fact that impure water is blue or green of course requires no proof, as it is obvious.

At atmospheric pressure water freezes at 0° C. and boils at 100° C., these points of the thermometric scale being in fact fixed as the *melting-point of ice* and the *boiling-point of water*.

The *density* of water is taken as unity, i.e. the weight of 1 c.c. of water at its point of maximum density (4° C.) is taken as the *unit of weight*, 1 gram. In the same way the capacity of water for heat is used in fixing the *unit of heat*; thus the calorie is the amount of heat required to raise the temperature of 1 gram of water through 1° C.

Water is an excellent *solvent*, and will dissolve practically every substance, at least in traces. It is, therefore, very difficult to obtain pure. Pure water is usually prepared by distillation in apparatus made of block tin or of silver, with addition of a little potassium permanganate to oxidize any volatile organic matter. It may still contain carbon dioxide, from which it can be purified by redistillation, after addition of a little barium hydroxide. Water obtained in this way is called *conductivity-water*, as it is used in experiments on the electrical conductivity of aqueous solutions.

Pure water is practically a non-conductor; the purest specimen hitherto obtained had a specific conductivity (p. 132) of $0{\cdot}4 \times 10^{-7}$ reciprocal ohms. The concentration of hydrogen ions in water at ordinary temperatures is equal to that of the hydroxyl ions, and is about 10^{-7} *gram-ions* per litre, i.e. 10^{-7} grams of $H^{\cdot}$ ions and 17×10^{-7} grams of hydroxyl ions, since the atomic weight of H = 1 and the molecular weight of the hydroxyl group is 17.

Small as it is, this ionization of water is of great importance, since it leads to the **hydrolysis** of many salts of weak acids and bases in solution. Thus when sodium carbonate is dissolved in water the solution has an alkaline reaction, a phenomenon which can be explained by supposing that the water has partially *hydrolysed* the substance, with formation of caustic soda and carbonic acid; the latter being a weak acid has scarcely any effect on litmus, whereas caustic soda is a strong base and turns litmus blue—an alkaline reaction.

$$Na_2CO_3 + 2H_2O \rightleftharpoons 2NaOH + H_2CO_3.$$

In terms of the ionic theory we have seen that the hydrolysis is really brought about by the *ions of water*, and will proceed until so much carbonic acid has been formed that the

concentration of hydrogen ions from it is equal to the concentration of hydrogen ions caused by the dissociation of water, $H_2O \rightleftharpoons H^{\cdot} + OH'$, that is, 10^{-7} gram-ions per litre.

Many examples of the hydrolysis of salts will be found in this book; hydrolysis, however, is not confined to salts but occurs with various other compounds as well. Thus phosphorus pentachloride is hydrolysed in the presence of water, first to phosphorus oxychloride and then to phosphoric acid—

(i) $PCl_5 + H_2O = POCl_3 + 2HCl$.
(ii) $POCl_3 + 3H_2O = H_3PO_4 + 3HCl$.

The *hydrolysis of esters* is important in organic chemistry. Esters form a class of compounds of which ethyl acetate, $CH_3.COOC_2H_5$, is an example. When heated with water they are slowly hydrolysed, e.g.—

$$CH_3.COOC_2H_5 + H_2O \rightleftharpoons \underset{\text{Acetic acid.}}{CH_3.COOH} + \underset{\text{Ethyl alcohol.}}{C_2H_5OH}.$$

The action is reversible; the forward action may be made to go to completion by use of a large excess of water, or by adding caustic soda to take up the acetic acid as soon as it is formed and hence prevent the reverse action. The hydrolysis of an ester (in absence of alkali) is greatly accelerated catalytically by the addition of a dilute acid. As any dilute acid will do, the catalysis is probably due to the *hydrogen ions* of the acid, and a method of determining the "strength" of an acid (i.e. its degree of ionization) is to measure its catalytic effect upon the rate of hydrolysis of an ester such as methyl or ethyl acetate.

Hydration.—Hydrolysis must be carefully distinguished from *hydration*. Many substances have the power of combining directly with water, to form compounds in which the water is more or less loosely held. These compounds are called *hydrates* and will generally give up their "water of hydration" on heating. In many cases hydrates are crystalline compounds which lose their crystalline form when the water is driven off: these are called crystalline hydrates and the water in them is called "*water of crystallization*." Copper sulphate crystals, for example, are copper sulphate *penta-*

hydrate, $CuSO_4.5H_2O$, while barium chloride crystals have the constitution $BaCl_2.2H_2O$.

A characteristic property of crystalline hydrates is that at a definite temperature they show a perfectly definite *vapour-pressure of water*, which can easily be measured by introducing a little of the hydrate into the Torricellian vacuum. The vapour pressure of a hydrate increases on rise of temperature and falls with a lowering of temperature.

Many crystalline hydrates *effloresce* on exposure to air; that is, they lose some or all of their water of crystallization and fall to a powder. Experiment has shown that hydrates will effloresce if their vapour-pressure is greater than the partial pressure of water-vapour in the atmosphere. It sometimes happens, therefore, that a salt that is not efflorescent when the relative humidity of the air is high will effloresce when the air is drier.

Deliquescence is a somewhat similar phenomenon but is not confined to hydrates, it may be shown by any substance which is very soluble in water. A deliquescent substance absorbs moisture from the air and gradually turns to an aqueous liquid; common examples are calcium chloride and caustic potash. Deliquescence occurs when the substance can form a saturated solution whose vapour-pressure is less than the vapour-pressure of water in the atmosphere, and will proceed until the solution is diluted to such an extent that its vapour-pressure is equal to that of the water in the air. The efficacy of a "drying-agent" for gases therefore depends largely upon its power of forming with water a solution (or a compound) having a low vapour-pressure of water.

Thermal Dissociation.—When steam is strongly heated it partially dissociates into hydrogen and oxygen—

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

This can be shown by blowing a rapid current of steam over a white hot platinum spiral and collecting the gases over water, when the steam condenses and a mixture of hydrogen and oxygen is left. At 2,500° about 10 per cent. of the steam is dissociated.

Hardness.—Water that will not readily lather with soap is said to be *hard*. Soap consists mainly of *sodium stearate*, $C_{17}H_{35}.COONa$, the sodium salt of an organic acid, stearic acid, $C_{17}H_{35}.COOH$. It is soluble in water, the solution having a "soapy" feel and lathering readily. If, however, soap is added to hard water, a curdy precipitate is obtained, and much more soap is needed to produce the lather. Analysis of the curdy precipitate shows that it consists chiefly of calcium stearate, although it may contain magnesium stearate as well. We may therefore conclude that hardness in water is due to the presence of soluble calcium or magnesium compounds which decompose the soap and thus prevent the formation of a lather until sufficient soap has been added to precipitate all the calcium and magnesium as stearates—

$$2C_{17}H_{35}COONa + \text{Ca salt} = \underset{\text{Calcium stearate, curdy precipitate.}}{(C_{17}H_{35}COO)_2Ca\downarrow} + 2\text{Na salt.}$$

It is obvious that the hardness of water will depend on the weight of *calcium* or *magnesium* per litre and will be independent of the nature of the acid radical with which the metal is combined. The hardness of water is therefore usually expressed in grams of calcium per 100 litres (or in other units technically).

The chief salts which cause hardness are the bicarbonates and sulphates. The former are present in water which has percolated through limestone or dolomitic (p. 244) rocks. Although calcium and magnesium carbonates are insoluble in pure water they dissolve in water containing carbon dioxide, owing to the formation of the bicarbonates, which are soluble—

$$CaCO_3 + H_2O + CO_2 = Ca(HCO_3)_2.$$

Natural water always contains carbon dioxide, which it has acquired in its passage, as rain, through the air, or which it has absorbed from the soil, where carbon dioxide is constantly present. Hence if natural water flows over carbonate rocks it becomes hard.

Hardness due to calcium or magnesium sulphate occurs only in those districts in which these compounds are present

in the soil; calcium sulphate is fairly widely distributed and hence is a common cause of hardness.

Hardness may be estimated by titrating a measured volume of the water with a standard soap-solution until a "permanent" lather is obtained on shaking. (Permanency here means a duration of two minutes.) The soap-solution is standardized against a standard solution of calcium chloride.

"*Softening*" *of Hard Water.*—Water may be softened (that is, its hardness may be removed) by removal of the calcium and magnesium salts which it contains. In the case of hardness due to bicarbonates, merely boiling the water is sufficient, since the bicarbonates decompose on heating and the normal carbonates are precipitated—

$$Ca(HCO_3)_2 = CaCO_3 + CO_2 + H_2O.$$

Such hardness is therefore said to be *temporary*, as opposed to that caused by the sulphates. These cannot be removed by boiling the water and the hardness caused by them is called *permanent*.

The softening of the water used in large towns is an important problem, since very hard water is in many ways objectionable not only for domestic use but also in industry. It is obviously impossible to soften the whole of a town's water supply by the process of boiling. Other methods are therefore employed. CLARK'S method for removing temporary hardness consists in adding to the water just sufficient *lime* to convert all the bicarbonate into normal carbonate (we may therefore call it the "homœopathic" process!)—

$$Ca(HCO_3)_2 + CaO = 2CaCO_3 \downarrow + H_2O.$$

Care must be taken, of course, not to add too much lime, or the last state of that water will be worse than the first.

Permanent hardness is removed by the addition of the calculated quantity of sodium carbonate to bring about the reaction—

$$CaSO_4 + Na_2CO_3 = Na_2SO_4 + CaCO_3 \downarrow.$$

A more modern method of softening hard water is the *permutite* process. "Permutite" consists of a sodium

aluminium silicate. When hard water is allowed to flow through a tube containing this substance the calcium and magnesium are retained as calcium and magnesium aluminium silicates; the spent permutite can be regenerated by pouring on to it a strong solution of salt and washing out the calcium and magnesium chlorides so formed.

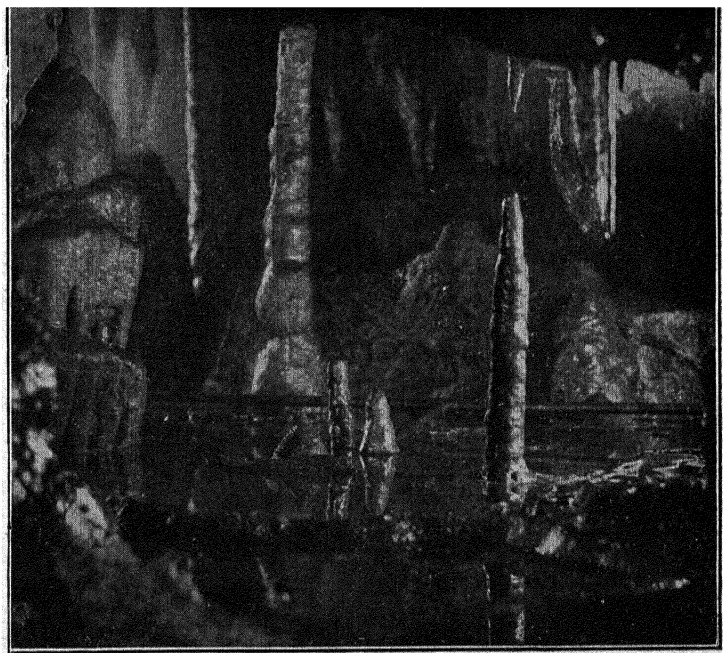


FIG. 96.—Formation of Stalactites and Stalagmites (Cox's Cave, Cheddar).

Very soft water is unsuitable for a general water-supply, since not only does it taste "flat" (owing to absence of carbon dioxide), but it also dissolves lead from the lead pipes through which it almost always flows at one part or another of its course. The action of the water on the lead in the presence of air results in the formation of lead hydroxide, $Pb(OH)_2$,

which is appreciably soluble. Lead salts are distinctly poisonous, and, as they do not pass out of the body, continued use of drinking-water containing lead would finally produce symptoms of lead-poisoning. With hard water, however, a coherent lining of lead carbonate is formed on the pipes and further solution of lead is therefore prevented.

The "furring" of kettles and the formation of "boiler-scale" are caused by the precipitation of calcium carbonate on boiling temporarily hard water. The formation of stalactites and stalagmites in caves in limestone districts (Cheddar, etc.) is due to the slow decomposition of calcium bicarbonate in the water which drips from the roof of the caves, with consequent deposition of calcium carbonate—part being deposited on the roof (stalactite) and part on the floor when the drops fall (stalagmite).

Recognition.—Water may be recognized by its physical constants and also by the fact that it turns anhydrous copper sulphate, which is white, to the *blue* hydrated salt, $CuSO_4.5H_2O$.

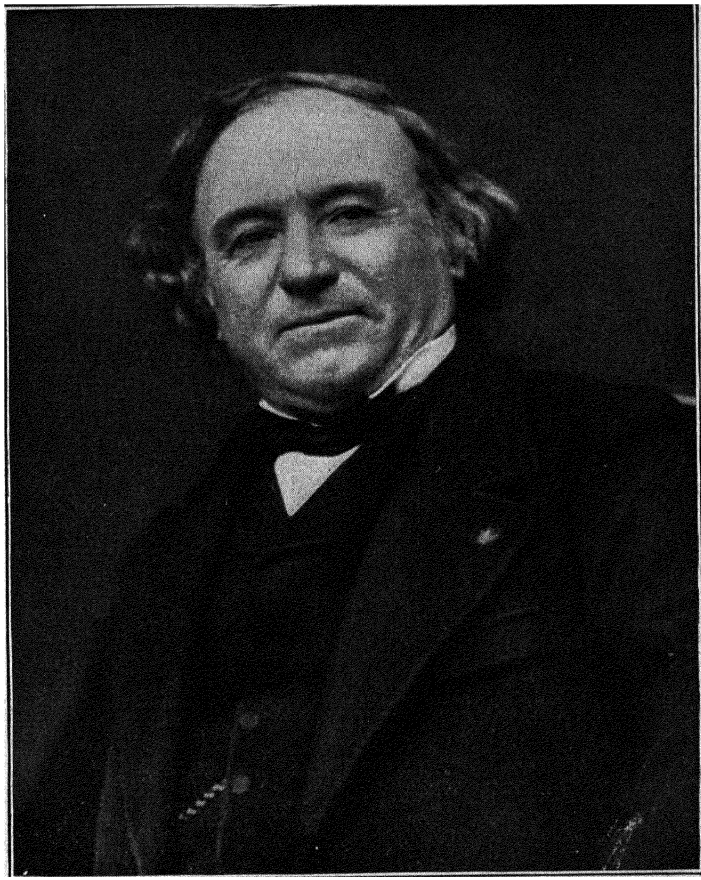
Water-Analysis.—The analysis of "water," i.e. detection and estimation of the impurities in it, is a subject in itself and cannot be adequately described within the limits of this book. Reference should be made to Sutton's *Volumetric Analysis* and to the technical books.

Air

The atmosphere.—Air consists chiefly of a mixture of nitrogen and oxygen in the approximate proportion by volume of 4 to 1. That it is a *mixture* and not a compound is shown by the following considerations—

(i) The composition of the air, although fairly constant, does show slight variations, too large to be assigned to experimental error.

(ii) Although the percentage composition by weight corresponds roughly to a formula N_4O (N = 77 per cent.; O = 23 per cent.), air cannot have this formula, for if it had its vapour density would be $\frac{4 \times 14 + 16}{2} = 36$, whereas the experimental value is 14·4.



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(iii) This value, 14·4, is that which would be given by a mixture of 4 volumes of nitrogen, V.D. 14, with 1 volume of oxygen, V.D. = 16.

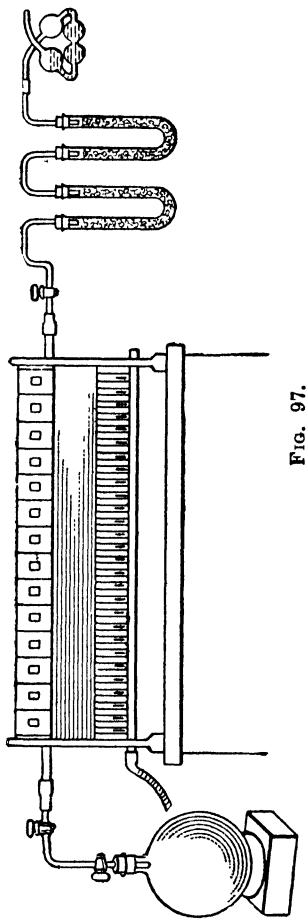


Fig. 97.

(iv) The oxygen and nitrogen may be separated by mechanical means, e.g. fractional distillation of liquid air, diffusion, dissolving in water, etc.

(v) The chemical and physical properties of air are those that would be expected of a mixture of nitrogen and oxygen in the proportions in which they occur in air.

(vi) A gas closely resembling ordinary air may be made, without evolution or absorption of heat, by mixing 4 volumes of nitrogen with 1 volume of oxygen.

The composition of dry air, free from carbon dioxide, may be found—

(i) *Gravimetrically*, by the method of DUMAS and BOUSSINGAULT. Air is sucked first through a bulb-tube containing caustic potash solution to absorb carbon dioxide, then through a series of tubes containing pumice soaked in concentrated sulphuric acid, to remove moisture, and finally through a tube containing red-hot copper turnings (weighed), into a weighed evacuated copper globe (Fig. 97).

The copper combines with the oxygen to form copper oxide, while the nitrogen passes on into the globe.

Therefore, the increase in weight of the copper turnings is equal to the weight of oxygen which was mixed, in air, with the weight of nitrogen given by the increase in weight of the copper globe.

It is hardly necessary to point out that the figure does not represent Dumas' actual apparatus (since Bunsen burners were not invented in 1843, the year of Dumas and Boussingault's experiment), but a modification suitable for the laboratory repetition of the experiment by an elementary student.

(ii) *Volumetrically*, by enclosing the air over mercury in a graduated tube containing a copper wire which may be electrically heated to redness. The volume of air taken is noted, the wire heated to redness for a few minutes, and the apparatus allowed to cool. A decrease in volume will be observed, since the copper will have combined with the oxygen to form copper oxide, the volume of which is practically the same as that of the copper wire itself and therefore may be neglected. After any necessary corrections for temperature and pressure, the volumetric composition of the air may therefore be calculated directly. The residual gas is nitrogen.

Water-vapour is present in the atmosphere, and is an essential constituent as far as life is concerned. The percentage of water-vapour in the air may be determined by a physical process (*hygrometry*, see textbooks of Heat), or chemically by aspirating a known volume of air through a weighed calcium chloride tube ; the increase in weight is due to absorption of the water-vapour of the air which has passed through. A cubic metre of air saturated with water-vapour at 25° C. contains 22·8 grams of water. The *relative humidity* of air at a given temperature is the ratio of the weight of water-vapour *actually* contained in 1 cubic metre of it to the maximum weight of water-vapour which 1 cubic metre of it *could* contain at that temperature.

Carbon dioxide is present in the atmosphere in the propor-

tion of 0·03 per cent. by volume. In spite of the fact that enormous quantities of this gas are continually being thrown into the air, from the combustion of carbonaceous fuels and the respiration of animals and plants, the percentage of carbon dioxide in the air remains remarkably constant. This is accounted for by the following facts—

(i) Carbon dioxide is soluble in water, so that any excess of the gas is dissolved by the sea.

(ii) Carbon dioxide is the chief *food* of green plants. Plants do not, of course, *breathe* carbon dioxide; they breathe oxygen, as do all other living things. They can, however, build up their tissues very largely from carbon dioxide and water; this is an endothermic reaction and the necessary energy is supplied by the light of the sun. The active agent or catalyst in this process of *carbon assimilation* or *photosynthesis* is the green colouring-matter *chlorophyll*, a complicated organic magnesium compound related in structure to the red colouring-matter, *hæmoglobin*, of the blood.

The percentage of carbon dioxide in the air is most conveniently determined by taking a definite volume of a standard solution of baryta-water, adding a few drops of phenolphthalein and then forcing air through the liquid by means of a pump which delivers a known volume of air at each stroke. If the number of strokes necessary just to decolourize the solution is counted, the weight of carbon dioxide in a known volume of the air can be calculated.

PETTENKOFER'S method is easy to carry out in the laboratory as it does not require special apparatus. A Winchester bottle is filled with water and the water then poured into a measuring cylinder. This gives the capacity of the bottle. Fifty c.c. of a dilute standard solution of baryta are then put in the bottle, the cork replaced and the bottle well shaken. The carbon dioxide in the air in the bottle will react with some of the barium hydroxide—

$$\text{(i)}\quad Ba(OH)_2 + CO_2 = BaCO_3 + H_2O.$$

If the residual liquid is now titrated, still in the bottle, with

a dilute standard solution of oxalic acid, using phenolphthalein as indicator, the weight of unused barium hydroxide may be found—

$$\text{(ii)}\quad Ba(OH)_2 + \underset{\text{Oxalic acid.}}{H_2C_2O_4} = BaC_2O_4 + 2H_2O.$$

The difference between the weight of barium hydroxide taken and the weight of that left is the weight of the barium hydroxide which has reacted with the carbon dioxide of the air in the bottle. From equation (i) above, it follows that 171 grams of barium hydroxide react with 44 grams of carbon dioxide, hence the weight of the carbon dioxide in the air may be calculated.

Other Gases, etc.—Air contains traces of hydrogen, ammonia, nitric acid, oxides of nitrogen, hydrogen peroxide and ozone as well as bacteria, dust, spores and small quantities of various organic compounds. In addition, it contains about 1 per cent. of the inactive gases, Helium, Neon, Argon, Krypton and Xenon, which are described in Chapter XVIII, p. 187.

The average composition of the air in the latitude of London is as follows:—

	Per cent. by volume.
Nitrogen	77·32
Oxygen	20·80
Argon, etc.	0·93
Carbon dioxide	0·03
Water-vapour	0·92

Sulphur

Group in Periodic System: VI; *Symbol:* S; *Atomic Weight:* 32·06; *Valency:* 2, 4, or 6; *Specific Gravity:* 1·98–2·06; *Boiling Point:* 444·6°.

History.—The word *sulphur* shows us that this element and one of its most characteristic properties have been known for some thousands of years, for "sulphur" is the Latin form of the Sanskrit word *sulvari* or "*enemy of copper.*" The Hindoos of 3000–2000 B.C. were therefore acquainted with

sulphur and with the fact that it "destroys" copper when the two are heated together. To the Greeks and Romans sulphur was well known, since it occurs naturally in Sicily and other volcanic regions of the Mediterranean. The alchemists of Islam called it *kibrīt*, and to them is due the theory that all metals are composed of *kibrīt* and *zībaq* (sulphur and mercury)—a theory that was later modified into the phlogiston theory of Becher and Stahl.

The properties of sulphur were thoroughly investigated in the Middle Ages, and many sulphur compounds described. The elementary nature of sulphur was shown by LAVOISIER in 1777.

Occurrence.—Sulphur in the elementary state occurs in Sicily and Italy and, at a depth of about 700 feet, in Louisiana (U.S.A.). Combined as *sulphates* and *sulphides*, sulphur is very widely distributed. The chief sulphides are *iron pyrites*, FeS_2, *copper pyrites*, $CuFeS_2$ or $Cu_2S.Fe_2S_3$, *galena*, PbS, *zinc blende*, ZnS, *realgar*, As_2S_2, *orpiment*, As_2S_3, and *cinnabar*, HgS. All these substances are of commercial importance, mostly on account of the metal they contain, although iron pyrites is used as a source of sulphur in the manufacture of sulphuric acid. The chief sulphate naturally occurring is *gypsum*, $CaSO_4.2H_2O$.

Sulphur is a common constituent of living matter and is probably essential.

Extraction.—The native sulphur of Sicily is mixed with silica, limestone and other impurities. It is interesting, if somewhat disappointing, to find that the method used in its extraction is the same now as it has been for the last 1,000 years; only in detail have chemists been able to suggest any improvement. The sulphur ore is piled in heaps, called *calcaroni*, with the largest lumps at the bottom. Air-passages are left, and the floor slopes downwards so that the molten sulphur produced may flow out and be collected. The heaps of ore are covered with the residue from a previous operation, and are then set alight by the introduction from the top of burning wood. Part of the sulphur burns and melts the rest, which sinks to the bottom of the heap and flows out.

It is collected in wet wooden boxes (Fig. 98). In this process, about 35 per cent. of the sulphur is lost by combustion.

An improved kiln was invented by ROBERT GILL (1880); here the ore is heated in brick-work chambers arranged in groups of two or, more recently, six, in such a way that there is a minimum loss of heat and of sulphur. Even in the Gill kiln, however, there is a loss of 20–25 per cent.

In 1891, a method for extracting sulphur by the use of superheated steam under pressure was patented. This had previously been suggested by PAYEN and GILL in 1867, but the practical difficulties at that time proved insurmountable. Owing to the high price of coal, this method is not much used in Sicily, but is employed in the Romagna.

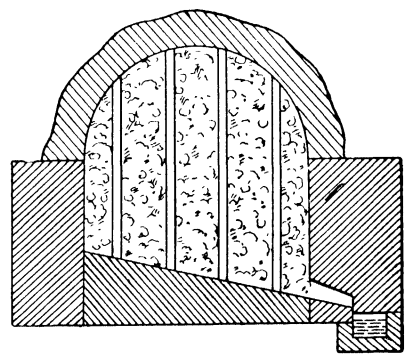


FIG. 98.

Refinement. — The crude Italian and Sicilian sulphur is refined partly in the Romagna, but chiefly at Marseilles and Antwerp. The plant employed was invented by MICHEL in 1808 and improved by LAMY (1844) and DUJARDIN (1890). The crude sulphur is melted in iron pots (A, Fig. 99) and then flows into shallow iron retorts (B), where it is boiled. The vapour is passed into a large brickwork chamber (C), where it condenses (i) to a powder (flowers of sulphur), if the temperature of the walls of the chamber is below 100°, or (ii) to a liquid when the temperature rises above 114°.

The flowers of sulphur first formed are scraped out and sold as such. The liquid sulphur that later collects on the floor of the chamber is run out and allowed to solidify in cylindrical moulds, forming the so-called "roll-sulphur."

Louisiana Process.—Until the end of the nineteenth century

practically all the sulphur on the market came from Sicily, but the discovery of a way to extract the sulphur in the Louisiana deposits resulted in a fall of some 45 per cent. in the sales of the Sicilian sulphur in 1912 and a still further fall in subsequent years. FRASCH (1903) made a boring of about 1 foot diameter through the overlying rock until he reached the sulphur at a depth of some 600–800 feet. Superheated water was then blown down and the molten sulphur

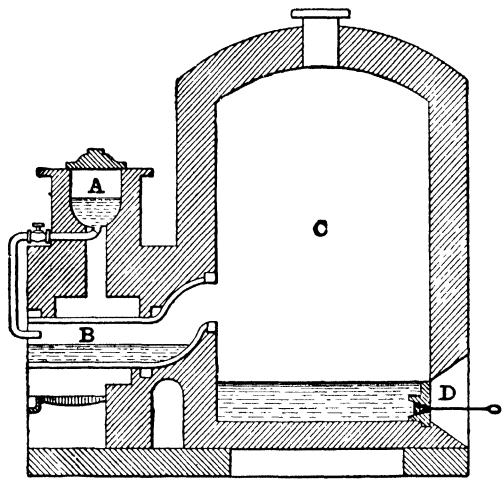


FIG. 99.—Sulphur Refining.

thus produced forced up by means of compressed air. A single well may produce as much as 500 tons daily. The sulphur obtained in this way is very pure (over 99 per cent.), and as the deposits are estimated at 40,000,000 tons, the supply of sulphur for the next century or so seems well assured. Large deposits have recently been discovered in Alaska, but they are not yet worked.

Recovery of Sulphur from various Manufacturing Processes.

(*a*) *Manufacture of Coal-gas.*—Crude coal-gas contains sulphuretted hydrogen (from the sulphurous compounds in

coal). It is passed over wet iron rust, when the sulphuretted hydrogen is removed—

$$2Fe(OH)_3 + 3H_2S = Fe_2S_3 + 6H_2O.$$

The iron sulphide so obtained is exposed to moist air for some time, when

$$2Fe_2S_3 + 6H_2O + 3O_2 = 4Fe(OH)_3 + 6S.$$

The sulphur produced may be extracted with carbon disulphide, in which it is soluble, or may be burnt and thus converted into sulphur dioxide, which is commercially valuable.

(*b*) *From the residues of the Leblanc soda industry* (CHANCE-CLAUS METHOD). See Manufacture of Sodium Carbonate, p. 204. [N.B.—The Leblanc process is now obsolete.]

The *alkali-waste*, containing calcium sulphide, CaS, in suspension in water, was treated with a stream of " chimney-gas " or " limekiln-gas " (carbon dioxide and nitrogen), when calcium carbonate and sulphuretted hydrogen were produced—

$$CaS + CO_2 + H_2O = CaCO_3 + H_2S.$$

The gas was collected in large gasometers and was then mixed with insufficient air for complete combustion and passed over heated iron oxide in a brickwork chamber called the *Claus kiln*—

$$2H_2S + O_2 = 2H_2O + 2S.$$

Sulphur was left in the kiln, and the iron oxide was unchanged; it probably acted as a catalyst. Sometimes the sulphur was burnt to sulphur dioxide for use in the lead-chamber process for the manufacture of sulphuric acid.

In this way nearly 100,000 tons of sulphur were recovered annually, and not only was much money saved but the mountainous heaps of alkali-waste no longer poisoned the air for miles around.

Properties.—Sulphur exists in a large number of allotropic forms. Ordinary sulphur is called *α*-sulphur or *rhombic* sulphur (since its crystals belong to the rhombic system).

α-Sulphur.—The naturally occurring form; rhombic crystals

melting at 114·5° C. Soluble in carbon disulphide, from which it crystallizes out in the same form. Specific gravity, 2·06. It is the stable form of sulphur at ordinary temperatures; all other forms of sulphur change into it more or less quickly. If, however, the temperature is raised above 95·6° C., α-sulphur becomes less stable than β-sulphur, into which it therefore passes.

β-Sulphur, monoclinic, or prismatic sulphur can be conveniently prepared by melting α-sulphur in a crucible, allowing the liquid to cool until a thin crust has just formed, piercing this with two holes and pouring out the remaining liquid through one of these while air enters through the other. If the crust is now removed the crucible will be found to be lined with long, transparent, needle-like crystals of β-sulphur. This form has a specific gravity 1·96 and melts at 119°. Above 95·6° β-sulphur is stable under atmospheric pressure, but below 95·6° it slowly passes into α-sulphur. α-sulphur, on the other hand, is stable below 95·6°, but unstable above. *At* 95·6°, α- and β-sulphur are equally stable, and this temperature is called the *transition-point* for the two forms.

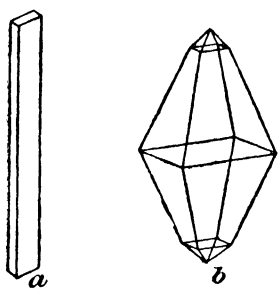


FIG. 100.—Crystals of Sulphur.
a. Monoclinic. *b*. Rhombic.

Here, then, we have an example of a substance that exists in two allotropic forms, either of which can be converted into the other by merely altering the temperature. These substances are called *enantiotropic* ("moving in opposite ways"), as opposed to *monotropic* substances, such as phosphorus and iodine chloride.

Phosphorus, for example, is capable of existing as yellow phosphorus and as red phosphorus. Now at all temperatures below the melting-point of the yellow form the latter is unstable with respect to the red, into which it passes slowly at ordinary temperatures but more quickly on heating. Hence

there is no transition-point between red and yellow phosphorus, that is, no temperature at which both are equally stable, and below which one is the stable form while above it the other form is the stable one. A mere change of temperature is sufficient, therefore, to change yellow phosphorus into red, but not the red into yellow: phosphorus is therefore called a *monotropic* substance.

Equilibria between various Forms of Sulphur in Terms of the Phase Rule.—The Phase Rule (p. 146) is P + F = C + 2. The constituent of all phases here is sulphur only; hence C = 1 and the rule becomes P + F = 3. If therefore we have three phases the system is non-variant, with two phases the system is univariant, and with one phase bivariant. Let us consider the phases α-sulphur, β-sulphur, liquid sulphur, and sulphur vapour. Below 95·6 we have α-sulphur and sulphur vapour (although the vapour pressure of α-sulphur is very small), that is, we have two phases and the system will therefore be univariant. In other words, if we fix the temperature, the pressure of sulphur vapour will adjust itself to a definite value for that temperature.

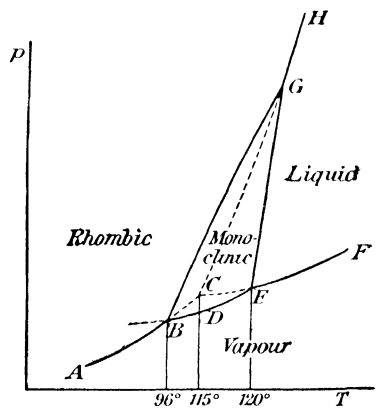


FIG. 101.—Phase Rule Diagram for Sulphur.

In figure 101, AB represents the vapour-pressure curve for α-sulphur, and as α-sulphur if heated quickly may be taken beyond the transition-point (95·6°) and melted at 114·5°, BC is the continuation of the vapour-pressure curve of this form as far as its melting-point. Above 95·6°, however, α-sulphur is unstable, and changes slowly into β-sulphur. If this change has taken place, then BE represents the vapour-pressure curve of

β-sulphur from the transition-point up to the melting-point of this form, 120°. At 95·6° we have the three phases α-sulphur, β-sulphur, and sulphur vapour; the system is therefore non-variant. EF is the vapour-pressure curve of liquid sulphur, and EG the curve showing the effect of pressure upon the melting-point of β-sulphur. BG shows the effect of pressure upon the transition-point of α- and β-sulphur, and CG the effect of pressure upon the melting-point of α-sulphur.

We see therefore that β-sulphur can exist in a stable form only within the limits shown by the triangle BGE. At G, α- and β-sulphur and liquid sulphur are in equilibrium; at E, β-sulphur, liquid sulphur, and sulphur vapour; at C, α-sulphur, liquid sulphur, and sulphur vapour, although at this point α-sulphur is unstable with respect to β-sulphur. B, C, E, and G all therefore represent non-variant systems.

Other Allotropic Forms.—*Nacreous* sulphur may be obtained by heating sulphur to 150°, cooling the liquid to 98°, and scratching the sides of the containing vessel with a glass rod. It is a modification of β-sulphur.

Colloidal sulphur has been obtained from the sulphur which is precipitated by addition of sodium thiosulphate to cold concentrated sulphuric acid.

Amorphous sulphur is present in small quantity in ordinary flowers of sulphur. It is insoluble in carbon disulphide and hence may be obtained by extraction of flowers of sulphur with this liquid; the rhombic sulphur dissolves and amorphous sulphur is left. It is a white powder.

Plastic sulphur can be obtained by pouring molten sulphur into cold water. It is an elastic substance readily changing into the rhombic and amorphous forms. It is considered to be a supercooled liquid, that is, a liquid taken so quickly to far below its freezing point that it has not had time to crystallize. Glass is another example of a supercooled liquid.

ϕ-Sulphur is an orange-yellow crystalline form prepared by adding ice-cold concentrated hydrochloric acid to a cold solution of sodium thiosulphate and shaking the liquid with the organic liquid toluene ($C_6H_5.CH_3$).

Milk of Sulphur is a white precipitate of sulphur obtained

by adding dilute hydrochloric acid to a solution of calcium polysulphide (CaS_x) prepared by dissolving sulphur in boiling milk of lime.

λ-Sulphur and *μ-Sulphur.*—When sulphur is melted, Sλ and Sμ are formed ; Sλ is of a pale amber colour and is mobile ; it is stable up to 160°. Above 160° liquid sulphur contains chiefly Sμ which is dark in colour and viscous. It is said that Sμ is formed only if the sulphur used is slightly impure. Other allotropic forms of sulphur have been described, e.g. Sρ (" Engel's sulphur "), obtained by adding hydrochloric acid to sodium thiosulphate solution, filtering, extracting the filtrate with chloroform, and evaporating the chloroform extract. Sρ is probably S_6.

Sulphur boils at 444·6°, and vapour-density determinations have shown that at temperatures just above the boiling-point many of the molecules are octatomic (S_8). On raising the temperature the vapour density gradually falls, the molecules dissociating into S_6, S_4, S_3, and S_2, while at 2,000° the vapour contains even the monatomic molecules S. The colour of the vapour changes in the process : at 450° it is orange-red, at 500° deep red, and above 600° pale yellow. BILTZ has shown that at 650° sulphur vapour consists chiefly of S_3 molecules.

Atomic Weight.—The equivalent of sulphur was determined by STAS, who passed sulphur vapour over a weighed quantity of pure silver. He found that 107·88 parts by weight of silver will combine with 16·035 of sulphur. The least weight of sulphur found in the gram-molecular weight of any of its compounds is $2 \times 16{\cdot}035$ gms. Hence the atomic weight of the element is $2 \times 16{\cdot}035 = 32{\cdot}07$.

COMPOUNDS OF SULPHUR.

Sulphuretted hydrogen, H_2S.—This compound is alternatively called hydrogen sulphide or, since its aqueous solution has an acid reaction, *hydrosulphuric acid.* It is formed synthetically when hydrogen is passed through boiling sulphur—

$$H_2 + S = H_2S.$$

When hydrogen and sulphur vapour are heated together,

equilibrium is set up between hydrogen, sulphur, and sulphuretted hydrogen—

$$H_2 + S \rightleftharpoons H_2S.$$

Since the latter substance is exothermic we should expect by Le Chatelier's principle that raising the temperature would diminish the proportion of sulphuretted hydrogen in the equilibrium mixture; this is found to be the case. At 1,700° the gas contains practically no undissociated sulphuretted hydrogen.

Sulphuretted hydrogen occurs naturally in certain volcanic gases, and it is possibly by the incomplete combustion of this substance that the sulphur deposits in volcanic regions have been formed—

$$2H_2S + O_2 = 2H_2O + S$$

or

$$2H_2S + 3O_2 = 2SO_2 + 3H_2O$$

followed by $2H_2S + SO_2 = 2H_2O + 3S$, since sulphuretted hydrogen immediately reacts with moist sulphur dioxide when the two gases are mixed.

In the laboratory sulphuretted hydrogen is made by the action of dilute hydrochloric acid upon ferrous sulphide—

$$FeS + 2HCl = FeCl_2 + H_2S.$$

A purer gas is obtained from antimony sulphide and concentrated hydrochloric acid—

$$Sb_2S_3 + 6HCl = 2SbCl_3 + 3H_2S.$$

As the gas is very often required in the laboratory, forms of apparatus have been devised which are automatic in action; sulphuretted hydrogen is produced when the tap is turned on and the action stopped when the tap is turned off. The well-known apparatus devised by KIPP is generally used.

Properties.—Sulphuretted hydrogen is a colourless gas with a sweetish and somewhat unpleasant odour of rotten eggs. It is a poisonous substance and, if inhaled, rapidly produces headache. It will burn in air with a blue flame, forming steam and sulphur dioxide if the supply of air be sufficient—

$$2H_2S + 3O_2 = 2H_2O + 2SO_2.$$

If the supply of air is insufficient sulphur is deposited.

The gas reacts with chlorine water, bromine water, or iodine suspended in water, yielding a precipitate of sulphur and a solution of halogen hydracid—

$$H_2S + X_2 = 2HX + S, \text{ where } X = Cl, Br, \text{ or } I.$$

When sulphuretted hydrogen is sparked, it is decomposed into hydrogen and solid sulphur. The volume of the residual hydrogen is found to be equal to the original volume of sulphuretted hydrogen. Hence, by Avogadro's hypothesis, 1 molecule of the gas contains 1 molecule of hydrogen, H_2, $\therefore$ formula is H_2S_x.

The vapour density is 17, $\therefore$ M. Wt. = 34. But of these 34 parts 2 are hydrogen, $\therefore$ 32 are sulphur.
But the atomic weight of sulphur = 32,

$$\therefore x = 1, \text{ and the formula is } H_2S.$$

Sulphuretted hydrogen dissolves in water to the extent of 290 c.c. in 100 c.c. of water at 20° C. The solution reacts feebly acid and is of great importance in analytical chemistry. Sulphuretted hydrogen is a dibasic acid and in solution ionizes in two stages—

$$\text{(i) } H_2S \rightleftharpoons H^{\cdot} + HS'$$
$$\text{(ii) } HS' \rightleftharpoons H^{\cdot} + S''$$

The second stage occurs to only a very small extent. In the presence of an acid, even the first stage is almost completely suppressed, whereas addition of an alkali, by removing hydrogen ions to form un-ionized water, will increase the formation of HS′ and S″ ions. Many metals form sulphides that are insoluble in water; they can be divided into two groups, (*a*) those whose sulphides are so insoluble that even the small concentration of S″ ions present in an acidified solution of sulphuretted hydrogen is large enough to cause their precipitation from solutions of the metallic salts, and (*b*) those whose sulphides are more soluble but still so slightly soluble that the concentration of S″ ions in an *alkaline* solution is sufficient to precipitate them, while that in acid solutions is insufficient. The former metals, lead, mercury, bismuth, copper, cadmium, arsenic, antimony and tin,

are precipitated as sulphides in Group II of the analytical tables; the latter metals include iron, cobalt, nickel, zinc and manganese, the last four of which are precipitated as sulphides in Group IV, the iron having been previously removed by another process in Group III.

Hydrogen persulphide, H_2S_2, is known. It is analogous to H_2O_2 and is prepared as a yellow oil with a pungent smell by adding a cold solution of calcium polysulphide slowly to well-cooled hydrochloric acid.

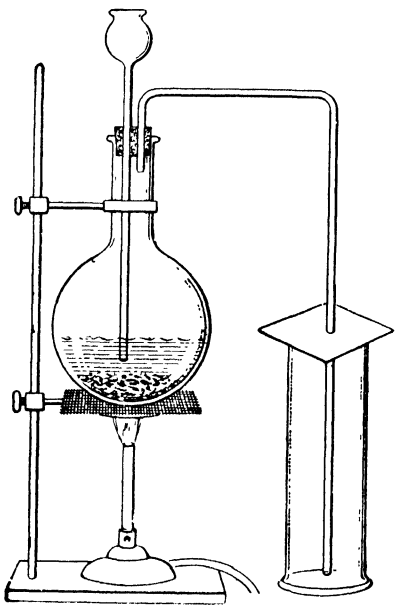


FIG. 102.—Preparation of Sulphur Dioxide.

Oxy-Compounds of Sulphur.

Sulphur forms four oxides—

S_2O_3, sulphur sesquioxide.

SO_2, sulphur dioxide or sulphurous anhydride.

SO_3, sulphur trioxide or sulphuric anhydride.

S_2O_7, sulphur heptoxide or persulphuric anhydride.

Sulphur dioxide, SO_2.—This gas was first prepared by PRIESTLEY in 1774, who made it by the action of hot concentrated sulphuric acid upon mercury—

$$Hg + 2H_2SO_4 = HgSO_4 + 2H_2O + SO_2.$$

LAVOISIER in 1777 showed that it is an oxide of sulphur.

Preparation.—Sulphur dioxide is formed when sulphur burns in air or oxygen, but prepared in this way is always mixed with traces of solid sulphur *tri*oxide, SO_3, which may cause the gas to have a cloudy appearance. Sulphur dioxide

is usually prepared by heating copper with strong sulphuric acid. The first reaction that occurs may be--

$$Cu + H_2SO_4 = CuSO_4 + H_2.$$

The " nascent " hydrogen then finds two things to reduce, viz., the excess of sulphuric acid and the copper sulphate, and reduces some of each—

$$\text{(i)}\ H_2SO_4 + H_2 = 2H_2O + SO_2.$$
$$\text{(ii)}\ 2CuSO_4 + 9H_2 = Cu_2S + 8H_2O + H_2S.$$

Sulphur dioxide results from the reduction of the sulphuric acid, and black copper sulphide from the reduction of the copper sulphate. The mixture left in the flask is therefore coloured black. It contains also some unreduced copper sulphate.

Many other substances will reduce sulphuric acid if heated with it, e.g., carbon—

$$C + 2H_2SO_4 = 2SO_2 + 2H_2O + CO_2.$$

This process is often used for the commercial preparation of sulphur dioxide.

Sulphur dioxide is generally prepared commercially by roasting iron pyrites, FeS_2, in a current of air. It is formed, too, by the action of a dilute acid upon a sulphite, bisulphite, or thiosulphate—

$$\text{(i)}\ Na_2SO_3 + 2HCl = 2NaCl + H_2O + SO_2.$$
$$\text{(ii)}\ NaHSO_3 + HCl = NaCl + H_2O + SO_2.$$
$$\text{(iii)}\ Na_2S_2O_3 + 2HCl = 2NaCl + H_2O + S + SO_2.$$

Properties.—Sulphur dioxide is a colourless gas with the pungent smell and taste of " burning sulphur." It is 2·3 times heavier than air, and may therefore be conveniently collected by downward displacement. It dissolves in water to give an acid solution containing some sulphurous acid, H_2SO_3—

$$H_2O + SO_2 = H_2SO_3.$$

The following equilibria occur in the system—

$$\underset{\text{Gas.}}{SO_2} \rightleftharpoons \underset{\text{Dissolved.}}{SO_2 + H_2O} \rightleftharpoons \underset{\text{Sulphurous acid.}}{H_2SO_3} \rightleftharpoons H^{\cdot} + HSO_3' \rightleftharpoons H^{\cdot} + H^{\cdot} + SO_3''$$

When sulphur dioxide solution is boiled, sulphur dioxide is driven off, and sulphurous acid has never been isolated.

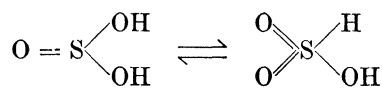
Sulphur dioxide is readily liquefied; it forms a colourless, mobile liquid which is put on the market in "syphons." When the valve of such a syphon is loosened, sulphur dioxide gas comes off, while if the syphon is inverted liquid sulphur dioxide can be run out.

Sulphurous acid.—This acid is known only in dilute solution and in the form of its salts, the *sulphites*. It is a weak acid, although stronger than carbonic (it liberates carbon dioxide from carbonates), and is a reducing agent since it is easily oxidized to sulphuric acid—

$$H_2SO_3 + \text{oxygen} = H_2SO_4.$$

Moist sulphur dioxide and sulphurous acid bleach many colouring matters; the bleaching process is usually a reduction, resulting in the dye taking up two atoms of hydrogen per molecule with the formation of a colourless substance called the *leucobase* of the dye. Generally the leucobase of a dye is very readily oxidized back again to the dye itself, so that sulphur dioxide bleaching is often not permanent. Straw hats, for example, are bleached with sulphur dioxide, in order that a few weeks' wear may be enough for the yellow colour to return, thus necessitating a new hat every season. Yet some people ask of what use chemistry is to the business man!

Sulphurous acid probably exists in two forms in its aqueous solution—



(Cf. hydrogen peroxide, p. 436.)

Calcium bisulphite, $Ca(HSO_3)_2$, is the most important salt of sulphurous acid. Some 190,000 tons of sulphur are annually converted into this salt, which is employed in the manufacture of paper from wood. Wood consists chiefly of two things, *lignin* (30 per cent.) and *cellulose* (70 per cent.). Paper is made from cellulose, and the calcium bisulphite is used to dissolve out the lignin from wood, leaving the cellulose.

Sodium metabisulphite, $Na_2S_2O_5$, a salt much used in photography, is made by evaporating a solution of sodium bisulphite, $NaHSO_3$—

$$2NaHSO_3 = Na_2S_2O_5 + H_2O.$$

Sodium bisulphite itself is used in organic chemistry for the separation and purification of aldehydes and ketones, with which it forms addition compounds—



Benzaldehyde. "Bisulphite compound" of benzaldehyde.

The " bisulphite compounds " of aldehydes and ketones are usually beautifully crystalline.

Sulphur dioxide and sulphites are used as *antichlors* because they react with chlorine and will thus remove the last traces of chlorine from fabrics that have been bleached with this gas—

$$SO_2 + 2H_2O + Cl_2 = H_2SO_4 + 2HCl.$$

With barium chloride, sulphur dioxide solution gives a slight precipitate of barium sulphite—

$$SO_2 + H_2O + BaCl_2 = BaSO_3 + 2HCl.$$

If, however, a little potassium permanganate solution is added first, the colour of the permanganate is discharged since the sulphurous acid is oxidized to sulphuric acid and the permanganate reduced. The solution with barium chloride now gives a heavy white precipitate of barium sulph*ate*—

(i) $SO_2 + H_2O +$ oxygen from permanganate $= H_2SO_4$
(or $K_2Mn_2O_8 + 5SO_2 + 2H_2O = K_2SO_4 + 2MnSO_4 + 2H_2SO_4$).

(ii) $H_2SO_4 + BaCl_2 = BaSO_4 \downarrow + 2HCl$.

Sulphur trioxide, SO_3.—Sulphur trioxide is a white substance crystallizing in fine needles. It is prepared by the oxidation of sulphur dioxide by means of oxygen, a catalyst being employed to accelerate the reaction.

When sulphur dioxide is heated with oxygen, slow combination of the two gases occurs, but the reaction is reversible—

$$2SO_2 + O_2 \rightleftharpoons 2SO_3.$$

The forward reaction is exothermic ; increase of temperature will therefore result in a lower proportion of the trioxide in the equilibrium mixture. Thus at 400° the proportion of trioxide at equilibrium is 98·5 per cent. ; at 700° it is 60 per cent., and at 900° it is practically *nil*. 400° then would seem to be the highest temperature at which a good yield of the trioxide can be expected, but the unaided reaction is slow at this temperature. However, platinized asbestos acts as an efficient catalyst, and a practically quantitative yield can be obtained in this way.

Sulphur trioxide dissolves in water with a hissing noise, forming sulphuric acid, of which it is therefore the *anhydride*—

$$H_2O + SO_3 = H_2SO_4.$$

Sulphuric acid, H_2SO_4.—It is probable that this compound was known to JABIR IBN HAYYAN (eighth century A.D.). It has certainly been known for several hundreds of years and was prepared by the alchemists by strongly heating green vitriol (ferrous sulphate). "The first sulphuric acid works was erected by WARD in 1740 at Richmond, near London. He heated a mixture of sulphur and saltpetre in iron capsules and collected the sulphuric acid vapours in glass vessels of 300 litres capacity, containing a little water. The product was concentrated by heating the glass vessels in a sand-bath, but great inconvenience was caused by the facility with which the vessels were broken. In order to avoid this trouble ROEBUCK and GARBETT in 1746 replaced them by receptacles or chambers of lead about two metres wide, in which a furnace in the centre produced the acid from sulphur and saltpetre. In 1766 this method was first introduced into France by HOLKER (at Rouen) ; in 1774 LA FOLLIE also passed a jet of steam into the lead chamber ; and in 1793 CLÉMENT and DÉSORMES showed the importance of a current of air in the lead chamber, which facilitated the formation of sulphuric acid and effected a notable saving of nitre and sulphur. Thus, before that time only 130 kilos of sulphuric acid were obtained from 100 kilos of sulphur, whereas to-day this yield is more than doubled. They had then already correctly

interpreted the process of sulphuric acid formation, and said that the nitric acid was merely a means of fixing (by means of nitrous vapours) the oxygen of the air which transformed the sulphur dioxide into sulphur trioxide. . . . Until about the year 1835, Sicilian sulphur had always been employed for the manufacture of sulphuric acid, but when the government of Ferdinand II of Bourbon, at Naples in 1858, conceded the monopoly of sulphur-mining to the House of Taix-Aycard and Co., of Marseilles, a concession which raised the price from 9*s.* 7*d.* to 28*s.* per ton, all Europe endeavoured to obtain sulphur from other sources, especially from pyrites." [1]

Sulphuric acid is the most important chemical of commerce. It is used directly or indirectly in practically every art and trade. About 10,000,000 tons are produced annually.

MANUFACTURE OF SULPHURIC ACID.

1. LEAD-CHAMBER PROCESS.—The theory of this process is very simple, although attempts have been made to complicate it—

(i) $H_2O + SO_2 + NO_2 = H_2SO_4 + NO$

(ii) NO + oxygen from air = NO_2.

A hot mixture of air and sulphur dioxide, containing also oxides of nitrogen, has a fine spray of water projected into it, when sulphuric acid is formed. Nitric oxide acts as an oxygen-carrier, combining with atmospheric oxygen and handing it on to the sulphur dioxide, thus forming sulphur trioxide, which is immediately converted by the water present into sulphuric acid. The above equations show that there is no loss of nitric oxide in the operation; from this point of view, therefore, nitric oxide may be said to act as a catalyst on the reaction.

The above theory, however, appeared to be too simple for many chemists, who set to work to see if they could not produce more complicated explanations of the reactions. Needless to say they succeeded, but it is refreshing to find that, after all, the simple equations given above really represent the reactions that go on better than the more complicated

[1] Molinari, *General and Industrial Inorganic Chemistry*, p. 254 (1912).

ones which have been suggested. If insufficient moisture be present in the reaction chambers, a crystalline solid separates. This compound is called "chamber crystals," or *nitrososulphuric acid*, $HSO_4.NO$; with water it gives sulphuric acid, nitric oxide, and nitrogen peroxide—

$$2HSO_4.NO + H_2O = 2H_2SO_4 + NO + NO_2.$$

There is, however, no evidence to show that chamber crystals are an intermediate stage under normal working conditions. RASCHIG assumed that nitrososulphonic acid ($HSO_3.NO$) and nitrosisulphonic acid (H_2NSO_5) were formed as intermediate products, but this theory has since been proved incorrect, by DIVERS and by REYNOLDS and TAYLOR.

The sulphur dioxide required for the process is obtained by roasting iron pyrites, FeS_2, in a current of air. The gas issuing from the pyrites burners contains about 7 per cent. of sulphur dioxide, 83 per cent. nitrogen, and 10 per cent. oxygen. A small supply of oxides of nitrogen is now fed into the gas, to make up for the inevitable slight losses of these substances which occur in working. The oxides of nitrogen are prepared by the catalytic oxidation of ammonia by means of heated platinum in the presence of oxygen; they were formerly prepared by the action of concentrated sulphuric acid upon nitre. Nowadays, the oxides of nitrogen are occasionally introduced by adding nitric acid in the Glover tower.

The mixture of air, sulphur dioxide, nitrogen and *small* amounts of oxides of nitrogen now passes up the GLOVER tower, which is made of brickwork lined with lead, inside which again is another lining of fireproof bricks. The tower is packed with broken flints, and down it trickles a mixture of (*a*) dilute "chamber" acid (65 per cent. H_2SO_4) and (*b*) concentrated sulphuric acid (containing dissolved oxides of nitrogen) from the GAY-LUSSAC tower at the other end of the plant. As the hot gases pass up the Glover tower they are cooled to the proper temperature for reaction, they take up the necessary oxides of nitrogen by driving these out from the descending acid (remember that the oxides of nitrogen

previously introduced are *only to make up for loss*; the main quantity of these oxides is taken up in the Glover tower), and they concentrate the acid which flows down the tower.

After the gases leave the Glover tower, they pass into a series of lead chambers, where the main portion of the sulphuric acid is formed. (Some is formed in the Glover tower.) A fine spray of water is blown into the chambers from the roof, and "chamber acid" collects on the floor, whence it can be drawn off. Chamber acid is never allowed to reach a concentration of more than 70 per cent. H_2SO_4, since stronger acid would dissolve the lead of the chambers.

The number and size of the chambers are so arranged that the conversion of sulphur dioxide into sulphuric acid is practically complete by the time the gases leave the last chamber. The residual gases consist chiefly of nitrogen and oxides of nitrogen. To recover the latter the GAY-LUSSAC tower is used. This is filled with broken coke, down over which a stream of cold concentrated sulphuric acid flows. This dissolves the oxides of nitrogen, probably forming a compound with them, while the nitrogen passes on into the chimney stack. The acid from the Gay-Lussac tower is then returned to the Glover tower, in which it loses its oxides of nitrogen as already described.

The dilute sulphuric acid (65–70 per cent.) which collects in the chambers is concentrated, if required, by passing a stream of hot air over the liquid heated in silica pans, or (GAILLARD process) by passing the liquid in a fine spray down a tower (made of acid-resisting lava) through which a current of hot gases from a coke generator passes in the opposite direction. An acid of 92–97 per cent. H_2SO_4 collects at the base of the tower. 100 per cent. sulphuric acid may be made by adding sulphur trioxide, or sulphuric acid containing dissolved sulphur trioxide, to the 92–97 per cent. acid.

Impurities in Chamber Acid.—The chief impurities in commercial sulphuric acid are arsenious oxide, As_2O_3 (from the pyrites), lead sulphate, $PbSO_4$ (from the chambers), and oxides of nitrogen (chiefly N_2O_3). The arsenic is removed by diluting the acid and passing a stream of sulphuretted

hydrogen through, when the arsenic is precipitated as arsenious sulphide—

$$As_2O_3 + 3H_2S = As_2S_3 \downarrow + 3H_2O$$

Arsenic may also be removed by adding just sufficient hydrochloric acid to convert the arsenious oxide present into arsenic trichloride, $AsCl_3$, and then blowing air through the liquid, when the chloride is carried off. The dark colour

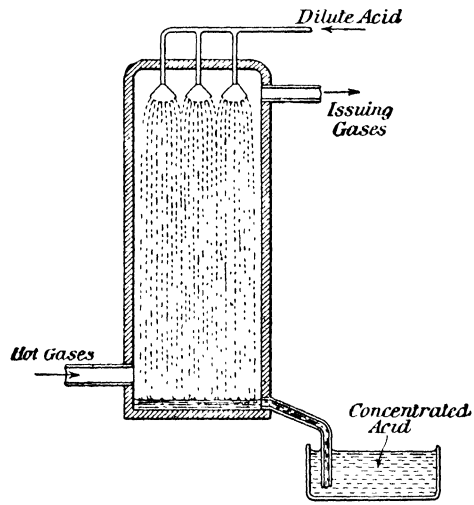


FIG. 103.—Concentration of Sulphuric Acid (Gaillard Tower).

often shown by commercial sulphuric acid is due to the charring of organic impurities.

2. CONTACT PROCESS.—The reaction $2SO_2 + O_2 \rightleftharpoons 2SO^3$ has already been discussed (p. 467). It should be noted in addition that since a contraction of volume takes place when sulphur trioxide is formed from sulphur dioxide and oxygen, increase of pressure will aid the formation of the trioxide (Le Chatelier). The law of mass action, again, will show us that to convert *all* the sulphur dioxide into trioxide an excess of oxygen must be used. To sum up, we may say that to get a good yield of sulphur trioxide—

(i) The temperature must be as low as conveniently possible, since a rise in temperature favours the reverse action, $2SO_3 \longrightarrow 2SO_2 + O_2$.

(ii) A catalyst is therefore necessary to make the reaction proceed at a reasonable rate.

(iii) An increase of pressure would aid the formation of trioxide.

(iv) An excess of oxygen should be used, to ensure complete conversion of the dioxide into trioxide.

Since sulphur trioxide forms sulphuric acid when it combines with water, if the formation of the trioxide could be carried out on a commercial scale we should have a new process for the manufacture of sulphuric acid.

Attempts to make sulphuric acid in this way were made over 100 years ago at Bristol by a vinegar manufacturer named PHILLIPS, but a successful process was not worked out until the end of the nineteenth century, when a firm of German chemical manufacturers, the *Badische Anilin und Soda Fabrik*, solved the problem.

At the present day, the lead-chamber process is obsolescent, and will no doubt be completely superseded by the " contact " process at no very remote date. Various modifications of this process are in use; some of the most important are described below.

(i) *Badische Anilin und Soda Fabrik Method.*—Sulphur dioxide from pyrites burners, mixed with excess of air, is passed into chambers called " scrubbers " ; into these chambers jets of steam are blown, when each particle of dust in the gases becomes the centre of a tiny drop of water. These drops of water are allowed to settle and the purified gas passed through coke soaked in strong sulphuric acid, where it is dried. This preliminary purification is necessary, as the dust contains arsenious oxide and other substances which would " poison " the catalyst (i.e. stop its action).

The pure dry gas, consisting of sulphur dioxide and excess of air, is now passed through a series of tubes containing the catalyst, which consists of platinized asbestos, that is, asbestos which has been soaked in platinum chloride solution and then

strongly heated, when the platinum chloride loses its chlorine and the platinum is left in a state of extremely fine division throughout the asbestos. In these tubes the reaction occurs. The reaction is exothermic, so that when it has been started by external heat it proceeds automatically, the rate of flow of the gases through the tubes being regulated in such a way that the heat evolved is just sufficient to keep the temperature at 400–450°.

The sulphur trioxide so produced is absorbed in 98 per

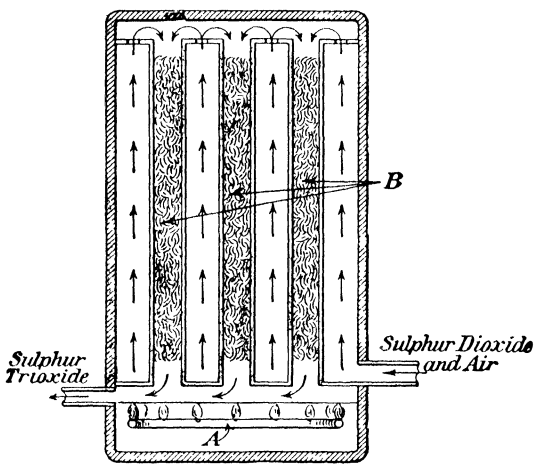


FIG. 104.—Diagram of the Badische Contact Process.
A. Ring of gas burners. *B*. Catalyst.

cent. sulphuric acid in a large vat, water being run in at the same time at such a rate that the concentration of the acid in the vat remains constant at 98 per cent. When the vat is nearly full, the water may be turned off and the concentration of acid raised to 100 per cent. If sulphur trioxide is still passed it dissolves in the 100 per cent. acid and forms *fuming sulphuric acid* or *oleum*, a solution of the trioxide in sulphuric acid.

At first attempts were made to dissolve the sulphur

trioxide in water directly, but this produced a mist of sulphuric acid that filled the works and proved extremely unpleasant to the workmen; moreover, much of the trioxide was converted into a glassy modification that dissolves in water much more slowly than the ordinary form.

(ii) *The Schröder-Grillo Process.*—This differs from the Badische process only in the form of the catalyst. Instead of employing platinized asbestos, magnesium sulphate crystals ($MgSO_4.7H_2O$) are taken, soaked in a solution of platinum chloride, and then heated in sulphur dioxide, when a spongy mass is obtained covered with very finely divided platinum. This mass is used as the catalyst.

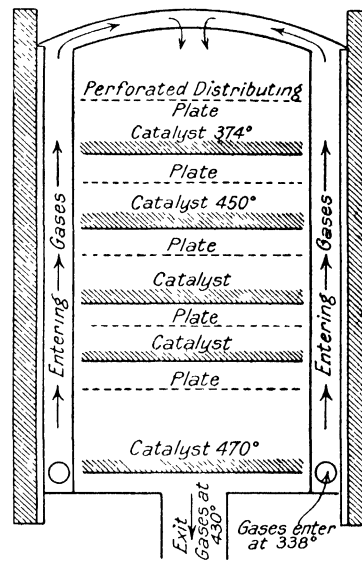


FIG. 105.—Grillo Plant.

(iii) *The Verein chemischer Fabriken (Mannheim) Process.*—In this process the contact agent or catalyst is burnt pyrites, which consists chiefly of ferric oxide, Fe_2O_3. Combination of the sulphur dioxide and oxygen is only partial (60 per cent.) in this case, and has to be completed by platinized asbestos.

(iv) *The Selden Process*, developed in America, uses oxides of vanadium as catalyst. These are much cheaper than platinum and not so susceptible to "poisons." A different form of contact chamber is employed, of greater efficiency.

Comparison of Lead-chamber and Contact Processes.—The lead-chamber process is the cheaper of the two, but produces a less pure acid. As for many purposes sulphuric acid is not required to be of a high degree of purity, chamber acid

still has a wide sale (e.g. in the manufacture of "superphosphate" fertilizers); but if the contact acid can be lowered in price it will probably kill the sale of lead-chamber acid completely. At the present day, contact acid is mainly employed in the manufacture of chemicals, explosives and dyes (especially indigo), and also in certain processes with food-materials such as beer.

Properties.—Sulphuric acid is a colourless oily liquid that can be frozen to white crystals melting at 10·5°. The purest commercial acid (known as *monohydrate*, i.e., the monohydrate of sulphur trioxide, $SO_3.H_2O$) contains about 97 per cent. H_2SO_4 and 3 per cent. H_2O. The most concentrated acid obtainable by distillation under atmospheric pressure boils at 330° and contains 98·3 per cent. H_2SO_4. A very characteristic property of sulphuric acid is its great avidity for water; so much heat is evolved when the two are mixed that in diluting the acid the latter must always be added to the water, and *never water to the acid.* Addition of water to concentrated sulphuric acid might cause the first few drops of water to be converted into steam, the expansion of which would scatter the acid explosively.

Evolution of heat is a very general sign of chemical reaction; we should therefore expect that when sulphuric acid is added to water combination of the two occurs. In point of fact two *hydrates* of sulphuric acid, $H_2SO_4.H_2O$ and $H_2SO_4.4H_2O$, have been isolated. The great avidity of sulphuric acid for water makes it an excellent drying agent for gases (*except* ammonia, with which it combines to form ammonium sulphate, and sulphuretted hydrogen, which it oxidizes to sulphur).

Sulphuric acid will often remove the *elements of water* from substances containing them; thus it chars sugar—

$$C_{12}H_{22}O_{11} = 12C + 11H_2O,$$

leaving a black mass of carbon. Paper, $(C_6H_{10}O_5)_n$, is similarly charred, while alcohol, C_2H_5OH, is converted into ethylene, C_2H_4—

$$C_2H_5OH = C_2H_4 + H_2O.$$

Vapour-density determinations show that the vapour of sulphuric acid consists chiefly of sulphur trioxide and water—

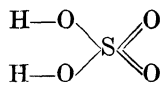
$$H_2SO_4 \rightleftharpoons H_2O + SO_3.$$

Sulphuric acid is a " strong " acid (p. 139), but only about half as strong as hydrochloric and nitric acids. It has, however, the great advantage over them of boiling at a much higher temperature (330°); it is therefore able to liberate them (and many other acids) from the corresponding metallic salts, on heating.

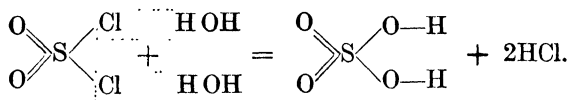
It is a dibasic acid and forms two series of salts, e.g., with sodium it forms *sodium hydrogen sulphate*, $NaHSO_4$, and *normal sodium sulphate*, Na_2SO_4.

When passed through a red-hot silica tube sulphuric acid is split up into water, sulphur dioxide and oxygen.

The *constitution of sulphuric acid* is probably



since it is formed when water acts upon ***sulphuryl chloride***, SO_2Cl_2 (p. 480).



Sulphur heptoxide, S_2O_7, was obtained in 1877 by BERTHELOT, by continued sparking of a mixture of sulphur dioxide and oxygen—

$$4SO_2 + 3O_2 = 2S_2O_7.$$

It is a white crystalline solid that dissolves in water to give *persulphuric acid*, $H_2S_2O_8$, of which it is therefore the anhydride.

Persulphuric acid, $H_2S_2O_8$, can be obtained as a white crystalline solid by the action of chlorosulphonic acid (p. 481) on 100 per cent. hydrogen peroxide—

$$2Cl.SO_2.OH + H_2O_2 = H_2S_2O_8 + 2HCl.$$

It can be prepared in aqueous solution by electrolysis of fairly

dilute (1 : 1) sulphuric acid, using a very small anode. The HSO_4 groups that are liberated at the anode combine together to form persulphuric acid—

$$2HSO_4 = H_2S_2O_8.$$

The potassium, sodium and ammonium salts may be made by substituting the corresponding acid sulphate for sulphuric acid in the electrolysis.

Ammonium persulphate, $(NH_4)_2S_2O_8$, is used commercially as a bleaching agent. If heated with concentrated nitric acid it yields a mixture of ozone and oxygen.

Persulphuric acid and the persulphates are strong oxidizing agents. The constitution of the acid is $\begin{matrix} O.SO_2.OH \\ | \\ O.SO_2.OH \end{matrix}$.

Caro's acid, $SO_2\begin{matrix} \diagup O.OH \\ \diagdown OH \end{matrix}$ (sometimes called per*mono*sulphuric acid to distinguish it from ordinary persulphuric acid, which is per*di*sulphuric acid), was discovered in 1898 by Caro. He made it by the action of concentrated sulphuric acid upon potassium persulphate. It is a *monobasic* acid and a powerful oxidizing agent.

Thionic Acids.—These are comparatively unimportant acids of the general formula $H_2S_xO_6$, where $x = 2, 3, 4, 5$, or 6. A mixture of some of them is formed when sulphuretted hydrogen is passed into a solution of sulphur dioxide. The product is called "WACKENRODER'S solution."

Thiosulphuric acid, $H_2S_2O_3$, is chiefly of importance in the form of its sodium salt, *sodium thiosulphate*, $Na_2S_2O_3.5H_2O$ —the "*hypo*" of photographers. This is made by boiling a solution of sodium sulphite with sulphur and is a white crystalline solid. It is used in volumetric analysis for the estimation of iodine, with which it reacts to form sodium iodide and *sodium tetrathionate*—

$$2Na_2S_2O_3 + I_2 = 2NaI + Na_2S_4O_6.$$

It is also used to "fix" photographic plates and prints by

dissolving out unchanged silver halides, with which it forms soluble "mixed" thiosulphates—

$$AgBr + Na_2S_2O_3 = NaAgS_2O_3 + NaBr.$$

Sodium thiosulphate will react with chlorine—

$$Na_2S_2O_3 + 4Cl_2 + 5H_2O = Na_2SO_4 + H_2SO_4 + 8HCl,$$

and hence is employed as an *antichlor* for fabrics after chlorine-bleaching. The reaction with bromine is similar (*contrast* action with iodine, above).

It was formerly manufactured from the alkali-waste of the Leblanc soda process (p. 201). On exposure of the waste (CaS) to air in presence of water calcium thiosulphate is formed—

$$2CaS + 2O_2 + H_2O = CaS_2O_3 + Ca(OH)_2.$$

On addition of sodium carbonate calcium carbonate is precipitated and a solution of sodium thiosulphate left—

$$CaS_2O_3 + Na_2CO_3 = CaCO_3 \downarrow + Na_2S_2O_3.$$

As the supplies of alkali-waste will soon be exhausted, alternative methods of manufacture have been initiated. These include (i) the action of sulphur dioxide upon a solution of sodium carbonate containing suspended sulphur—

$$H_2SO_3 + Na_2CO_3 = Na_2SO_3 + H_2O + CO_2$$
$$Na_2SO_3 + S = Na_2S_2O_3$$

and (ii) the action of sulphur dioxide upon a mixture of sodium bisulphite and sodium sulphide—

$$2NaHSO_3 + 2Na_2S + 2SO_2 = 3Na_2S_2O_3 + H_2O.$$

Hydrosulphurous acid, $H_2S_2O_4$, is important commercially in the form of its sodium salt, $Na_2S_2O_4$, which is extensively employed in dyeing with indigo. It is made by the action of zinc upon a solution of sodium bisulphite, and is a white crystalline solid with powerful reducing properties.

$$Zn + 4NaHSO_3 = ZnSO_3 + Na_2SO_3 + 2H_2O + Na_2S_2O_4.$$

Sulphur sesquioxide, S_2O_3, is a blue solid made by the action of flowers of sulphur upon molten sulphur trioxide. It is decomposed by water into sulphuric acid, thiosulphuric acid and sulphur.

Halogen Compounds of Sulphur.—Sulphur forms the following compounds with the halogens. They are of little importance. SF_6, sulphur hexafluoride, colourless gas; S_2Cl_2, sulphur monochloride, yellow liquid; SCl_4, sulphur tetrachloride, reddish brown liquid; S_2Br_2, sulphur monobromide, red liquid.

The *oxyhalogen* compounds of sulphur are more important. The chief are thionyl chloride, $SOCl_2$; sulphuryl chloride, SO_2Cl_2; and chlorosulphonic acid, $HO.SO_2.Cl$.

Thionyl chloride, $SOCl_2$, is a colourless fuming liquid made by the action of sulphur trioxide upon sulphur monochloride—

$$SO_3 + S_2Cl_2 = SOCl_2 + S + SO_2,$$

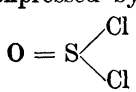
or by the action of phosphorus pentachloride upon sulphur dioxide—

$$SO_2 + PCl_5 = SOCl_2 + POCl_3.$$

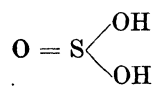
It is decomposed by water, giving a mixture of sulphurous and hydrochloric acids—

$$SOCl_2 + 2H_2O = H_2SO_3 + 2HCl.$$

The relationship between thionyl chloride and sulphurous acid is expressed by the following structural formulæ—



Thionyl chloride.

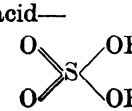


Sulphurous acid.

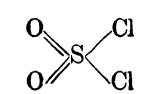
Compounds derived from acids by replacement of hydroxyl groups of the latter by chlorine are called *acid chlorides*; thus *acetyl chloride*, $CH_3.CO.Cl$, is the acid chloride of acetic acid, $CH_3.CO.OH$, and *benzoyl chloride*, $C_6H_5.CO.Cl$, is similarly related to benzoic acid, $C_6H_5.CO.OH$.

Thionyl chloride is therefore the acid chloride of sulphurous acid.

Sulphuryl chloride, SO_2Cl_2, is the acid chloride of sulphuric acid—



Sulphuric acid.



Sulphuryl chloride.

It can be made synthetically by the action of chlorine upon sulphur dioxide, preferably in the presence of camphor as a catalyst—

$$SO_2 + Cl_2 = SO_2Cl_2.$$

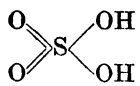
It is also formed when phosphorus pentachloride, PCl_5, acts upon concentrated sulphuric acid—

$$H_2SO_4 + 2PCl_5 = SO_2Cl_2 + 2POCl_3 + 2HCl.$$

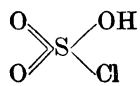
Sulphuryl chloride is a colourless fuming liquid, the structure of which is sufficiently proved by its synthesis. It is decomposed by water, forming sulphuric and hydrochloric acids—

$$SO_2Cl_2 + 2H_2O = H_2SO_4 + 2HCl.$$

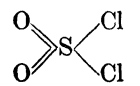
Chlorosulphonic acid, $HO.SO_2.Cl$, is intermediate in structure between sulphuric acid and sulphuryl chloride—



Sulphuric acid.



Chlorosulphonic acid.



Sulphuryl chloride.

It can be made synthetically by the action of hydrochloric acid gas on sulphur trioxide—

$$SO_3 + HCl = HO.SO_2.Cl,$$

and in other ways. It is a colourless fuming liquid that reacts with water to form sulphuric and hydrochloric acids—

$$HO.SO_2.Cl + H_2O = H_2SO_4 + HCl.$$

Chlorosulphonic acid is used to some extent in the manufacture of dyes. It is prepared commercially by passing hydrochloric acid gas into oleum (p. 474).

Questions

1. What is the origin of the word *sulphur*? Describe the properties of the element.
2. Give an account of the extraction of sulphur.
3. Is the classification of oxygen with sulphur justified by the chemical behaviour of these two elements?
4. Discuss the phenomenon of allotropy, with special reference to the allotropes of sulphur and oxygen.
5. Explain the use of sulphuretted hydrogen in qualitative analysis.

6. Contrast the bleaching action of chlorine with that of sulphur dioxide.

7. How is sulphuric acid manufactured ?

8. What do you know of the oxyacids of sulphur, excluding sulphuric and sulphurous acids ?

9. Show, by means of formulæ, the relationship between sulphuryl chloride, chlorosulphonic acid, thionyl chloride, sulphurous acid and sulphuric acid.

CHAPTER XXVII

GROUP VI, Sub-group A

Chromium, Molybdenum, Tungsten, Uranium

In chemical properties these elements show many resemblances to one another, but scarcely any to the other members of the group. They are similar in many respects to iron, cobalt, and nickel.

CHROMIUM

Group in Periodic System: VI; *Symbol:* Cr; *Valency:* 2, 3, or 6; *Atomic Weight:* 52·0; *Melting-point:* 1,700°; *Specific Gravity:* 6·8–7·1.

History.—A mineral called *crocoisite* was discovered by Lehmann, in 1762. Vauquelin and Klaproth, in 1797, showed it to be the lead salt of a peculiar acid. From this acid Vauquelin succeeded in isolating an impure specimen of a new metallic element which was later called *chromium* on account of its characteristic property of forming coloured compounds. In 1857 Deville prepared the metal in a state of approximate purity, but it was not until 1894 that chemically pure chromium was made, by Moissan.

Occurrence.—The chief ore of chromium is *chromite* or *chrome iron ore*, $FeO.Cr_2O_3$. *Crocoisite*, $PbCrO_4$, occurs in smaller quantities and is rarer.

Preparation.—Chromium of a high degree of purity may easily be made by the *thermite* process. Chromium sesquioxide, Cr_2O_3, is mixed with a slight excess of aluminium powder in a fireclay crucible, and the mixture fired by igniting

a small heap of powdered potassium chlorate and magnesium powder placed on the top. A very intense heat is produced, and the chromium oxide is reduced to chromium, which is found after the reaction as a mass of metal at the bottom of the crucible—

$$Cr_2O_3 + 2Al = 2Cr + Al_2O_3.$$

Properties.—Chromium is a greyish metal with a silvery lustre. Its specific gravity is 6·8, melting-point about 1,700°, and boiling-point 2,200°. It is stable in moist air at ordinary temperatures, but burns with a bright flame when strongly heated. It is soluble in dilute hydrochloric and sulphuric acids, even in the cold, forming *chromous* salts; concentrated nitric acid renders it *passive* (p. 551), probably owing to the formation of a thin coherent and protective coating of oxide.

Alloys of chromium with iron, and with iron and nickel, are used industrially for armour-plating and many other purposes. "Chrome steel" is very hard and exceedingly tough, and is extremely resistant to acids. The so-called "stainless steel" is not a true steel, but an alloy of chromium, iron, and sometimes molybdenum containing about 12–15 per cent. of chromium. *Chromium-plating* is carried out by the electrolytic deposition of chromium from a solution of chromic acid and chromium sulphate (p. 486) to which chromium carbonate has been added. Useful as it is, there are indications that it may be replaced by cadmium plating. Chromium compounds (e.g. chrome alum and sodium dichromate) are used in tanning leather, in the manufacture of dyes and pigments, and in the photographic industry.

Compounds of Chromium.—Chromium forms three oxides, two of which are basic and one acidic:

Chromous oxide, CrO. Basic.
Chromium sesquioxide, Cr_2O_3. Basic.
Chromium trioxide, CrO_3. Acidic.

Chromous oxide, CrO, is obtained as a black powder when chromium amalgam is allowed to oxidize in the air.

Chromous hydroxide, $Cr(OH)_2$, is a yellow powder precipitated by addition of caustic soda to a solution of

chromous chloride. It is unstable and readily oxidizes into chromic hydroxide—

$$2Cr(OH)_2 + H_2O + \text{oxygen} = 2Cr(OH)_3.$$

Chromous chloride, $CrCl_2$, is formed when chromium dissolves in dilute hydrochloric acid, but is usually prepared by the reduction of chromic chloride with nascent hydrogen, e.g., with zinc and hydrochloric acid.

$$2CrCl_3 + H_2 \text{ (nascent)} = 2CrCl_2 + 2HCl.$$

The anhydrous salt is conveniently made by heating chromic chloride in a current of hydrogen; it is a white crystalline solid.

Aqueous solutions of chromous salts, and the hydrated salts themselves, are blue; the anhydrous salts vary in colour, for while chromous chloride is white, *chromous acetate* is red.

Chromium sesquioxide or chromic oxide, Cr_2O_3, can be made in a number of ways, the easiest being to heat ammonium dichromate—

$$(NH_4)_2Cr_2O_7 = Cr_2O_3 + 4H_2O + N_2.$$

Obtained in this way it is a voluminous green powder. It is used as a paint ("*chrome-green*") and also for making coloured glass, to which it imparts a fine green colour.

Chromic hydroxide, $Cr(OH)_3$, is obtained as a bluish-green gelatinous precipitate on addition of caustic alkali to a solution of a chromic salt. Under suitable conditions it will dissolve in excess of caustic soda or potash to form *salts*, the *chromites*; it will also dissolve in dilute acids to form chromic salts, and is therefore both basic and acidic.

Chromic chloride, $CrCl_3$, is prepared anhydrous by heating a mixture of chromium sesquioxide and carbon in a current of chlorine—

$$Cr_2O_3 + 3C + 3Cl_2 = 2CrCl_3 + 3CO.$$

The chromic chloride sublimes over in pale violet crystalline scales. A remarkable property of anhydrous chromic chloride is that it will not dissolve in water, even on heating, unless a

trace of chrom*ous* chloride is present, when it dissolves easily, forming a green solution from which green crystals of the hexahydrate $CrCl_3.6H_2O$ may be obtained.

Chromic chloride hexahydrate exists in three isomeric forms. In aqueous solution one form yields *three* chlorine ions per molecule, the second gives *two*, and the third only *one*. To account for this behaviour, WERNER assumes that some or all of the water of crystallization forms an integral part of the molecule and is not split off in solution ; he then represents the first form as the anhydrous chloride of the tervalent group $[Cr(H_2O)_6]$, the second as the monohydrated chloride of the bivalent group $[Cr(H_2O)_5Cl]$, and the third as the dihydrated chloride of the univalent group $[Cr(H_2O)_4Cl_2]$, or

(i) $[Cr(H_2O)_6]Cl_3$.
(ii) $[Cr(H_2O)_5Cl]Cl_2.H_2O$.
(iii) $[Cr(H_2O)_4Cl_2]Cl.2H_2O$.

For further information on this point, and on Werner's Theory of Valency in general, the student is referred to larger textbooks.

Chromic sulphate, $Cr_2(SO_4)_3$, may be made by dissolving the hydroxide in sulphuric acid. It forms violet crystals containing 16 or 18 molecules of water of crystallization according to the method of extraction. It is most often met with in the form of its double salt with potassium sulphate, *chrome alum,* $K_2SO_4.Cr_2(SO_4)_3.24H_2O$. Chrome alum is a dark purple crystalline substance that is usually prepared by passing sulphur dioxide into a solution of potassium dichromate acidified with sulphuric acid—

$$K_2Cr_2O_7 + 3SO_2 + H_2SO_4 = K_2SO_4 + Cr_2(SO_4)_3 + H_2O.$$

On evaporation of the solution, chrome alum separates. It is isomorphous with alum, $K_2SO_4.Al_2(SO_4)_3.24H_2O$, and is a *double salt,* i.e., in solution it gives all the ions which would be given by its constituent salts separately. (Contrast a typical *complex salt,* such as potassium ferrocyanide, $K_4Fe(CN)_6$, which gives none of the ionic reactions of ferrous iron.)

Chrome alum has become of considerable importance of

late years in the tanning of leather. Leather which has been soaked in chrome alum solution (" chrome-leather ") is much more durable than leather tanned in the ordinary way; it is said that the boots of Chicago policemen needed repairing three times as seldom when they were shod with chrome leather as when they wore the ordinary kind. The author, however, is uncertain whether there *are* any policemen in Chicago.

Crystals of chrome alum are often found in the cells of a " Bichromate " battery that needs recharging.

Chromium trioxide, CrO_3, separates in the form of delightful red needles on adding concentrated sulphuric acid to a concentrated solution of sodium or potassium dichromate and allowing the liquid to stand in a cool place. The crystals are deliquescent and dissolve in water to give a strongly acid solution containing *dichromic acid*—

$$H_2O + 2CrO_3 \rightarrow H_2Cr_2O_7$$

One might have expected to get *chromic acid*, H_2CrO_4 (especially as salts of this acid are well known)—

$$H_2O + CrO_3 = H_2CrO_4;$$

cryoscopic and conductivity experiments on the solution, however, show that it is the dichromic acid which is formed.

When heated to 250°, chromium trioxide splits up into chromic oxide and oxygen—

$$4CrO_3 = 2Cr_2O_3 + 3O_2,$$

and the readiness with which this oxygen is lost makes chromium trioxide a strong oxidizing agent. Thus, a suspension of it in acid must be filtered through glass wool, since it chars paper, while if alcohol is dropped on the solid trioxide the mixture inflames.

Chromates and Dichromates.—These compounds are salts of two different acids, neither of which has been isolated, and one of which (chromic acid) is unknown even in solution The *chromates* are salts of *chromic acid*, H_2CrO_4, and the *dichromates* are salts of *dichromic acid*, $H_2Cr_2O_7$. It will be at once apparent that it is incorrect to call the potassium salt

of dichromic acid potassium *bi*-chromate, as is so often done; potassium *bi*chromate does not exist, but if it did it would have the formula $KHCrO_4$, corresponding to potassium bisulphate, $KHSO_4$.

Potassium chromate, K_2CrO_4, may be made by neutralizing a solution of *di*chromic acid or potassium dichromate with potash—

$$K_2Cr_2O_7 + 2KOH = 2K_2CrO_4 + H_2O.$$

On evaporation of the solution the potassium chromate separates in the form of yellow crystals. In solution, potassium chromate is used as a reagent in qualitative analysis, since it gives precipitates of insoluble chromates with many metals, e.g., silver (brick red), lead (yellow), barium (yellow).

Potassium dichromate, $K_2Cr_2O_7$, is manufactured from chrome iron ore by fusing the ore in a reverberatory furnace with sodium carbonate and lime with free access of air—

$$4FeO.Cr_2O_3 + 8Na_2CO_3 + 8CaO + 7O_2 = 2Fe_2O_3 + 8Na_2CrO_4 + 8CaCO_3.$$

The fused mass, after cooling, is powdered and treated with a warm dilute solution of sodium carbonate (to decompose any calcium chromate present), the insoluble matter allowed to settle, and the clear liquid just acidified with sulphuric acid and evaporated to crystallization. This yields the *sodium* salt, $Na_2Cr_2O_7.2H_2O$.

$$2Na_2CrO_4 + H_2SO_4 = Na_2SO_4 + Na_2Cr_2O_7 + H_2O.$$

To obtain the potassium salt, the solution of sodium dichromate is mixed, before evaporation, with potassium chloride; the mixture of salt and potassium dichromate so formed can be separated by fractional crystallization. Electrolytic processes are now coming into use.

Potassium dichromate forms orange-red anhydrous crystals. It dissolves in water, and the acidified solution is used as an oxidizing agent, especially in organic chemistry and

in volumetric analysis. In the presence of sulphuric acid the oxidizing action may be represented by the equation

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

Ferrous salts may be estimated in solution by titration with dichromate in presence of sulphuric acid, using potassium ferricyanide as external indicator.

Sodium dichromate is much cheaper and much more soluble than the potassium salt, and is equally good for ordinary oxidations, e.g., preparation of acetaldehyde. It is not so convenient for volumetric analysis, as it is deliquescent and therefore cannot be weighed out directly.

All chromates and dichromates are excessively poisonous, owing to the fact that they destroy the red corpuscles of the blood.

Distillation of a mixture of potassium dichromate, salt, and concentrated sulphuric acid yields dark red vapours which condense to a red liquid, called *chromyl chloride*, CrO_2Cl_2. This substance may be regarded as the " acid chloride " of chromic acid—

Chromic acid, $O_2Cr(OH)_2$; *Chromyl chloride,* O_2CrCl_2.

It boils at 117° and readily reacts with water, giving hydrochloric and dichromic acids. With a concentrated solution of potassium chloride it reacts to form the red crystalline compound called PÉLIGOT'S salt or *potassium chlorochromate*, $CrO_2(Cl)(OK)$

$$CrO_2Cl_2 + KCl + H_2O = CrO_2(Cl)(OK) + 2HCl.$$

Perchromic acid, $HCrO_5$ (?)—On addition of hydrogen peroxide to a solution of potassium dichromate acidified with sulphuric acid, a deep blue compound is produced that rapidly decomposes in aqueous solution but is much more

stable in ether. This blue compound is called "*perchromic acid*" and was considered by MOISSAN (who isolated certain of its salts) to have the composition $HCrO_5$; it may, however, be H_3CrO_8, since crystals of this substance, with two molecules of water of crystallization, have been prepared by the action of nearly pure hydrogen peroxide upon chromium trioxide dissolved in an inert organic solvent at low temperatures.

QUESTIONS

1. Exercise your chemical ingenuity by justifying the grouping of chromium with oxygen and sulphur.
2. Describe the preparation and properties of potassium dichromate.
3. How would you make (*a*) chromyl chloride, (*b*) chromium trioxide, from potassium dichromate?
4. Write an account of the preparation and properties of chromic chloride.

CHAPTER XXVIII

GROUP VII

TYPICAL ELEMENTS: **Fluorine, Chlorine.**
Sub-group A: **Manganese.**
Sub-group B (similar to typical elements): **Bromine, Iodine.**

FLUORINE, CHLORINE, BROMINE, IODINE

The "halogen" elements, fluorine, chlorine, bromine and iodine, form a very well-marked family of elements, closely similar in chemical and physical properties. Manganese, however, would never be classed with the halogens on the ground of chemical relationship.

The student will find it a useful exercise to tabulate the resemblances of the halogens to one another; he may also tax his ingenuity in finding points of similarity between the halogens and manganese, other than the fact that chlorine forms an oxide Cl_2O_7 and manganese an oxide Mn_2O_7.

It may be well to point out here that examiners are very fond of the question, "Why are the elements (this, that and the other) classified together?" since they can thus test the candidate's knowledge of the chemistry of several elements in an economical way. The most popular elements for this purpose are the alkali-metals, halogens, and nitrogen group.

FLUORINE

Group in Periodic System: VII; *Symbol:* F; *Valency:* 1; *Atomicity:* 2; *Atomic Weight:* 19·0.

History.—In the form of its compound with calcium, CaF_2 (calcium fluoride, or *fluorspar*), fluorine has been known since the days of "BASIL VALENTINE" (about 1600). SCHEELE was the first (1771) to prepare hydrofluoric acid, which was more fully investigated by GAY-LUSSAC and THÉNARD. Fluorine was first prepared in the elementary state by MOISSAN in 1886.

Occurrence.—In common with the other halogen elements, fluorine is too active to be found in nature in the uncombined state. It occurs chiefly as *fluorspar*, CaF_2, which is found in many parts of the world, especially in Derbyshire and Mexico; as *cryolite* or "ice-stone" (Na_3AlF_6), which occurs in quantity in Greenland; and in *fluor-apatite* ($CaF_2.3Ca_3(PO_4)_2$). In small quantities it is very widely distributed in sea-water, the enamel of teeth, oyster-shells, etc.

Preparation.—The preparation of fluorine proved to be a very difficult task. Methods analogous to those used in the preparation of chlorine (*q.v.*) proved useless, owing to the fact that the fluorine, even if liberated, was so active that it immediately entered into combination again with some of the other substances present. The French chemist Moissan, following DAVY, tried to prepare it by electrolysis of an aqueous solution of hydrofluoric acid, HF, but found that ozonized oxygen, and not fluorine, was obtained at the anode. He therefore tried again with pure anhydrous hydrofluoric acid, kept liquid by being surrounded with a freezing-mixture. This method was also unsuccessful, since anhydrous liquid hydrofluoric acid proved to be a non-conductor. To overcome this difficulty, Moissan at length hit on the happy idea of dissolving some potassium hydrogen fluoride (KHF_2) in the liquid hydrofluoric acid, thus rendering the liquid a conductor. He found that on electrolysis this solution gave at the anode a pale yellow gas which proved to be fluorine.

The apparatus Moissan employed was a platinum U-tube, fitted with side delivery-tubes and closed by stoppers made of transparent fluor-spar. Into this U-tube dipped the electrodes, which were made of an alloy of platinum and iridium. The tube was of about 160 c.c. capacity, and in

it were placed 100 c.c. of anhydrous liquid hydrofluoric acid and 20 grams of potassium hydrogen fluoride. On electrolysis by means of a current of 15 ampères and 50 volts, Moissan obtained fluorine at the rate of 5 litres per hour. The U-tube was kept at a temperature of — 23° C. by immersion in a bath of boiling liquid methyl chloride. [See Fig. 106.]

Moissan afterwards found that a copper tube (but not copper electrodes) could be used in the preparation of fluorine, since the copper soon becomes covered by a coherent coating of copper fluoride, CuF_2, which prevents further action.

To show that the gas he obtained was fluorine, and nothing else, Moissan absorbed a certain weight of it in sodium, and weighed the sodium fluoride formed.

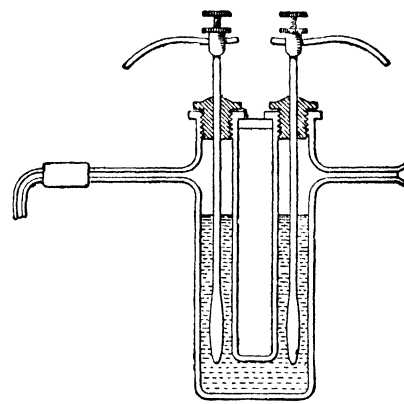


FIG. 106.—Preparation of Fluorine.

Properties.—Fluorine is a pale greenish-yellow gas of density 19 (H = 1), corresponding to the formula F_2. Liquid fluorine, first obtained by Moissan and Dewar in 1897, is a transparent yellow liquid boiling at —187° C., and freezing at —233° C. to a pale yellow solid. Fluorine is one of the most chemically active elements known; it combines with practically all other elements except nitrogen, chlorine, and the inactive gases, forming fluorides. Metals, especially when heated, take fire in fluorine; so do sulphur, phosphorus and even carbon in a finely divided state. Fluorine and hydrogen combine with explosion even in the dark, forming hydrofluoric acid. Water is decomposed by fluorine, hydrofluoric acid and ozonized oxygen resulting. Perfectly dry fluorine attacks glass only extremely slowly, if at all, but if even a trace of moisture be present rapid action takes

place, and silicon tetrafluoride (SiF_4) and water are formed.

The atomic weight of fluorine has been determined in many ways, e.g., by the conversion of sodium fluoride into sodium sulphate, and by the formation of sodium chloride from sodium fluoride by passing a current of dry hydrochloric acid gas over the latter substance. The value adopted is F = 19·0.

COMPOUNDS OF FLUORINE.

Hydrofluoric acid or Hydrogen fluoride, HF.

Preparation.—This substance may be obtained by the direct union of its elements and in other ways, but it is generally prepared by the action of strong sulphuric acid upon calcium fluoride—

$$CaF_2 + H_2SO_4 = CaSO_4 + 2HF.$$

The operation is usually carried out in a lead retort, and the acid which comes off is collected in a cooled receiver, or, if an aqueous solution is desired, the gas may be passed into water. The pure anhydrous acid is prepared from the aqueous solution as follows: the solution is divided into two equal parts, one of which is then neutralized with caustic potash solution. This gives a solution of potassium fluoride, KF—

$$HF + KOH = KF + H_2O.$$

To this solution the other half of the original hydrofluoric acid solution is added, when

$$KF + HF = KHF_2, \text{ or } KF.HF$$

Potassium hydrogen fluoride.

The solution of potassium hydrogen fluoride is evaporated until the crystals of the salt separate out; these are then carefully dried in a vacuum desiccator and the dry salt placed in a platinum retort connected to a platinum condenser and receiver, the latter being placed in a freezing mixture. On heating, the acid fluoride splits up into potassium fluoride and hydrofluoric acid—

$$KHF_2 = KF + HF,$$

and the latter is condensed to a colourless, mobile, volatile liquid which collects in the receiver. It must be kept in

strong platinum bottles, the stoppers of which can be firmly clamped.

Properties.—Hydrofluoric acid is usually met with as a gas, which condenses at 19° to a colourless fuming mobile liquid. It is readily soluble in water, forming a strongly acid solution. The anhydrous acid is not so active as the moist acid; thus perfectly dry hydrofluoric acid has no action upon glass, whilst in the presence of moisture (even in minute quantity) rapid action takes place and the glass is attacked. It is this property of moist hydrofluoric acid which is made use of for the *etching* of glass. The glass article to be etched is covered with wax and the desired pattern then drawn on the wax with a sharp instrument so that the glass is exposed in those places where etching is required. It is then placed over a trough containing aqueous hydrofluoric acid, or a mixture of calcium fluoride and concentrated sulphuric acid, the hydrofluoric acid fumes attack the glass in the exposed parts, and the glass is etched.

As an acid, hydrofluoric acid is not so strong as the corresponding acids of the other halogens (HCl, HBr, HI). It has, however, a greater action on organic material. Its formula has been proved by Moissan (among others) who measured the volumes of hydrogen and fluorine liberated during the electrolysis of anhydrous liquid hydrofluoric acid (containing a little potassium hydrogen fluoride to make it conduct), and found that they were equal. Hence by Avogadro's Hypothesis the formula must be $(HF)_n$. At a temperature of about 75° the vapour density is 10, therefore the molecular weight is 20 and $n = 1$; the formula of the gas here is HF. At lower temperatures *association* takes place, that is, two or more molecules combine to form a more complex one, and the mixture of these more complex molecules with the simple HF ones gives a higher vapour density.

Silver fluoride differs from silver chloride, bromide and iodide in being soluble in water. Many fluorides will combine directly with hydrofluoric acid to form acid fluorides, e.g., KHF_2, so that hydrofluoric acid can act as a dibasic acid, although it is usually monobasic. HF, of course, *must* be

monobasic; the apparent dibasicity must be attributed to unusual stability of the associated H_2F_2 molecules or to the fact that fluorine is occasionally capable of acting as a polyvalent element.

CHLORINE

Group in Periodic System: VII; *Symbol:* Cl; *Valency:* 1; *Atomicity:* 2; *Atomic Weight:* 35·46.

History.—The history of elementary chlorine dates from 1774, in which year it was prepared by SCHEELE by the action of *muriatic acid* (HCl) upon *pyrolusite* (MnO_2). Chlorine in the form of its compounds, however—especially sodium chloride, NaCl—has been known from prehistoric times. *Aqua regia*, a mixture of hydrochloric and nitric acids, was prepared by the Arabian chemists in the early Middle Ages, by heating a mixture of salt, saltpetre and alum, or sal-ammoniac, saltpetre, copper sulphate and clay. GLAUBER (1648) prepared *aqua regia* by heating a mixture of *aqua fortis* (nitric acid) and salt, and *spiritus salis* (spirit of salt, or hydrochloric acid solution) by heating salt with concentrated sulphuric acid and dissolving the fumes in water. An earlier preparation of *spiritus salis* is that of LIBAVIUS (1595), who made the acid by strongly heating a mixture of salt and clay.

In 1772 PRIESTLEY collected hydrochloric acid gas by means of a mercury pneumatic trough, and called it *marine acid air* on account of its preparation from sea-salt; the name *muriatic acid* was given to it for the same reason. In 1774 Scheele heated a solution of marine acid air, or muriatic acid, with pyrolusite and obtained a greenish yellow gas which he called *dephlogisticated marine acid air*, as he considered it to be muriatic acid from which phlogiston had been removed by the pyrolusite. BERTHOLLET (1785) showed that an aqueous solution of Scheele's gas on exposure to light yielded bubbles of oxygen and a solution of muriatic acid. From this and other observations LAVOISIER (1789) called the gas *oxymuriatic acid* and regarded it as a compound of oxygen and muriatic acid; he supposed the latter compound to be an oxide, MuO_2, of a new element *murium*, and Scheele's gas to be MuO_3.

GAY-LUSSAC and THÉNARD (1809), from their researches on these substances, supported Lavoisier's theory, but also pointed out that the facts agreed equally well with the theory that oxymuriatic acid was an element.

SIR HUMPHRY DAVY, in 1810, observed that if oxymuriatic gas was a compound, as maintained by Lavoisier, it should be possible to split it up, and made many experiments with this aim. He heated metallic sodium in dry oxymuriatic acid but obtained nothing but sodium muriate, whereas if the gas were a compound, oxygen or water would probably have been formed. From these and many other results, Davy concluded that Scheele's gas was an element, and since "oxymuriatic acid" was obviously an inappropriate name for an element, after consultation with other chemists he re-named it *chlorine*, from the Greek χλωρὸς, greenish-yellow.

Within the last few years, it has been shown that ordinary chlorine is a mixture of two isotopic elements, one of atomic weight 35 and the other of atomic weight 37. Neither of the isotopes has yet been obtained free from the other.

Occurrence.—Owing to its great chemical activity, chlorine does not naturally occur in the free state. The *chlorides* of sodium, potassium and magnesium are widely distributed in large quantities. *Sodium chloride*, NaCl, is found as *rock-salt* or *halite* (cubical crystals), in very large deposits in England (Cheshire), Galicia (near the town of Wielickza), and Germany (Stassfurt deposits). It is also found dissolved, in brine-springs (Droitwich, etc.) and in the sea. Potassium and magnesium chlorides are found in the solid state at Stassfurt, and in solution in sea-water. *Silver chloride*, AgCl, or *horn silver*, is also found native. Chlorine is essential to the life of both plants and animals.

Preparation.—In the laboratory chlorine is prepared generally by the oxidation of hydrochloric acid—

$$2HCl + \text{oxygen} = H_2O + Cl_2.$$

Practically any oxidizing agent will do; the choice is governed by convenience and economy. Manganese dioxide

and potassium permanganate are commonly employed. If manganese dioxide is used it is mixed with concentrated hydrochloric acid in a round-bottomed flask fitted with a cork carrying a thistle funnel (through which more acid may be added if required) and a delivery tube.

On heating, chlorine is evolved—

(i) $MnO_2 + 4HCl = MnCl_4 + 2H_2O$ (in the cold).

(ii) $MnCl_4 = MnCl_2 + Cl_2$ (on heating).

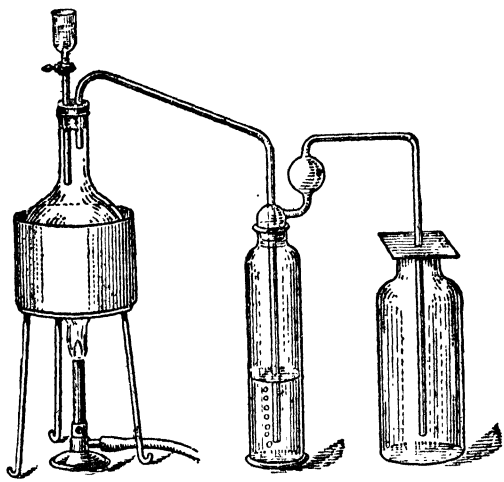


FIG. 107.—Preparation of Chlorine from Manganese Dioxide.

With potassium permanganate, action takes place in the cold. The permanganate is placed in a flask fitted with a cork carrying a dropping-funnel and delivery tube; concentrated hydrochloric acid is run in slowly from the funnel, and a steady stream of chlorine comes off without the application of heat—

$$2KMnO_4 + 16HCl = 2KCl + 2MnCl_2 + 8H_2O + 5Cl_2.$$

The gas is collected by downward displacement or over brine; if required dry it is passed through a Drechsel bottle containing strong sulphuric acid and collected by downward

displacement. It cannot be collected over mercury, as it attacks this metal, with formation of mercuric chloride.

Chlorine may also be prepared by the action of a dilute acid upon bleaching-powder, $CaOCl_2$.

$$CaOCl_2 + H_2SO_4 = CaSO_4 + H_2O + Cl_2.$$

Pure chlorine may be made by the electrolysis of fused silver chloride (SHENSTONE) using a carbon anode, or by the

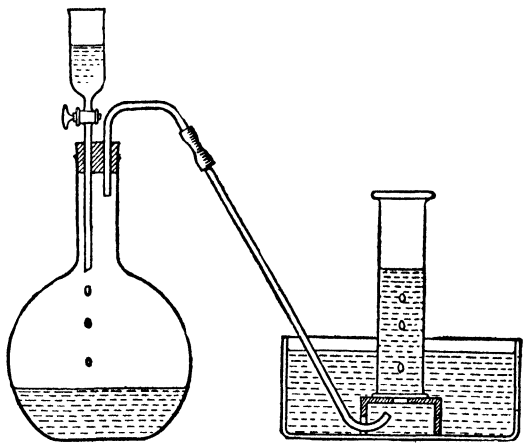


FIG. 108.—Preparation of Chlorine from Potassium Permanganate.

action of heat upon carefully dried and recrystallized gold chloride, $AuCl_3$—

$$2AuCl_3 = 3Cl_2 + 2Au.$$

Manufacture.—Chlorine is important commercially, and is manufactured from salt or from hydrochloric acid.

DEACON'S PROCESS.—This process employs atmospheric oxygen to oxidize hydrochloric acid gas to chlorine. The forward reaction $4HCl + O_2 \rightleftharpoons 2H_2O + 2Cl_2$ is exothermic, and is therefore favoured by low temperature; but at ordinary temperatures the velocity of the reaction is slow. Hence the conditions for successful operation are—

(i) The rate of reaction must be so far increased that the change takes place as quickly as possible.

(ii) The temperature must not be so high that equilibrium is appreciably moved to the left in the above equation.

(iii) As much of the hydrochloric acid as possible must be converted into chlorine.

In order to realize conditions (i) and (ii) a catalyst is employed. Many substances were tried, but the best was found to be *cupric chloride*, $CuCl_2$. In order to get a large surface of catalyst with least expenditure, broken bricks are soaked in a solution of the copper chloride and then dried. In this way the chloride is left in a finely divided state throughout the porous clay of which the bricks are made. It has been suggested that the action of the catalyst consists in the alternate formation and decomposition of *cuprous chloride*, CuCl—

(i) $2CuCl_2 = 2CuCl + Cl_2$.

(ii) $2CuCl + 2HCl +$ atmospheric oxygen $= 2CuCl_2 + H_2O$.

It should be remembered, however, that other substances, for which the above kind of explanation is not admissible, will act as catalysts on the reaction.

The best temperature is found to be 450–500°, and in practice about 70 per cent. of the hydrochloric acid is oxidized in one passage through the apparatus; the remaining 30 per cent. is absorbed in water and used again.

The hydrochloric acid gas formerly used came from the salt-cake furnaces in the manufacture of sodium carbonate by the LEBLANC process. It was absorbed in water in a tower filled with coke, and then again set free from the aqueous solution by addition to concentrated sulphuric acid. In this way the impurities contained in the crude gas from the furnaces were removed.

The purified hydrochloric acid gas obtained from this or other sources is mixed with excess of air (condition (iii) above) and the mixed gases heated in pipes to about 450°, after which they pass into another series of tubes that contain the catalyst and are maintained at a temperature of about 480–500° by the

heat of the reaction between the hot gases. The issuing gas is passed up a tower filled with coke over which water trickles; the unused hydrochloric acid is dissolved and the remaining gas dried by passing through concentrated sulphuric acid.

The chlorine obtained in this way is very dilute, being mixed with about fifteen times its own volume of residual air and nitrogen; it is therefore not suitable for compression but is used directly for bleaching or for conversion into bleaching-powder (p. 248).

The catalyst loses its power after about ten days and has to be renewed. Nowadays a mixture of cupric chloride and common salt is used instead of pure cupric chloride; this does not require renewal so often. With the disuse of the Leblanc process and the general adoption of the electrolytic process (p. 197), the Deacon process is gradually becoming obsolete.

WELDON'S PROCESS.—When concentrated chlorine is required on a small scale it is still occasionally made by a process first successfully worked by WELDON in 1866. Formerly the Weldon process was of much more importance than it is now; at the present day it has been almost entirely superseded by the Electrolytic process.

Pyrolusite (mineral manganese dioxide, about 80 per cent. MnO_2) is treated with concentrated hydrochloric acid in stone chambers heated by steam, when a fairly pure chlorine is evolved.

$$MnO_2 + 4HCl = MnCl_2 + 2H_2O + Cl_2.$$

Manganese dioxide is expensive, and therefore to obtain the chlorine at a reasonable cost the manganese has to be *recovered* from the chloride, or reconverted into manganese dioxide which may be used again. The recovery is carried out by mixing the manganese chloride solution with a large (33-40 per cent.) excess of lime and blowing air into the liquid at a temperature of 60°. Under these conditions the manganese chloride is converted first into manganous hydroxide by the lime—

$$MnCl_2 + Ca(OH)_2 = Mn(OH)_2 + CaCl_2,$$

and this into manganese dioxide by the atmospheric air—

$$2Mn(OH)_2 + O_2 = 2MnO_2 + 2H_2O.$$

The manganese dioxide then combines with excess of lime to form *calcium manganite*, $CaMnO_3$, or $CaO.MnO_2$, which settles to the bottom as a black mud, *Weldon mud*. This is then run into the chlorine stills and used instead of fresh pyrolusite. If *excess* of lime is not used in the recovery process, *trimanganic tetroxide*, Mn_3O_4, is formed, which means that only *one-third* of the manganese is reconverted into the state of oxidation of manganese dioxide ($Mn_3O_4 = 2MnO.MnO_2$).

It is clear that since the Weldon mud contains lime as well as manganese dioxide (calcium manganite = $CaO + MnO_2$), there is a serious loss of hydrochloric acid in the form of calcium chloride—

$$CaMnO_3 + 6HCl = CaCl_2 + MnCl_2 + 3H_2O + Cl_2,$$

only 33 per cent. of the hydrochloric acid being converted into free chlorine.

Electrolytic Processes.—Most of the chlorine used commercially is now prepared electrolytically, in the manufacture of caustic soda, p. 197. Electrolytic chlorine is very pure, which is a great advantage in all cases except for the manufacture of bleaching-powder, for which a dilute chlorine is best.

Chlorine is put on the market as a liquid, contained under pressure in steel cylinders. To liquefy the gas it is strongly cooled and then compressed; it must be carefully dried first, since moist chlorine attacks the steel cylinders.

Properties.—Chlorine is a greenish-yellow gas with a characteristic pungent and irritating smell. It is very poisonous, and was largely employed in the war of 1914–18 as a weapon of offence: sometimes with boomerang effects upon its users. The gas-masks used against it contained a mixture of charcoal and potassium permanganate.

The vapour density of chlorine is 35·5 at ordinary temperatures, corresponding to the formula Cl_2; at higher temperatures the vapour density diminishes *slightly*, showing that partial dissociation has occurred (Cf. iodine, p. 530).

Chlorine was first liquefied by FARADAY; it forms a golden yellow liquid boiling at — 33·6° and solidifying on further cooling to a yellow crystalline solid, M.P. — 102°.

Chlorine combines directly with most metals, forming salts called chlorides (" halogen," salt producer), and also with many non-metals. In general, absolutely dry chlorine is much less active than the ordinary moist, or not specially dried, gas; water seems to act as a catalyst in these, as in many other, reactions.

With hydrogen, chlorine combines explosively in the presence of bright sunlight, and more slowly in diffused light, to form hydrochloric acid gas—

$$H_2 + Cl_2 = 2HCl.$$

The reaction is very exothermic. Hydrogen and chlorine also explode if heated to about 260°. Owing to the great affinity of chlorine for hydrogen, many hydrocarbons, that is, compounds that consist of hydrogen and carbon only, will burn in the element, forming clouds of hydrochloric acid gas and depositing the carbon as soot—

$$C_xH_y + \frac{y}{2}Cl_2 = yHCl + xC.$$

Thus a piece of filter-paper soaked in boiling turpentine takes fire spontaneously in chlorine, the turpentine burning with a reddish smoky flame—

$$C_{10}H_{16} + 8Cl_2 = 10C + 16HCl.$$

Similarly a burning wax taper goes on burning if put into chlorine, since wax is a hydrocarbon of the type C_nH_{2n+2}.

$$C_nH_{2n+2} + (n + 1)Cl_2 = nC + (2n + 2)HCl.$$

In other cases of the reaction of chlorine with hydrocarbons the chlorine may combine directly with the hydrocarbon to form an *addition product*, e.g.—

$$\underset{\text{Ethylene.}}{C_2H_4} + Cl_2 = \underset{\text{Ethylene dichloride.}}{C_2H_4Cl_2},$$

or may replace all or part of the hydrogen in the hydrocarbon forming *substitution products*, e.g.—

$$\underset{\text{Methane.}}{CH_4} + Cl_2 = \underset{\text{Chloromethane, or methyl chloride.}}{CH_3Cl} + HCl.$$

Many metals burn when heated in chlorine, and if finely-divided may even ignite spontaneously in the gas at ordinary temperatures. Powdered antimony takes fire when sprinkled into a jar of chlorine, forming antimony chlorides, but sodium has to be heated in the gas before it will burn, although slow combination occurs in the cold. The anhydrous chlorides of metals may often be conveniently made in this *synthetic* way (e.g. ferric chloride, aluminium chloride).

Phosphorus melts and ignites spontaneously in chlorine, forming phosphorus pentachloride, PCl_5, mixed with the trichloride, PCl_3.

Chlorine will combine directly with carbon monoxide, CO, forming *phosgene* gas or carbonyl chloride, $COCl_2$; and with sulphur dioxide, SO_2, forming *sulphuryl chloride*, SO_2Cl_2. A catalyst is necessary to make these reactions proceed quickly; camphor, for example, acts as a suitable catalyst on the second change, while finely divided charcoal is generally used in the first.

Chlorine is soluble in water, the solution, which has the colour and smell of the gas, being called *chlorine water*. If cooled to 0°, chlorine water yields greenish yellow crystals of *chlorine hydrate*, $Cl_2.xH_2O$ where x is generally said to be 8. It was by heating this substance in a bent sealed tube, one arm of which was cooled in a freezing-mixture, that Faraday first liquefied chlorine; the hydrate decomposes on heating, liberating chlorine.

Chlorine and chlorine-water are good bleaching agents; chlorine used for bleaching must be moist, as the dry gas usually has no action. The bleaching in all cases is an *oxidation process*; sometimes the chlorine itself combines with the colouring matter to form colourless compounds, but in general the process is due to the action of *hypochlorous acid*, HClO, which is slowly formed by the action of chlorine on water—

$$H_2O + Cl_2 = HCl + HClO,$$

and readily yields its atom of oxygen to the dye, which is split up thereby into colourless substances. Note that the active bleaching agent is not "nascent oxygen," as is so often

stated, but hypochlorous acid; although it is correct, of course, to say that the bleaching is brought about by oxidation.

CHLORINE AND ALKALIS.—When chlorine is passed into cold dilute caustic soda solution, *sodium chloride* and *hypochlorite* are formed—

$$Cl_2 + 2NaOH = NaCl + NaClO + H_2O.$$

Analogous reactions occur with caustic potash and dilute milk of lime—

$$Cl_2 + 2KOH = KCl + KClO + H_2O.$$
$$2Cl_2 + 2Ca(OH)_2 = CaCl_2 + Ca(ClO)_2 + 2H_2O.$$

With hot concentrated alkalis or milk of lime, however, the *chloride* and *chlorate* of the metal are formed—

$$3Cl_2 + 6NaOH = 5NaCl + NaClO_3 + 3H_2O.$$
$$3Cl_2 + 6KOH = 5KCl + KClO_3 + 3H_2O.$$
$$6Cl_2 + 6Ca(OH)_2 = 5CaCl_2 + Ca(ClO_3)_2 + 6H_2O.$$

COMPOUNDS OF CHLORINE.

Hydrochloric acid, or hydrogen chloride, HCl.—The history of this gas has already been given (p. 496). It is obtained commercially by heating common salt with concentrated sulphuric acid, when

(i) $NaCl + H_2SO_4 = NaHSO_4 + HCl$,
(ii) $NaCl + NaHSO_4 = Na_2SO_4 + HCl$.

The gases are passed up through a tower filled with coke, where the hydrochloric acid is absorbed in a downward-flowing stream of water. By running the dilute acid thus obtained down over the coke again it absorbs more of the gas and so becomes more concentrated. The strongest hydrochloric acid solution obtainable is about 43 per cent. by weight. The chief impurities in the commercial product are *chlorine*, *ferric chloride* ($FeCl_3$), *sulphur dioxide* (SO_2), *arsenic chloride* ($AsCl_3$), *sulphuric acid* (H_2SO_4), and *common salt* (NaCl). The purification of hydrochloric acid is difficult, hence the much lower price of the "commercial" acid.

In the laboratory, hydrochloric acid gas is prepared by the action of sulphuric acid upon a chloride, generally common

salt. The reaction takes place in the cold, but is hastened, as usual, by heat. The products are sodium *bi*sulphate and hydrochloric acid gas—

$$NaCl + H_2SO_4 = NaHSO_4 + HCl.$$

The reaction $2NaCl + H_2SO_4 = Na_2SO_4 + 2HCl$ takes place only at much higher temperatures.

The apparatus used is similar to that for preparing sulphur dioxide (see p. 464). The gas may be dried by bubbling through concentrated sulphuric acid and collected by downward displacement or over mercury. If a solution of hydro-

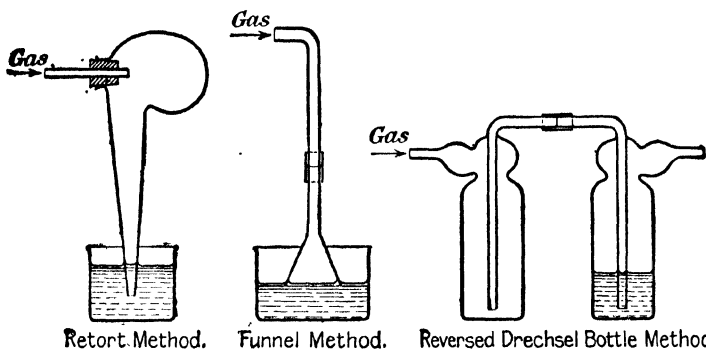


FIG. 109.—Methods of preventing "Sucking Back."

chloric acid is required, the gas is passed into distilled water, using one of the many devices for preventing "sucking back," which is always liable to occur in making a solution of a very soluble gas.

Properties.—Hydrochloric acid is a colourless gas with a pungent smell. It fumes strongly in moist air, owing to the formation of tiny drops of hydrochloric acid solution. It can be liquefied by cold and pressure to a colourless liquid boiling at —83° and solidifying to a white crystalline solid at —115°; it was first liquefied by FARADAY in 1846. It is very soluble in water, 1 volume of which will dissolve 450 volumes of the gas at 15° C. The solution possesses strongly acid pro-

perties, in contrast to the anhydrous *liquid acid* just mentioned, which shows scarcely any acid reactions—it will not act upon metals nor even upon carbonates. The solution, however, readily dissolves many metals with evolution of hydrogen, e.g.—

$$Zn + 2HCl = ZnCl_2 + H_2,$$

the other products being *chlorides*.

Hydrochloric acid is highly ionized in solution, and is, in fact, the strongest acid known, being about as strong as nitric acid and about one and a half times as strong as sulphuric. (See *strengths of acids*, p. 139.) The most concentrated solution of hydrochloric acid obtainable at 15° C. has a specific gravity of 1·212, and contains 43 per cent. by weight of HCl. On distilling this solution hydrochloric acid is given off and the solution becomes weaker, the temperature gradually rising to 110°, when no further change takes place and the solution distils over unchanged. The composition of this *constant-boiling solution* of hydrochloric acid is 20·24 per cent. HCl by weight. If a more dilute solution be distilled, water comes off first, the temperature of the boiling-point gradually rising till it reaches 110°, when the constant-boiling solution is obtained, which distils over unchanged. These results are shown in the figure (Fig. 110).

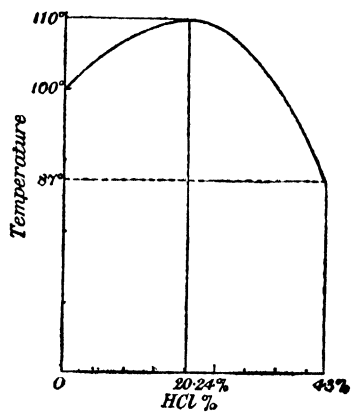


FIG. 110.—Boiling-point curve for Hydrochloric Acid solutions.

This constant-boiling solution was at one time considered to be a compound, since its percentage composition (20·24 per cent. HCl) is approximately that required by the formula $HCl.8H_2O$, but it was shown that the composition of the constant boiling solution *varies with the pressure*, whereas,

of course, the composition of a *compound* is independent of the physical conditions. Hence the constant-boiling solution is a *mixture* and not a compound.

CHLORIDES.—Most metallic chlorides are soluble in water, the chief exceptions being those of silver, mercury (mercur*ous* chloride, Hg_2Cl_2; mercuric chloride, $HgCl_2$, is soluble) and lead (slightly soluble); these metals are therefore precipitated as their chlorides when hydrochloric acid is added to a solution containing them (Group I, qualitative analysis). Metallic chlorides in general are not hydrolysed by water (*exceptions* —antimony and bismuth chlorides, etc.), and ionize readily in aqueous solution (*exceptions*—mercuric and cadmium chlorides). On heating with sulphuric acid they yield hydrochloric acid gas; with a mixture of manganese dioxide and sulphuric acid chlorine is given off on application of heat—

$$2NaCl + MnO_2 + 3H_2SO_4 = 2NaHSO_4 + MnSO_4 + 2H_2O + Cl_2.$$

(This reaction is sometimes used for the preparation of chlorine.)

The chlorides of non-metals are generally colourless liquids, for example, phosphorus trichloride, carbon tetrachloride, nitrogen trichloride. They are often, but not always, hydrolysed when added to water; thus phosphorus trichloride yields *phosphorous acid* and hydrochloric acid—

$$PCl_3 + 3H_2O = H_3PO_3 + 3HCl.$$

A rough test for deciding whether an element is a metal or non-metal is therefore to find the effect of water upon its chloride—

Metal chloride + *water* = ionized solution, no hydrolysis.
Non-metal chloride + *water* ⟶ hydrolysis, with formation of hydrochloric acid.

(Note, however, the exceptions mentioned above.)

Certain chlorides on heating lose chlorine, being reduced to a lower chloride or suffering complete decomposition into their elements. Thus platinum chloride, $PtCl_4$, yields platinum

and chlorine, $Pt + 2Cl_2$; cupric chloride, $CuCl_2$, gives cuprous chloride and chlorine—

$$2CuCl_2 \rightleftharpoons Cu_2Cl_2 + Cl_2;$$

phosphorus pentachloride gives the trichloride and chlorine—

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2,$$

and nitrogen chloride gives nitrogen and chlorine with explosion—

$$2NCl_3 = N_2 + 3Cl_2.$$

Other chlorides yield the corresponding *oxides* if heated in a current of air or oxygen; thus ferric chloride goes to ferric oxide—

$$4FeCl_3 + 3O_2 = 2Fe_2O_3 + 6Cl_2.$$

Practically all metallic chlorides are reduced to metal if heated strongly in a current of hydrogen.

Constitution of hydrochloric acid.—(i) When a mixture of 1 volume of hydrogen and 1 volume of chlorine is exploded, the hydrochloric acid gas formed on cooling is found to occupy the same volume as the original mixture, namely 2 volumes. Hence, by Avogadro's Hypothesis, two molecules of hydrochloric acid gas contain 1 molecule of hydrogen and 1 of chlorine, ∴ 1 molecule of hydrochloric acid gas contains ½ molecule of hydrogen and ½ molecule of chlorine. If we may assume that the molecules of hydrogen and chlorine are diatomic, the hydrochloric acid molecule will be HCl.

(ii) This is confirmed by a vapour density determination, which gives a V.D. of 18·25 and ∴ a M.W. of 36·5. The atomic weight of chlorine is 35·5, ∴ the hydrochloric acid molecule is HCl.

(iii) By shaking up a known volume of hydrochloric acid gas with sodium amalgam the acid is decomposed, yielding hydrogen (gas) and sodium chloride (solid) (Fig. 111). The volume of the residual hydrogen is found to be exactly half that of the hydrochloric acid gas taken, ∴ by Avogadro's Hypothesis, 1 molecule of hydrochloric acid gas contains ½ mol. of hydrogen,

$\therefore$ the hydrochloric acid molecule is HCl_x. x is found from (ii) the vapour density.

(iv) Electrolysis of concentrated hydrochloric acid solution, using a carbon anode, yields hydrogen (cathode) and chloride (anode). After the liquid has become saturated with chlorine, it will be found that the volume of hydrogen which comes off from the cathode in a given time is exactly equal to the volume of chlorine evolved from the anode in that time. The same sort of argument as used in the previous examples may be applied here.

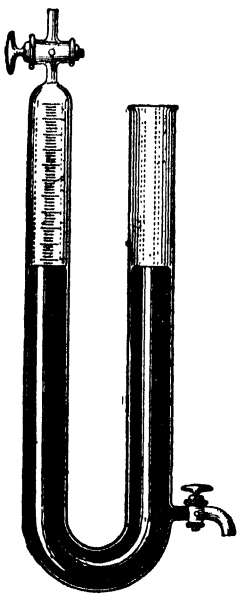


FIG. 111.

The *composition by weight* of hydrochloric acid is of great importance, since it yields the equivalent weight of chlorine (and also its atomic weight, since its valency is 1), upon which the atomic weights of so many elements depend. It has been determined by burning a known weight of pure hydrogen in pure chlorine and finding the weight of hydrochloric acid gas formed. By weighing also the chlorine used, the accuracy of the experiment could be checked. The student is advised to read the original papers in which this work is described. [*Phil. Trans.*, **205** A, 169, *1905*; *ibid.*, **209** A, 1, *1908*.]

Oxides of Chlorine.—Although the two elements do not combine together directly, three compounds of oxygen and chlorine are known: chlorine monoxide, Cl_2O; chlorine peroxide, ClO_2; and chlorine heptoxide, Cl_2O_7. They are all explosive and endothermic.

Chlorine monoxide, Cl_2O.—This substance was discovered in 1834 by BALARD and is still best made by the method he employed, viz. the action of dry chlorine on dry mercuric

oxide in the cold. The mercuric oxide is prepared by adding caustic soda to mercuric chloride solution—

$$HgCl_2 + 2NaOH = 2NaCl + H_2O + HgO;$$

it is washed and dried and a stream of cold dry chlorine is passed over it, when chlorine monoxide and mercuric oxychloride are formed—

$$2HgO + 2Cl_2 = HgO.HgCl_2 + Cl_2O.$$

Chlorine monoxide is an orange-yellow gas that condenses to a reddish brown liquid if passed through a freezing-mixture. It explodes on heating and is a powerful oxidizing agent. It readily dissolves in water, most of it being converted into the weak *hypochlorous acid*, HClO, of which it is therefore the anhydride—

$$H_2O + Cl_2O \rightleftharpoons 2HClO \rightleftharpoons 2H^{\cdot} + 2ClO'.$$

The composition of the gas was shown by BALARD and GAY-LUSSAC, by exploding a known volume and measuring the volumes of chlorine and oxygen produced. They found that 2 volumes of chlorine monoxide gave 3 volumes of mixed chlorine and oxygen; on treatment with caustic potash solution the chlorine dissolved and 1 volume of oxygen was left; the volume of

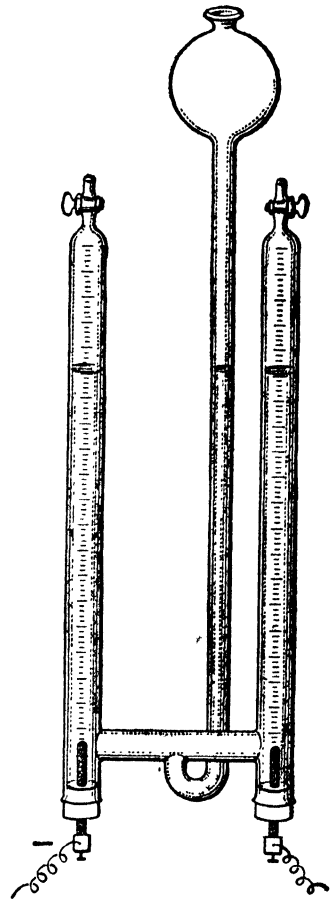


FIG. 112.—Electrolysis of Hydrochloric Acid.

the chlorine was therefore 3—1 = 2 volumes. Therefore by Avogadro's Hypothesis—

2 molecules of chlorine monoxide give 2 molecules of chlorine and 1 of oxygen.

∴ 1 molecule of chlorine monoxide gives 1 molecule of chlorine and ½ of oxygen.

∴ formula of the gas is Cl_2O.

Chlorine peroxide or **chlorine dioxide**, ClO_2, was first prepared by DAVY in 1815, by the action of concentrated sulphuric acid upon potassium chlorate—

(i) $KClO_3 + H_2SO_4 = KHSO_4 + HClO_3$.

(ii) $3HClO_3 = HClO_4 + 2ClO_2 + H_2O$.

The action takes place in two stages, as shown above. First (i) the acid and chlorate react to give potassium hydrogen sulphate and *chloric acid* ($HClO_3$); this then decomposes (ii) into *perchloric acid* ($HClO_4$), water, and chlorine peroxide.

BRAY'S method of preparing chlorine dioxide is to warm to 60° a mixture of powdered potassium chlorate, oxalic acid, and a little water. It has the advantage of not being dangerous.

Chlorine peroxide is a bright yellow gas with a characteristic smell. It is readily decomposed into its elements and is violently explosive. It can easily be liquefied, as was first shown by FARADAY in 1823. The liquid boils at 9 to 10° and freezes at —79° to orange-red crystals.

Chlorine peroxide is a strong oxidizing agent; phosphorus, sulphur, and many organic compounds such as sugar ignite spontaneously in the gas. The ignition of a mixture of potassium chlorate and sugar on addition of a drop of sulphuric acid is explained by the spontaneous combustion of a little of the sugar in the chlorine peroxide formed by the action of the acid on some of the chlorate; ignition thus started rapidly spreads through the whole mixture.

If some small pieces of phosphorus are placed under water and a few crystals of potassium chlorate added, the phosphorus may be made to burn under the water by introducing a little concentrated sulphuric acid through a thistle funnel on to the

crystals of the chlorate ; chlorine peroxide is evolved and the phosphorus burns in it.

Chlorine peroxide dissolves in water, yielding a solution which is acid, since chlorine peroxide combines with water to form a mixture of *chlorous acid* ($HClO_2$) and *chloric acid* ($HClO_3$)—

$$2ClO_2 + H_2O \rightleftharpoons HClO_3 + HClO_2.$$

It is therefore a *mixed anhydride*, like nitrogen peroxide (p. 366). The aqueous solution of chlorine peroxide is unstable in the light, gradually decomposing into chloric acid, chlorine, and oxygen—

$$6ClO_2 + 2H_2O = 4HClO_3 + Cl_2 + O_2.$$

Chlorine peroxide will dissolve in solutions of caustic alkalis, forming *chlorites* and *chlorates*—

$$2ClO_2 + 2KOH = KClO_2 + KClO_3 + H_2O,$$

as would be expected.

The constitution of chlorine peroxide was shown by Davy and by Gay-Lussac by decomposing a known volume of the gas into its elements and measuring the volumes of the chlorine and oxygen produced. They found that 2 volumes of chlorine peroxide gave 1 volume of chlorine and 2 of oxygen, whence, by Avogadro's Hypothesis, the formula for the gas must be ClO_2.

Chlorine heptoxide, Cl_2O_7.—This is the anhydride of *perchloric acid*, $HClO_4$. It was first made in 1900 by Michael and Conn, by addition of anhydrous perchloric acid to phosphorus pentoxide kept at a temperature of —10° by means of a freezing-mixture.

$$2HClO_4 + P_2O_5 = 2HPO_3 + Cl_2O_7.$$

After standing for 24 hours, at the same temperature, the mixture is heated to 82° when the chlorine heptoxide distils over as a colourless volatile oil.

Chlorine heptoxide is extremely explosive, and its preparation involves considerable danger. It is unstable, and gradually decomposes on standing. It is not so powerful an oxidizing agent as the other chlorine oxides, e.g. it does not

ignite sugar. With water it slowly reacts, to form perchloric acid—

$$Cl_2O_7 + H_2O = 2HClO_4.$$

"**Euchlorine**" is a mixture of chlorine peroxide and chlorine, made by the action of hydrochloric acid upon potassium chlorate. The composition of the mixture is variable. It was first prepared by DAVY (1811), who inclined to the view that it was a definite compound, but PÉBAL (1875) proved that it was a mixture.

Oxyacids of chlorine.

Chlorine forms four oxyacids; anhydrides are known of only two of them.

Acid.	*Acid Anhydride.*
Hypochlorous acid, $HClO$.	Chlorine monoxide, Cl_2O.
Chlorous acid, $HClO_2$.	Unknown
Chloric acid, $HClO_3$.	Unknown
Perchloric acid, $HClO_4$.	Chlorine heptoxide, Cl_2O_7.

(ClO_2 is the "mixed" anhydride.)

Hypochlorous acid, $HClO$.—The pure acid has not been isolated; an aqueous solution of it is made by dissolving chlorine monoxide in water—

$$Cl_2O + H_2O \rightleftharpoons 2HClO.$$

On attempting to concentrate the solution, decomposition occurs, the hypochlorous acid splitting up into oxygen and hydrochloric acid—

$$2HClO = 2HCl + O_2.$$

Hypochlorous acid in aqueous solution may also be made by treating bleaching-powder cautiously with the calculated quantity of dilute nitric acid and distilling under reduced pressure.

The nearest approach to pure hypochlorous acid yet recorded is that of GOLDSCHMIDT, who prepared a 25 per cent. solution by the distillation under reduced pressure of a mixture of chlorine hydrate and yellow mercuric oxide.

An aqueous solution of hypochlorous acid is yellow in colour and has the smell of chlorine monoxide. It is unstable, readily giving off oxygen, according to the equation given

above. Hypochlorous acid is a weak, monobasic acid, but is a powerful oxidizing agent owing to the readiness with which it loses oxygen. It probably has the constitution represented by the formula H—O—Cl.

The salts of hypochlorous acid, the *hypochlorites*, are very important since they are largely used in the bleaching industry. The solution of potassium chloride and hypochlorite made by passing chlorine into a cold dilute solution of caustic potash—

$$2KOH + Cl_2 = KCl + KClO + H_2O,$$

is called *eau de Javelle*, and has been in use as a bleaching agent since 1789. The corresponding solution made from caustic soda was first used in 1820 and was called *eau de Labarraque*. The bleaching action of hypochlorites in the presence of dilute acids is an oxidation process, as mentioned previously (p. 504).

Like the acid itself, hypochlorites slowly decompose in aqueous solution, with liberation of oxygen; the decomposition is hastened by the addition of cobalt or nickel salts as catalysts—

$$2NaClO = 2NaCl + O_2,$$

or, to show the reaction more generally—

$$2ClO' = 2Cl' + O_2.$$

An important derivative of hypochlorous acid is bleaching powder, $Ca\langle^{OCl}_{Cl}$. This is described in the section on calcium (p. 248). It can be regarded as a "mixed salt," half a chloride and half a hypochlorite, as shown by the formula.

Hypochlorites are difficult to prepare in the solid state, as they are so unstable; however *sodium hypochlorite*, $NaOCl.6H_2O$, was prepared in 1898 by MUSPRATT and SMITH, and *calcium hypochlorite*, $Ca(OCl)_2.4H_2O$, by KINGZETT in 1875.

They are white or slightly yellow crystalline solids.

Chlorous acid, $HClO_2$.—This acid, like hypochlorous acid,

is known only in solution. Mixed with chloric acid, it is formed when chlorine peroxide is dissolved in water—

$$2ClO_2 + H_2O = HClO_3 + HClO_2.$$

The *chlorites* of certain metals have been isolated; they are generally colourless, deliquescent, crystalline solids readily soluble in water. Sodium and potassium chlorites will bleach vegetable colours. The silver and lead salts are yellow, and only sparingly soluble. They explode when heated. A mixture of chlorite and chlorate is formed when chlorine peroxide is dissolved in a solution of caustic alkali (p. 513).

Chloric acid, $HClO_3$, can be obtained in aqueous solution by addition of the calculated weight of sulphuric acid to a solution of barium chlorate, and removing the precipitated barium sulphate—

$$Ba(ClO_3)_2 + H_2SO_4 = BaSO_4 + 2HClO_3.$$

By careful evaporation of the solution under reduced pressure it may be concentrated to a colourless syrupy liquid containing 30 to 40 per cent. chloric acid. The pure acid has not been prepared, since on further evaporation of the solution decomposition occurs, perchloric acid, oxygen and chlorine being formed—

$$8HClO_3 = 4HClO_4 + 3O_2 + 2Cl_2 + 2H_2O.$$

The aqueous solution of the acid is a powerful oxidizing agent; it sets fire to paper and many other organic substances, and converts phosphorus into phosphoric acid, sulphur into sulphuric acid, etc. The constitution of the acid is still unsettled; it may be HO—Cl$\begin{<}{O \atop O}$, since other compounds are known in which chlorine is tervalent.

The salts of chloric acid, the *chlorates*, are stable compounds, some of them being of considerable importance both in the laboratory and in industry.

Potassium chlorate, $KClO_3$, is described in the chapter on potassium, p. 213.

Barium chlorate, $Ba(ClO_3)_2$, and *calcium chlorate*, $Ca(ClO_3)_2$,

are white crystalline solids made by passing chlorine into a hot paste of the metallic hydroxide—

$$6Ca(OH)_2 + 6Cl_2 = 5CaCl_2 + Ca(ClO_3)_2 + 6H_2O.$$

The chlorate may be separated from the chloride by fractional crystallization; the chlorate, being much the less soluble salt, separates out first.

Chlorates decompose on heating, into the corresponding chlorides and oxygen—

$$Ba(ClO_3)_2 = BaCl_2 + 3O_2.$$
$$2KClO_3 = 2KCl + 3O_2.$$

They are good oxidizing agents, and are used commercially in the match industry, for making fireworks, and in the manufacture of dyes. They are manufactured chiefly by electrical processes (p. 213).

Perchloric acid, $HClO_4$.—This is the only oxyacid of chlorine which has been prepared in the pure state. It is made by distilling under reduced pressure a mixture of potassium perchlorate and concentrated sulphuric acid—

$$KClO_4 + H_2SO_4 = KHSO_4 + HClO_4.$$

The distillate of perchloric acid is purified by redistillation at a pressure of about 50–60 mm.

Perchloric acid is a colourless oily liquid that fumes strongly in moist air and is very hygroscopic. It readily dissolves in water, with evolution of heat; the solution is stable, but the anhydrous acid explodes if heated sufficiently or if dropped upon organic material such as wood or charcoal. It is an oxidizing agent, but not so active as chloric acid in this respect.

The *perchlorates* are well known and are quite stable. They may be made by neutralizing the acid with the hydroxides or oxides of the metals, or by double decomposition of barium perchlorate with a metallic sulphate, etc., and also electrolytically. *Potassium perchlorate*, $KClO_4$, is formed by careful heating of potassium chlorate. The chlorate is heated until it melts; shortly afterwards oxygen begins to come off, but after a time the evolution of gas ceases and the liquid becomes viscous. At this stage the fused mass consists of a mixture

of potassium perchlorate and chloride, which may be separated from one another by fractional crystallization—

$$4KClO_3 = 3KClO_4 + KCl$$

(or, since oxygen is evolved, $2KClO_3 = KClO_4 + KCl + O_2$).

Perchloric anhydride is *chlorine heptoxide*, p. 513.

Bromine

Group in Periodic System: VII; ***Symbol:*** Br; ***Valency:*** 1; ***Atomicity of Vapour:*** 2; ***Atomic Weight:*** 79·92; ***Boiling Point:*** 59°; ***Specific Gravity:*** 3·19.

History.—Bromine was first made in a salt factory in Germany, about the year 1820, and sent to the great German chemist Liebig for examination; he thought, however, that it was iodine chloride, and did not examine it very closely. The honour of the discovery of bromine must therefore be given to Balard, who obtained it in 1826 from the mother-liquors ("bittern") left after the recrystallization of salt from sea-water. He passed chlorine through these mother-liquors (which contain the bromides of sodium, potassium and magnesium) and noticed that a yellowish brown colouration was produced. Further experiments enabled him to isolate the coloured substance, which he obtained in the form of a dark brown liquid with a pungent smell. Balard, like Liebig, at first regarded it as iodine chloride, but failing to detect any iodine in it, he assumed it to be an element and called it originally *muride* but afterwards *bromine* (Greek, βρῶμος, a stench).

Occurrence.—Bromine does not occur free in nature. It is found in the form of *bromides*, chiefly those of sodium, potassium, and magnesium. These are contained in sea-water and in certain mineral springs, and occur also in the solid state in the *Stassfurt* deposits in North Germany.

Preparation.—Bromine may be prepared in the laboratory by heating a mixture of potassium bromide, manganese dioxide and sulphuric acid in a retort; bromine distils over and is collected in a cooled receiver—

$$2KBr + MnO_2 + 3H_2SO_4 = 2KHSO_4 + MnSO_4 + 2H_2O + Br_2.$$

Other bromides may be used, but the potassium salt is the one usually met with.

On the commercial scale, bromine is prepared by the action of chlorine upon the mother-liquors obtained in the recrystallization of the salts of the Stassfurt deposits. Since the war cut off the supplies of bromine from Germany, the manufacture of bromine in America (Ohio and the Saginaw Valley, Michigan) received a great impetus, and much bromine is now obtained commercially from the mother-liquors from the American springs. Bromine has also recently been extracted from sea-water on a commercially profitable scale.

The Stassfurt and Ohio mother-liquors contain the bromides of potassium and magnesium. The hot mother-liquors are

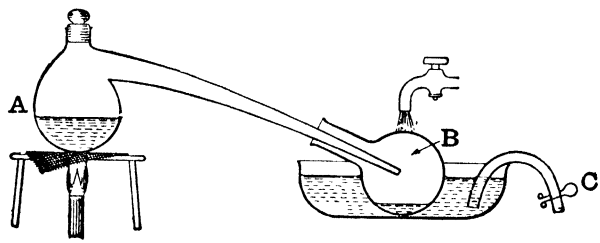


FIG. 113.—Preparation of Bromine.

allowed to flow down a tower filled with earthenware balls; here they meet an upward stream of chlorine, and bromine is liberated—$2KBr + Cl_2 = 2KCl + Br_2$.

The bromine vapour and excess of chlorine escape from the top of the tower and are passed through a spiral cooling-tube surrounded by water, where most of the bromine condenses and may be collected in a receiver. Any uncondensed bromine is trapped by passing through a small tower containing wet iron filings, where iron bromide is formed; this is used for making potassium bromide (p. 525). The spent mother-liquors that leave the bottom of the main tower carry a little of the chlorine and bromine with them; they are therefore allowed to circulate over sandstone shelves in a small chamber through which steam is blown. The chlorine and bromine are thus blown out of the solution and, mixing

with the main stream of chlorine from the chlorine generator, pass up the tower again.

The chief impurities in the bromine obtained in the commercial process are chlorine and water. The water may be removed by shaking with concentrated sulphuric acid ; if the dry bromine is then distilled over potassium bromide or iron bromide it is freed from chlorine, which replaces the bromine

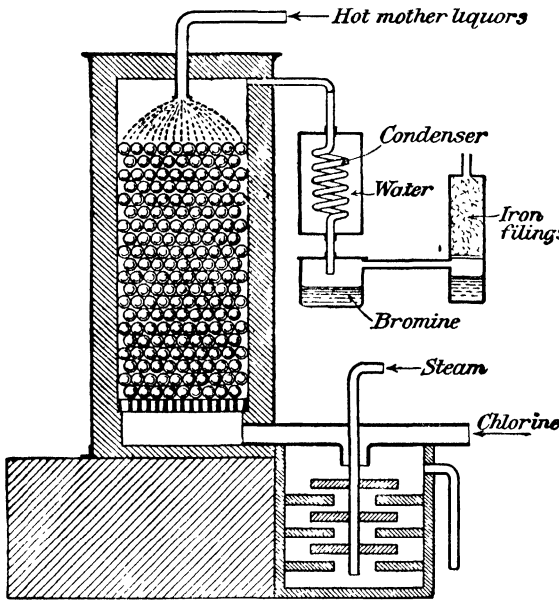


Fig. 114.—Manufacture of Bromine.

in the bromide added and is left behind as potassium or iron chloride—

$$2KBr + Cl_2 = 2KCl + Br_2.$$

Iodine, which sometimes occurs as an impurity, is removed by addition of a little starch paste, which absorbs it (p. 531).

The purest bromine hitherto obtained was made by Scott in 1913. [See Scott, *Trans. Chem. Soc.*, **131**, 847, *1913*.]

Properties.—Bromine is a reddish brown, heavy, volatile liquid, which boils at 59°, freezes at —7·3, and has a specific gravity of 3·19. It readily passes into vapour at ordinary temperatures; the vapour is red in colour and very irritating to the mucous membrane and the eyes. Liquid bromine produces yellow burns when dropped on the skin. The vapour density of bromine vapour shows that at first the molecules of the gas are Br_2 (V.D. = 79·92); as the temperature rises, however, partial dissociation occurs.

$$Br_2 \rightleftharpoons Br + Br.$$

Bromine dissolves slightly in water; the solution is called bromine-water, and on cooling to 0° deposits red crystals of bromine hydrate, $Br_2.8H_2O$. (Compare *chlorine hydrate*, p. 504.) Bromine is much more soluble in organic solvents such as chloroform, ether, carbon disulphide and benzene. It is absorbed by the siliceous earth called *kieselguhr*; the product gradually gives off bromine on exposure to air and is sold as a disinfectant under the (incorrect) name of *bromum solidificatum*, or solidified bromine.

In its chemical properties bromine closely resembles chlorine; it combines directly with *hydrogen* (to form hydrobromic acid gas), with *metals* (to form salts, the *bromides*—"halogen"), and with *phosphorus* (to form phosphorus tri- and penta-bromides). The reaction between metallic potassium and liquid bromine is explosive.

Owing to its affinity for hydrogen, bromine is an *oxidizing agent*, though less powerful than chlorine. It will bleach, though not very energetically, and turns starch-solution yellow (distinction from *iodine*, p. 531). Ordinary bromine consists of 2 isotopes, atomic weights 79 and 81.

The *atomic weight* of ordinary bromine is 79·92; it was determined by STAS by converting a known weight of pure silver into silver bromide, which was weighed, and by GUYE and also by MOLES, from the vapour density of pure hydrobromic acid gas.

Bromine is required in large quantities (several million pounds per annum) for addition—in the form of ethylene dibromide, $C_2H_4Br_2$—to "ethyl petrol." About 2 c.c.

ethylene dibromide is added to every gallon of petrol, its function being to provide bromine to convert the lead of the lead tetraethyl (p. 330) into lead bromide. The lead would otherwise foul the sparking-plugs.

COMPOUNDS OF BROMINE.

Hydrogen bromide, or Hydrobromic acid, HBr.—When hydrogen and bromine vapour are heated together in equal volumes, combination takes place with measurable velocity at about 250°, and at higher temperatures proceeds much more quickly and practically completely. At still higher temperatures, however, the hydrogen bromide dissociates again—

$$H_2 + Br_2 \rightleftharpoons 2HBr.$$

The best yield of hydrobromic acid, by the *synthetic* method, is therefore obtained by passing the mixture of

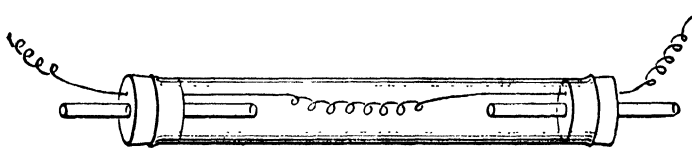


FIG. 115.—Preparation of Hydrobromic Acid.

hydrogen and bromine vapour over a catalyst heated to a moderately high temperature; e.g. by passing the mixture through a tube containing a platinum spiral electrically heated.

Hydrobromic acid *cannot* be obtained pure by heating sulphuric acid with a bromide (cf. preparation of hydrochloric acid), since it is a mild reducing agent, and on liberation reduces the hot sulphuric acid to sulphur dioxide, being itself oxidized to bromine—

i. $KBr + H_2SO_4 = KHSO_4 + HBr.$

ii. $H_2SO_4 + 2HBr = 2H_2O + SO_2 + Br_2,$

or $2KBr + 3H_2SO_4 = 2KHSO_4 + 2H_2O + SO_2 + Br_2.$

Some of the hydrobromic acid, it is true, escapes decomposition, but the mixture of gases evolved, hydrobromic acid,

sulphur dioxide and bromine, cannot be conveniently purified.

Hydrobromic acid is therefore generally prepared by the action of *water on phosphorus tribromide*, PBr_3—

$$PBr_3 + 3H_2O = \underset{\text{Phosphorous acid.}}{H_3PO_3} + 3HBr.$$

Similar reactions with the trichloride and tri-iodide of

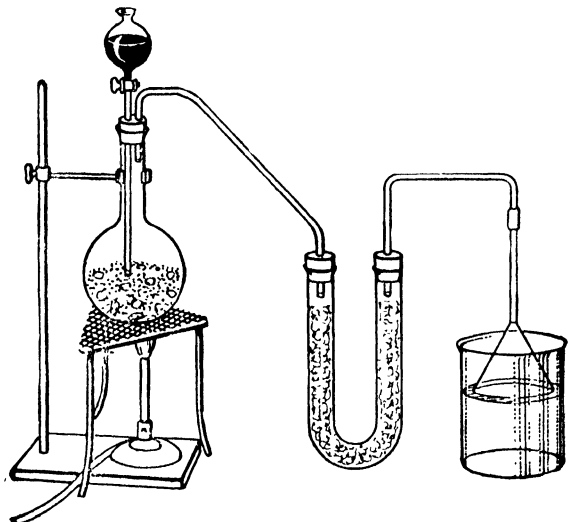


FIG. 116.—Preparation of Hydrobromic Acid.

phosphorus give hydrochloric acid and hydriodic acid; hydriodic acid indeed is prepared in this way, but the method is not used for hydrochloric acid since simpler ones are available.

Red phosphorus, water, and sand are stirred up together into a thin paste and put in a flask fitted with a cork carrying a dropping-funnel and delivery-tube. The delivery-tube is connected to a U-tube containing bits of broken glass smeared with a paste of red phosphorus and water. Bromine is placed in the funnel and allowed to run in slowly. As each drop

touches the phosphorus a bright flash occurs, and hydrobromic acid gas is given off. The bromine combines with the phosphorus to form phosphorus tribromide, and this is then decomposed by the water present, according to the equation given above.

Owing to the volatile nature of bromine, the gas that comes off from the delivery tube carries with it some bromine vapour; this is removed in the U-tube, where it is converted into hydrobromic acid by the water and phosphorus. The U-tube is, in fact, a secondary apparatus for producing hydrobromic acid.

The hydrobromic acid gas is then collected by downward displacement or over mercury, or if a solution of the hydrobromic acid is required, as in Fig. 109.

If larger quantities of the gas are required, it is better to use ERDMANN'S method, which is very simple to carry out. It consists in the addition of bromine to benzene (C_6H_6) in the presence of a catalyst, such as reduced iron or aluminium powder, when the following reaction occurs—

$$C_6H_6 + 2Br_2 = \underset{\text{Dibromobenzene.}}{C_6H_4Br_2} + 2HBr.$$

The benzene (which should be dry) is placed in a flask and a little reduced iron is added. Bromine is then gradually run in, when the action starts at once; it may be necessary to cool the flask, as the reaction is vigorous. The hydrobromic acid gas that is evolved carries over benzene vapour and bromine vapour with it; it is freed from the latter by passing through a U-tube containing ferric bromide, $FeBr_3$, and from the former by anthracene contained in a second U-tube.

The *aqueous solution* of hydrobromic acid may be made by dissolving the gas in water (taking the precautions usual in the case of a very soluble gas), or directly in one of the following ways—

(i) By passing sulphuretted hydrogen through bromine-water, and filtering off the precipitated sulphur—

$$H_2S + Br_2 = 2HBr + S.$$

(ii) By passing sulphur dioxide through bromine-water, or bromine covered by a layer of bromine-water—

$$SO_2 + Br_2 + 2H_2O = H_2SO_4 + 2HBr.$$

From the mixture of dilute sulphuric and hydrobromic acids obtained in this way, dilute hydrobromic acid may be made by distillation.

Properties.—Hydrobromic acid is a heavy colourless acid gas that fumes in moist air, dissolves readily in water giving a strongly acid solution, and in its general properties closely resembles hydrochloric acid. It can be condensed to a colourless liquid boiling at — 69° and freezing to a colourless crystalline solid at —86°.

The aqueous solution is highly ionized—

$$HBr \rightleftharpoons H^{\cdot} + Br'.$$

Hydrobromic acid, like hydrochloric acid (p. 507), forms a *constant-boiling mixture* with water. This at atmospheric pressure boils at 126° and contains 47·8 per cent. HBr by weight. In aqueous solution hydrobromic acid slowly decomposes on exposure to air and light, the solution turning yellow owing to liberation of bromine by oxidation—

$$O_2 + 4HBr = 2H_2O + 2Br_2.$$

A convenient way of obtaining the gas from the aqueous solution is to add an excess of anhydrous calcium bromide, or to drop the solution from a dropping funnel on to the anhydrous salt.

The salts of hydrobromic acid are called *bromides*. The most important is *potassium bromide*, KBr, which finds many applications in the laboratory, in medicine, and in photography. It is made from the iron bromide obtained in the manufacture of bromine (p. 519) by dissolving it in water and adding potassium carbonate solution; an iron hydroxide is precipitated, carbon dioxide is evolved, and a solution of potassium bromide is left from which the salt may be crystallized on evaporation.

$$2FeBr_3 + 3K_2CO_3 + 3H_2O = 2Fe(OH)_3 + 6KBr + 3CO_2.$$

As the iron bromide from the bromine works does not yield

sufficient potassium bromide to satisfy the demand, more is made by adding bromine to iron filings and is then converted into potassium bromide by the method described.

Potassium bromide may also be made by dissolving bromine in concentrated caustic potash solution, evaporating to dryness, and heating the residual mass of bromide and bromate with charcoal, or even alone—

$$3Br_2 + 6KOH = 5KBr + KBrO_3 + 3H_2O.$$
$$5KBr + KBrO_3 = 6KBr + \text{oxygen},$$

or, with charcoal,

$$5KBr + KBrO_3 + 3C = 6KBr + 3CO.$$

It is a white crystalline solid, soluble in water and is used in medicine as a sedative or sleeping-draught.

All metallic bromides are soluble in water except those of silver, lead and mercury (*ous*). The formation of pale-yellow insoluble silver bromide is used as a test for a bromide in qualitative analysis. Silver bromide is used in photography (p. 233).

Oxides of Bromine are unknown.

Oxyacids of Bromine.—Hypobromous acid, HBrO, and bromic acid, $HBrO_3$, are known, and there is some evidence for the existence of bromous acid, $HBrO_2$.

Hypobromous acid, HBrO.—BALARD prepared an aqueous solution of hypobromous acid by shaking bromine-water with yellow mercuric oxide. By further addition of bromine and mercuric oxide a solution can be obtained containing 6 to 7 per cent. of hypobromous acid. Distillation of this liquid under reduced pressure yields a pale yellow dilute solution of the acid.

$$2Br_2 + 2HgO + H_2O = 2HBrO + HgO.HgBr_2.$$

The pure acid has not been isolated; attempts at further concentration of the solution cause the acid to decompose into water, bromine, and oxygen.

Hypobromites, mixed with bromides, are formed when bromine is dissolved in cold dilute solutions of caustic alkalis—

$$2KOH + Br_2 = KBr + KBrO + H_2O.$$

They are very similar to the hypochlorites, but are even less stable; they have bleaching properties, and will liberate nitrogen from urea, for the estimation of which they are often employed.

Bromous acid, $HBrO_2$.—According to RICHARDS (1906) a solution of bromous acid is formed when a large excess of bromine water is added to silver nitrate solution.

Bromic acid, $HBrO_3$.—This acid is known only in dilute solution and in the form of its salts, the bromates. The aqueous solution of the acid has been prepared in many ways, e.g. by the action of bromine on a suspension of silver bromate in hot water (KÄMMERER, 1869)—

$$5AgBrO_3 + 3Br_2 + 3H_2O = 5AgBr\downarrow + 6HBrO_3,$$

or by addition of dilute sulphuric acid to a solution of barium bromate (BALARD, 1826)—

$$Ba(BrO_3)_2 + H_2SO_4 = BaSO_4\downarrow + 2HBrO_3.$$

The aqueous solution can be concentrated by distillation under reduced pressure to a syrupy colourless liquid containing 50·6 per cent. $HBrO_3$. Further concentration brings about decomposition—

$$4HBrO_3 = 2H_2O + 5O_2 + 2Br_2.$$

Bromic acid is a strong acid and a powerful oxidizing agent; thus it oxidizes hydrobromic acid to bromine—

$$HBrO_3 + 5HBr = 3H_2O + Br_2,$$

nitrous acid to nitric acid—

$$5HNO_2 + 2HBrO_3 = 5HNO_3 + H_2O + Br_2,$$

and sulphur dioxide solution to sulphuric acid—

$$2HBrO_3 + 5H_2SO_3 = Br_2 + H_2O + 5H_2SO_4.$$

The *bromates* show close similarity to the chlorates. A mixture of potassium bromide and bromate is made by adding bromine to hot concentrated caustic potash solution—

$$3Br_2 + 6KOH = 5KBr + KBrO_3 + 3H_2O.$$

The silver salt, being insoluble, may be prepared from a

solution of the potassium salt by precipitation. Bromates yield bromides and oxygen on heating.

Perbromic acid and *perbromates* do not exist.

IODINE

Group in Periodic System: VII; *Symbol:* I; *Valency:* 1; *Atomicity of Vapour:* 2; *Atomic Weight:* 126·93; *Melting Point:* 116·1°; *Specific Gravity:* 4·93.

History.—In 1812 a French saltpetre manufacturer, COURTOIS, found that on adding concentrated sulphuric acid to the mother-liquor of the sodium carbonate extracted from the ashes of seaweed, a black powder was precipitated, which on heating was converted into a violet vapour. Courtois sent some of his new substance to GAY-LUSSAC, who made a thorough investigation of it and showed that it was an element similar in many respects to chlorine. He called it *iodine*, from the violet colour of its vapour (Greek, *ἰοειδής*), and succeeded in preparing hydriodic acid, HI, from it. SIR HUMPHRY DAVY, who was passing through Paris at the time, also made investigations on the new element, a specimen of which was given to him by AMPÈRE, and confirmed Gay-Lussac's results.

[For an interesting account of the history of iodine, see *Chemical News*, **99**, 193 (1909).]

Occurrence.—Iodine is not found free in nature. It is, however, widely distributed (although in small quantities) in the form of *iodides*, and to a less extent, *iodates*. It occurs as *sodium iodate*, $NaIO_3$, mixed with sodium nitrate, in Chile saltpetre or *caliche* (about 0·3 per cent. $NaIO_3$), and as the iodides of sodium, magnesium and potassium in sea-water. It is an interesting fact that seaweeds have the power of absorbing iodine from sea-water; thus while the percentage of iodine in the sea is 0·001, the percentage in the dry matter of *Laminaria*, a deep-sea seaweed, is nearly 0·5. Sponges seem to possess this power to an astonishing degree; according to HUNDESHAGEN, tropical sponges may contain as much as 14 per cent. of iodine!

An organic compound of iodine is a constant constituent of the important *thyroid gland* in man (p. 531).

Extraction.—Iodine is obtained both from seaweeds and from caliche.

(i) *Extraction from Seaweed.*—The seaweed is dried during the summer months and then burnt, forming an ash known as *kelp* in this country and *varech* in Normandy. The kelp contains the sulphates, carbonates, chlorides, bromides and iodides of sodium and potassium, mixed with carbon. It is stirred up with hot water in iron pots, and the insoluble matter allowed to settle. The solution is then run off and

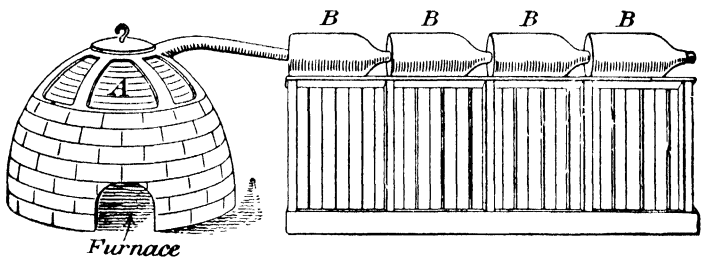


FIG. 117.—Manufacture of Iodine from Kelp.
A. Iron Pot. *BB*. Udells.

concentrated, when the sulphates, carbonates and chlorides separate out, being less soluble, while the bromides and iodides are left in the mother-liquor. (The proportion of bromides to iodides is small.)

The mother-liquor is mixed with manganese dioxide and concentrated sulphuric acid and heated in cast-iron pots, when the iodine distils over and is collected in specially-shaped condensers called *aludels* or *udells*. Towards the end of the reaction, bromine comes over, from the bromides present. It is collected, if present in sufficient quantity, otherwise it is allowed to go to waste.

The iodine obtained in this way is washed, dried, and purified by sublimation over potassium iodide.

(ii) *Extraction from Caliche.*—The crude sodium nitrate is

recrystallized from water, when the sodium iodate, $NaIO_3$, is left in the *aqua vieja* or mother-liquor. This is run into wooden or lead-lined vats and mixed with the calculated weight of sodium bisulphite, $NaHSO_3$, to precipitate all the iodine, according to the equations—

$$\text{(i)}\quad NaHSO_3 + NaIO_3 = Na_2SO_3 + HIO_3.$$

Here the *acid* sodium sulphite liberates *iodic acid* from some of the iodate.

$$\text{(ii)}\quad 3NaHSO_3 + HIO_3 = 3NaHSO_4 + HI.$$

The *reducing* properties of the sulphite convert iodic acid to hydriodic acid.

$$\text{(iii)}\quad 5HI + HIO_3 = 3H_2O + 3I_2\downarrow.$$

Iodic and hydriodic acids cannot exist together in solution. They immediately react to form iodine and water.

The black precipitate of iodine is filtered off, and purified as above, while the remaining liquid is used over again for the recrystallization of a fresh lot of caliche.

Modifications of this process are also employed in certain districts in South America.

In the laboratory iodine is generally made by heating a mixture of manganese dioxide and sulphuric acid with potassium iodide, in a retort. Iodine sublimes over into the neck of the retort.

$$2KI + MnO_2 + 3H_2SO_4 = 2KHSO_4 + MnSO_4 + 2H_2O + I_2.$$

Properties.—Iodine is a lustrous black crystalline solid, which sublimes if quickly heated, but if slowly heated melts at 116°. The liquid boils at 184° to a deep purple vapour, whose density at the boiling-point corresponds to the formula I_2. At 600° dissociation begins, and at 1,600° is complete, the molecules of the vapour then all being monatomic—

$$I_2 \rightleftharpoons I + I.$$

Iodine is only slightly soluble in water, but is much more soluble in organic solvents. It is also very soluble in *potassium iodide* solution; a certain amount of combination occurs, potassium tri-iodide being formed—

$$KI + I_2 \rightleftharpoons KI_3.$$

This substance has been isolated in the form of black crystals. It loses a molecule of iodine so readily in aqueous solution that a solution of iodine in potassium iodide may be regarded in volumetric analysis as containing as much *free* iodine as was dissolved. This fact is very convenient, since concentrated aqueous solutions of free iodine cannot be prepared in the usual way owing to the small solubility of the element.

Iodine has the usual halogen properties, but is less reactive than chlorine and bromine; however, a mixture of yellow phosphorus and iodine takes fire spontaneously, forming iodides of phosphorus. Iodine will also combine directly with many metals, forming salts, the *iodides*.

The most characteristic property of iodine is perhaps the reaction with starch. When iodine is added to starch solution a deep blue colour is produced; this reaction is so sensitive that 0·00001 grams of iodine in a litre of water may be detected by it. On heating, the blue colour disappears, but it reappears on cooling. It is permanently destroyed by addition of ammonia. The composition of the blue substance is unknown; it is probably an "adsorption compound" of iodine in starch, and is almost certainly not a true chemical compound.

Iodine is essential to the well-being of the human body. Its absence may lead to goitre or cretinism. Though normally supplied to the body in certain foods, e.g. spinach and lettuce among vegetables and butter and milk among animal foods, it is well to add small quantities of sodium iodide to table salt. Many salt manufacturers now make this addition as a matter of course. The body of a normal adult contains about 20 milligrams of iodine, approximately half the total quantity being present as the compound *thyroxin*, in the thyroid gland.

Compounds of Iodine.

Hydriodic acid, or Hydrogen iodide, HI.—If a mixture of hydrogen and iodine vapour is heated, partial combination takes place and an equilibrium between hydrogen, iodine, and hydrogen iodide is set up—

$$H_2 + I_2 \rightleftharpoons 2HI.$$

At 448°, the mixture contains 75 per cent. HI, but the rate of formation at this temperature is so slow that it is best to add a catalyst, such as platinum black, to accelerate the change.

Hydriodic acid gas, however, is generally prepared by the action of water upon phosphorus iodide—

$$PI_3 + 3H_2O = H_3PO_3 + 3HI.$$

In practice, an apparatus similar to that employed for the preparation of hydrobromic acid (p. 523) is used. Water is placed in the dropping-funnel and a mixture of red phosphorus and iodine in the flask. On adding the water, drop by drop, hydriodic acid gas comes off. Since the actual formation of phosphorus iodide in this reaction has not been observed, it may be better to write the equation as—

$$2P + 3I_2 + 6H_2O = 6HI + 2H_3PO_3.$$

As iodine is not very volatile at ordinary temperature, there is no necessity to have the U-tube on the delivery tube.

The hydriodic acid gas that comes off is collected by downward displacement (*not* over mercury, which it attacks).

An aqueous solution of hydriodic acid may be made by dissolving the gas in water (precautions for very soluble gas), or by passing sulphuretted hydrogen through iodine suspended in water—

$$I_2 + H_2S = 2HI + S.$$

(Cf. $Br_2 + H_2S = 2HBr + S$, and $Cl_2 + H_2S = 2HCl + S$.)

Hydriodic acid cannot be made by the action of concentrated sulphuric acid upon potassium iodide, since it is a reducing agent, and reduces the acid to sulphur, sulphuretted hydrogen and sulphur dioxide, being itself oxidized to iodine.

Properties.—Hydrogen iodide is a colourless heavy acid gas, fuming in moist air, and readily soluble in water, giving a strongly acid solution. It can be condensed to a colourless liquid, boiling at —35·5° and freezing at —51° to a colourless crystalline solid.

In general chemical properties it closely resembles hydrochloric and hydrobromic acids. Unlike them, however, it is

an *endothermic* substance and a powerful reducing agent; hydrochloric acid and hydrobromic acid are both strongly exothermic, and are not reducing agents under ordinary circumstances, although hydrobromic acid may sometimes show reducing powers (p. 522).

Like the other halogen acids, hydriodic acid forms a *constant-boiling mixture*, that formed at atmospheric pressure boiling at 127° and containing 57 per cent. HI. Aqueous hydriodic acid is used in organic chemistry as a reducing agent. When freshly prepared it is colourless, but rapidly goes brown owing to oxidation of the acid with liberation of iodine—

$$2HI + \text{oxygen} = H_2O + I_2.$$

The *iodides* are very similar to the chlorides and bromides. The formation of the insoluble yellow *silver* salt is used as a test for iodides in solution.

Oxides of Iodine.

Iodine forms three oxides—iodine dioxide, IO_2, iodine pentoxide, I_2O_5, and "iodine iodate," I_4O_2.

Iodine dioxide, IO_2 (or I_2O_4), was first prepared by MILLON (1844). It may be made by heating sulphuric acid with iodic acid, or by the action of concentrated nitric acid upon dry powdered iodine in the cold. It is a yellow crystalline solid that may be purified by recrystallization from concentrated sulphuric acid. It reacts with water to form iodic acid (HIO_3) and iodine—

$$5I_2O_4 + 4H_2O = 8HIO_3 + I_2.$$

Iodine dioxide, unlike chlorine dioxide, is not explosive.

Iodine pentoxide, I_2O_5, is the anhydride of iodic acid, from which it may be made by the action of gentle heat (220°)—

$$2HIO_3 \rightleftharpoons H_2O + I_2O_5.$$

It is a white crystalline solid that dissolves in water to form iodic acid. When exposed to a dull red heat it splits up into its elements. It is a strong oxidizing agent, converting carbon monoxide into the dioxide even at ordinary tempera-

tures, while on heating it will convert sulphur dioxide into the trioxide—

$$5CO + I_2O_5 = 5CO_2 + I_2.$$
$$5SO_2 + I_2O_5 = 5SO_3 + I_2.$$

Oxyacids of Iodine.—Iodine forms three oxyacids—
Hypoiodous acid, HIO.
Iodic acid, HIO_3.
Periodic acid, HIO_4 (or H_5IO_6, see below).

Hypoiodous acid, HIO.—When iodine is added to dilute caustic potash solution it forms a mixture of potassium iodide and potassium hypoiodite—

$$2KOH + I_2 = KI + KIO + H_2O.$$

Hypoiodous acid, however, is such a weak acid that unless a large excess of alkali is present the potassium hypoiodite is hydrolysed into *hypoiodous acid itself* and caustic potash—

$$KIO + H_2O \rightleftharpoons HIO + KOH.$$

A solution of hypoiodous acid may also be obtained by shaking a solution of iodine in alcohol with yellow mercuric oxide. (Compare hypochlorous and hypobromous acids, pp. 514 and 526.)

The free acid has not been isolated. The aqueous solution is yellow in colour and has oxidizing and bleaching properties.

Iodic acid, HIO_3, is made by heating iodine with a large excess of fuming nitric acid. The reaction is very slow, but is greatly accelerated if a stream of oxygen is bubbled through the reacting mixture.

Iodic acid is a white deliquescent crystalline solid. It was discovered by GAY-LUSSAC, who made it by passing a stream of chlorine through a suspension of iodine in water—

$$I_2 + 5Cl_2 + 6H_2O = 2HIO_3 + 10HCl.$$

It is a strong oxidizing agent, and also a strong acid, i.e. in aqueous solution is is highly ionized. Cryoscopic experiments on concentrated solutions of the acid indicate that it may have the double formula $(HIO_3)_2$ or $H_2I_2O_6$; the exist-

ence of *acid iodates* is additional evidence for the double formula.

Iodic acid and hydriodic acid react together in solution, forming iodine and water (see p. 530)—

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

The chief *iodate* is that of potassium, which is made by dissolving iodine in a hot concentrated solution of caustic potash—

$$3I_2 + 6KOH = 5KI + KIO_3 + 3H_2O.$$

It is a white crystalline solid, soluble in water, and splitting up into potassium iodide and oxygen on heating. (Cf. potassium chlorate and bromate.)

$$2KIO_3 = 2KI + 3O_2.$$

Periodic acid.—Several periodic acids are known; the chief are *meta-periodic acid*, HIO_4, and *para-periodic acid*, H_5IO_6. The barium salt of the *para* acid is formed when barium iodate is carefully heated—

$$5Ba(IO_3)_2 = Ba_5(IO_6)_2 + 4I_2 + 9O_2.$$

The potassium salt of the *meta* acid can be obtained by electrolysis of an alkaline solution of potassium iodate.

Free para-periodic acid may be made from the barium salt by addition of sulphuric acid—

$$Ba_5(IO_6)_2 + 5H_2SO_4 = 5BaSO_4 \downarrow + 2H_5IO_6.$$

Evaporation of the filtered solution produces crystals of the para-acid. On heating para-periodic acid to 100° at low pressures, it yields the meta-acid—

$$H_5IO_6 = HIO_4 + 2H_2O.$$

QUESTIONS

1. Show that fluorine, chlorine, bromine and iodine are justifiably grouped together.
2. Describe the preparation and properties of (*a*) fluorine, (*b*) hydrofluoric acid.
3. Give an account of the history of chlorine.
4. How is chlorine prepared in the laboratory? What are its properties?
5. Describe the manufacture of chlorine.

6. What is the action of chlorine upon alkalis ?
7. Write an account of the oxides and oxyacids of chlorine.
8. How is bromine manufactured ? What are its properties ?
9. Describe the preparation and properties of hydrobromic acid gas.
10. How does iodine occur in nature ? How is it manufactured ?
11. Compare and contrast the behaviour of sulphuric acid with (*a*) potassium chloride, (*b*) potassium bromide, and (*c*) potassium iodide.
12. How is iodic acid made ? What are its properties ?
13. Discuss the valency of the halogens.

CHAPTER XXIX

GROUP VII, Sub-group A

MANGANESE, MASURIUM (?), RHENIUM

Until 1925, manganese was an orphan element, occupying a position of splendid isolation in the Periodic System, and although it was forced into Group VII with the halogens it must have felt extremely uncomfortable among those fiery and excitable neighbours. However, in 1925, the existence of two new elements, *masurium* and *rhenium*, was inferred spectroscopically, and these metals would complete Group VII, sub-group A. There is still doubt as to the identity of masurium, but rhenium has now been isolated and its atomic weight (188·7) determined, while certain of its compounds have been carefully studied. Potassium per-rhenate, $KReO_4$, is already included in the manufacturer's lists. Rhenium occurs in certain tantalum and platinum minerals.

Manganese

Group in Periodic System: VII; *Symbol:* Mn; *Valency:* 2, 3, 4, 7; *Atomic Weight:* 54·93; *Melting Point:* 1,260°; *Specific Gravity:* 7·2–8·0.

History.—The ancient chemists confused pyrolusite, MnO_2, with magnetite, Fe_3O_4, but Pliny recognized it as a distinct substance and called it *magnesia nigra*. It was well known to the Arab chemists of the Middle Ages, who carefully distinguished between it and magnetite and *magnesia alba* (MgO). It has been used for centuries in glass manufacture, to take out the green colour caused by the presence

of iron. Pyrolusite was for long considered to be an ore of iron, but in 1774 SCHEELE showed that it contained a new metallic element, and shortly afterwards the metal was isolated by GAHN who reduced the pyrolusite with carbon.

Occurrence.—Maganese is found in nature chiefly as the dioxide, MnO_2, which is called *pyrolusite*. This mineral is found in Germany, Russia, India, Brazil, North America, Spain, the Caucasus and other countries. Other manganese ores are *manganese blende*, MnS; *Hausmannite*, Mn_3O_4; and *manganese spinel*, (Mn, Mg)(Fe, Mn)$_2O_4$.

Preparation.—Manganese is generally made nowadays either by reducing the oxide with powdered aluminium—

$$3MnO_2 + 4Al = 2Al_2O_3 + 3Mn,$$

or by the reduction of the dioxide with carbon in the electric furnace.

MOISSAN'S method gives a purer product. It consists of the electrolysis of a solution of manganous chloride, $MnCl_2$, by means of a powerful electric current. The cathode is of mercury and a manganese-mercury amalgam containing about 4 per cent. of manganese is obtained. This is carefully washed and dried and the mercury distilled off under reduced pressure.

Properties.—Pure manganese is a hard, brittle, greyish metal with a reddish tinge. The specific gravity is 7·39–8·0 according to the method of preparation; probably 7·39 is the most nearly correct value hitherto obtained. The metal melts at 1,260° and boils at 1,900°. It readily oxidizes in the air and is therefore kept under rock-oil, like sodium. It decomposes water in the cold with evolution of hydrogen, and is very soluble in dilute acids, less so in the concentrated acids. It combines directly with oxygen, nitrogen, chlorine, carbon, silicon, boron and phosphorus, when heated.

The atomic weight of the element has been determined by analysis of manganous bromide, $MnBr_2$, and chloride, $MnCl_2$. The value generally accepted is 54·93.

Manganese has recently become of great importance in the manufacture of alloys such as *ferro-manganese*, *manganese bronze*, *spiegeleisen*, *cupro-manganese*, *manganin*, *etc.* These

find various uses; manganese bronze, for example, is used for the propellers of ships while manganin is used in rheostats or resistance coils.

It is said that rats fed on a diet free from manganese lose all love for their offspring.

COMPOUNDS OF MANGANESE.—Manganese forms a whole family of oxides—

Manganous oxide, MnO, basic. Forms manganous salts.

Trimanganic tetroxide, Mn_3O_4. Resembles Fe_3O_4.

Manganic oxide, Mn_2O_3. Slightly basic, forming manganic salts.

Manganese dioxide, MnO_2. Slightly acidic, forming manganites.

Manganese trioxide, MnO_3. Acidic, forming manganates.

Manganese heptoxide, Mn_2O_7. This also is acidic, forming permanganates.

Manganese forms two series of salts, the *manganous* salts corresponding to the oxide MnO, and the *manganic* salts corresponding to the oxide Mn_2O_3. In the first series manganese is bivalent and in the second tervalent. The common salts of manganese are manganous salts.

Manganous oxide, MnO, is obtained as a bright green powder by heating manganese dioxide or manganous carbonate in a stream of hydrogen. It is soluble in dilute acids, forming manganous salts.

Manganous hydroxide, $Mn(OH)_2$, is formed as a white precipitate (rapidly going brown in the air, owing to oxidation) when caustic soda or potash solution is added to a solution of a manganous salt.

Manganous chloride is obtained in the form of pink crystals containing 4 molecules of water of crystallization, $MnCl_2.4H_2O$, by dissolving the metal, oxide, hydroxide, or carbonate in dilute hydrochloric acid and evaporating the solution.

Manganous carbonate, $MnCO_3$, is obtained as a dirty white precipitate when sodium carbonate is added to a solution of a manganous salt. It is unstable in moist air, slowly oxidizing to manganic hydroxide, $Mn(OH)_3$, and other substances.

Manganese dioxide, MnO_2, **is a** black powder. The native form, pyrolusite, contains on an average about 80 per cent. MnO_2. When pyrolusite is required for the manufacture of chlorine it is important from the buyer's point of view to know how much manganese dioxide it contains. This is determined by taking a known weight of the finely ground ore and boiling it with hydrochloric acid, until all black particles have disappeared.

$$MnO_2 + 4HCl = MnCl_2 + 2H_2O + Cl_2.$$

The chlorine which is evolved is passed through potassium iodide solution, where it liberates an equivalent weight of iodine. The weight of iodine set free is estimated by titration with standard sodium thiosulphate.

Manganese dioxide is a good oxidizing agent. It is used in the manufacture of chlorine, for decolourizing glass, as a depolarizer in Leclanché cells and dry batteries, and in the preparation of potassium and sodium permanganates.

It will dissolve in concentrated alkalis, forming salts called *manganites*, such as $CaMnO_3$, calcium manganite. (See Weldon's Process, p. 501.)

Manganates and Permanganates.—When manganese dioxide is fused with caustic potash or caustic soda in the presence of air or, better, with addition of a strong oxidizing agent such as potassium chlorate or nitrate, a dark green mass is obtained. This consists of impure *sodium* or *potassium manganate*—

$$2MnO_2 + 4KOH + O_2 = 2K_2MnO_4 + 2H_2O.$$

If the mass is dissolved in water a green solution is formed from which dark green crystals of the manganate, K_2MnO_4, may be obtained by careful evaporation under reduced pressure. Potassium manganate is isomorphous with potassium sulphate and potassium chromate.

On warming or largely diluting a concentrated solution of potassium manganate, a brown precipitate of hydrated manganese dioxide is thrown down and a purple solution of *potassium permanganate* is left—

$$3K_2MnO_4 + 3H_2O = 2KMnO_4 + 4KOH + MnO_2.H_2O.$$

A better yield of permanganate is obtained by blowing a current of carbon dioxide through the manganate solution, to combine with the alkali liberated. Concentration of the filtered solution yields dark purple crystals of the permanganate, isomorphous with those of potassium perchlorate, $KClO_4$. Potassium permanganate is a powerful oxidizing agent. On heating it splits up into potassium manganate, manganese dioxide, and oxygen—

$$2KMnO_4 = K_2MnO_4 + MnO_2 + O_2.$$

It is usually employed for oxidizing purposes dissolved in water. The reaction follows a different course in alkaline solution from that in acid solution—

A. *Alkaline Solutions.*—On boiling with an alkali solution, in presence of a substance that can be oxidized, the permanganate is first reduced to manganate—

$$4KMnO_4 + 4KOH = 4K_2MnO_4 + 2H_2O + O_2,$$

and the manganate is then further reduced to manganese dioxide which is precipitated—

$$2K_2MnO_4 + 2H_2O = 2MnO_2 + 4KOH + O_2.$$

It follows that 2 *molecules of potassium permanganate in alkaline solution yield* 3 *atoms of oxygen available for oxidation.*

Alkaline permanganate is used for oxidation purposes chiefly in organic chemistry; the acid solution is generally employed in inorganic work.

B. *Acid Solutions.*—If we write the formula for two molecules of potassium permanganate, $2KMnO_4$, in the form $K_2O.2MnO.5O$, we shall see that 2 *molecules of the salt in acid solution are capable of yielding* 5 *atoms of oxygen available for oxidation.* Sulphuric acid is used, since hydrochloric acid would be oxidized—

$$2KMnO_4 + 16HCl = 2KCl + 2MnCl_2 + 8H_2O + 5Cl_2.$$

In the presence of sulphuric acid, then, potassium permanganate is capable of acting in the following way, upon an oxidizable substance—

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

In acid solution, therefore, 316 grams of potassium permanganate yield 80 grams of available oxygen. The equivalent of the salt in grams is thus 31·6 gms.; hence N/10 potassium permanganate contains 3·16 gms. per litre.

Standard potassium permanganate in the presence of sulphuric acid is one of the most valuable volumetric solutions. It is used for the estimation of hydrogen peroxide, ferrous iron, oxalic acid (on heating to 70°), nitrites, and other oxidizable chemicals. The reactions which occur in the above examples are as follows—

(i) $5O + 5H_2O_2 = 5H_2O + 5O_2$.
(ii) $5O + 10FeSO_4 + 5H_2SO_4 = 5Fe_2(SO_4)_3 + 5H_2O$.
(iii) $5O + 5H_2C_2O_4 = 10CO_2 + 5H_2O$.
(iv) $5O + 5HNO_2 = 5HNO_3$.

The 5O in these equations is formed according to the equation above.

Sodium permanganate is the active agent in *Condy's Fluid.* The disinfecting and deodorizing properties of permanganates are due to the readiness with which these salts give up their oxygen.

Questions

1. What do you think of the position of manganese in the Periodic System? Make a considered statement as to the general success or failure of the Periodic System in its grouping of the elements.

2. Describe the preparation and properties of potassium permanganate. For what purposes is this substance employed in the laboratory?

CHAPTER XXX

GROUP VIII

The "Transition Elements."—Iron, Cobalt, Nickel; Ruthenium, Rhodium, Palladium; Osmium, Iridium, Platinum.

The transition elements fall into three groups, indicated by semi-colons in the above list. The members of each group are very similar to one another, and have nearly the same atomic weights: thus, in round numbers

(i)	(ii)	(iii)
Fe = 56	Ru = 102	Os = 191
Co = 59	Rh = 103	Ir = 193
Ni = 58	Pd = 107	Pt = 195

Groups (ii) and (iii) together are called the *platinum metals*. They are precious metals, extremely resistant to the action of acids and alkalis; osmium, for example, will not dissolve even in *aqua regia*. The use of platinum in the laboratory is well known.

The elements of group (i), iron, cobalt and nickel, are all *magnetic*.

IRON, COBALT, NICKEL

Iron

Group in Periodic System: VIII; *Symbol:* Fe; *Valency:* 2 and 3; *Atomic Weight:* 55·84; *Melting Point:* 1,500°; *Specific Gravity:* 7·84.

History.—In spite of the fact that it is difficult to extract iron from its ores, this metal has been known for some 5,000 years. In very early days it was more or less of a curiosity,

but later became widely used for making swords and other weapons of war, and was supposed by the alchemists to be astrologically connected with the planet Mars, ♂. About 100,000 talents (2,500 tons) of iron were used in the construction of SOLOMON'S temple (*circa* 1000 B.C.), and NEBUCHADREZZAR is said to have carried off into captivity in 604 B.C. a thousand blacksmiths from Damascus. Iron was worked in India from about 1000 B.C. and Indian steel was taken by sea to Oman and the Yemen where it was used by the Arabs for making fine blades.

In the *Old Testament* iron is called *barzil* (from the ancient Assyrian *barza*), and the name "Berzelaios" in JOSEPHUS apparently means "the man of iron"—an appropriate name for the chemist who first accurately determined the atomic weight of iron, BARON BERZELIUS! Iron is mentioned also in the *Qur'ān*, Chapter 57, v. 25, "ALLAH sent down iron, in which is both keen violence and advantages to men," whence the names "*The Violent*" and "*The Useful*" often given to the metal by the chemists of Islam, e.g., ABU'L-QĀSIM AL-'IRĀQĪ (*Book of the Mighty Secret of the Most Noble Stone*), "Iron is hot and dry, related essentially to Marrikh (Mars), ruler of the Fifth Heaven. Its symbol is ♂, and alternative names for it are *the Violent, Death, the Useful, the Black Slave*, and *Persian earth*."

"GEBER" (thirteenth century) says, "*Mars or Iron* is a *Metallick Body*, very livid, a little red, partaking of *Whiteneſs*, not pure, ſuſtaining *Ignition*, fuſible with no right fuſion, under the *Hammer* extenſible, and ſounding much. . . . *Mars*, among all the *Bodies*, is of leaſt *Perfection in Tranſmutation*, to be handled moſt difficult, and of exceeding long Labour."

Iron is the Scandinavian and Anglo-Saxon name for the metal.

Occurrence.—Iron forms about 4 per cent. of the earth's crust. It is found in small quantities free in nature, especially in meteorites, where it is usually associated with nickel. It occurs much more abundantly in the form of its oxides, sulphide, and carbonate—

Oxides. *Hæmatite*, Fe_2O_3; *magnetite*, Fe_3O_4; *limonite*, $2Fe_2O_3.3H_2O$.

Sulphide. *Iron pyrites* and *marcasite*, FeS_2.

Carbonate. *Spathic iron ore* or *siderite*, $FeCO_3$.

Iron is a constituent of the red colouring-matter of the blood (*hæmoglobin*); it is also essential to the life of green plants, although it is not present in chlorophyll.

Extraction.—The chief ores of iron are *hæmatite* (Lancashire, Belgium, North America), *magnetite* (Scandinavia, Germany, North America), *limonite* (South Wales), and *spathic iron ore* (mixed with clay as *clay ironstone*, in many parts of Great Britain). *Iron pyrites* is used chiefly as a source of *sulphur*.

Iron is prepared from its ores by reducing them with carbon monoxide in a blast furnace—

$$Fe_2O_3 + 3CO \rightleftharpoons 2Fe + 3CO_2.$$

The ore is first roasted to drive off any water present, to convert carbonate into oxide, to oxidize any sulphide to oxide, and to convert ferrous oxide (FeO) to ferric oxide (Fe_2O_3), according to the ore used.

The roasted ore is mixed with coke and limestone and the mixture introduced into the blast furnace through a cup and cone hopper at the top (see Fig. 118). The blast furnace is an iron tower lined with fire-resisting material, and is usually about 70–100 feet in height; it is maintained at a temperature of from 700° at the bottom to over 1,500° at the top, chiefly by the heat evolved in the reactions. Hot air (700°) is blown in at the bottom of the furnace through water-jacketed pipes called *tuyères* (" twyers "); this oxidizes the adjacent coke into carbon monoxide which then reacts with the ferric oxide according to the equation given above. The reduced iron melts and sinks to the bottom of the furnace, accompanied by a molten *slag* of calcium aluminium silicate, formed from the clay and silica of the ores and the lime produced by decomposition of the added limestone. In this way, *all* the ore is converted into substances that can be removed from the furnace (namely, iron, slag, and carbon

dioxide and monoxide), and the process is therefore continuous. Fresh material is fed in from time to time and the furnace kept in operation until it is worn out. An average furnace can produce about 500–600 tons of pig-iron a day.

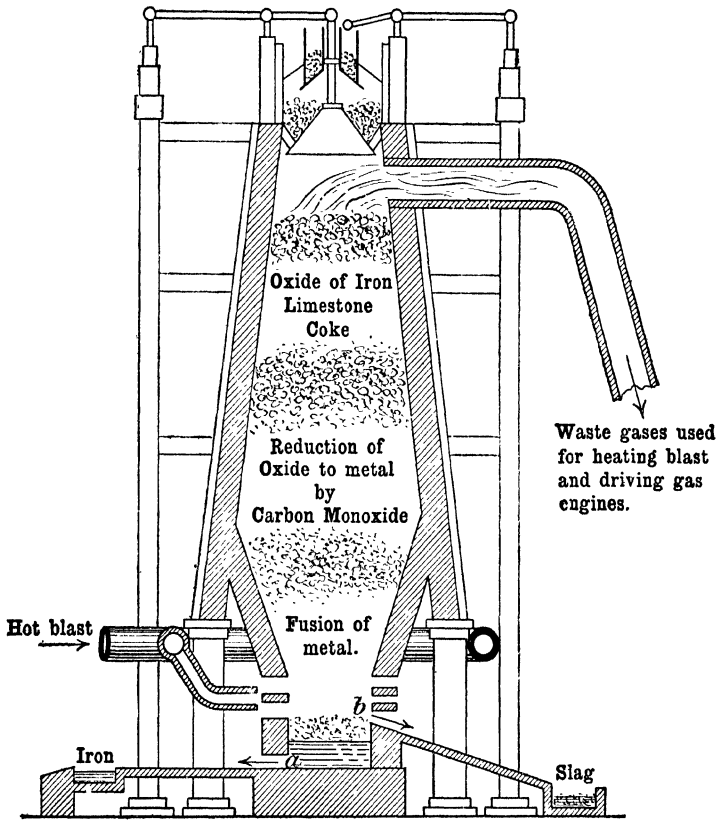


FIG. 118.—Blast Furnace.

The gases that escape from the furnace contain about 60 per cent. of nitrogen, 12 per cent. carbon dioxide, and 24 per cent. carbon monoxide. They are passed through flues into a *gas-cleaner* to remove the dust and are then burnt in

a brickwork "Cowper stove." When this is sufficiently heated the gases are turned into a second Cowper stove while air is passed through the first. The hot air is then delivered through the tuyères into the blast furnace. In this way one of the Cowper stoves is being heated while the other one is giving up its heat to the air-blast. This use of the "waste" gases effects a considerable saving of fuel.

The dust which collects in the flues contains potassium salts, often in sufficient quantity to make their extraction commercially profitable.

The molten iron that flows to the well of the furnace is run into moulds where it solidifies in blocks called *pig iron* or *cast iron*. It is very impure, containing as much as 4·5 per cent. of carbon and 1 to 2 per cent. of silicon, as well as smaller quantities of phosphorus, sulphur and other elements. Cast iron is brittle and cannot be welded; its use is therefore limited.

Wrought iron is made from pig iron by burning away the carbon, phosphorus, sulphur and silicon. The pig iron is melted in a reverberatory furnace lined with hæmatite (Fe_2O_3), when the impurities are oxidized—partly to gas (CO) and partly to a slag (SiO_2, P_2O_5, etc.). The iron then begins to go "pasty," since the pure metal has a higher melting-point than that of the crude pig iron. The pasty iron is stirred and finally removed in large lumps, which are hammered with a steam hammer to remove the slag and then rolled into sheets. Further hammering and rolling produce the characteristic fibrous structure of wrought iron.

Wrought iron is the purest form of commercial iron, containing about 99–99·5 per cent. Fe. It is very tough, has a high tensile strength, and can be welded (i.e. two pieces of it, when red-hot, can be joined together by hammering). It is used chiefly by blacksmiths and for the cores of electro-magnets.

Steel is a mixture of iron and *iron carbide* or *cementite*, Fe_3C.[1] The carbon content is from 0·2 to 1·5 per cent. Steel is now generally prepared by the SIEMENS-MARTIN open-hearth

[1] Hard steels are generally regarded as solid solutions of carbon in γ-iron.

process, but the *cementation* and BESSEMER processes are still occasionally employed and will therefore be described here.

(i) *Cementation Process.*—Bars of wrought iron are packed with charcoal and heated to about 1,000° for 11–14 days. Absorption of charcoal by the iron gradually takes place and the product is called "blister-steel." In *case-hardening* the iron is removed when only the surface layers of the metal

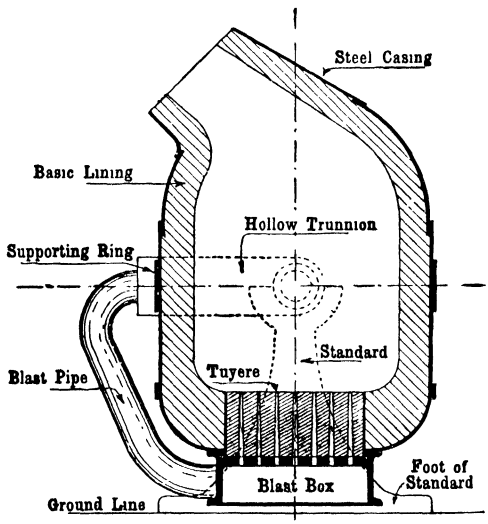


FIG. 119.—Bessemer Converter.

have been converted into steel. *Crucible steel* (used for tools) is made by melting cementation steel in graphite crucibles.

(ii) *The* BESSEMER *Process.*—Cast iron is melted in a Bessemer converter (Fig. 119), and air is then blown through the molten metal to oxidize the carbon, phosphorus and other impurities. The converter is lined with a mixture of lime and magnesia (made by heating dolomite, $CaCO_3.MgCO_3$), which absorbs the phosphorus pentoxide, forming *Thomas slag* or *basic slag* (crude calcium phosphate). The pure molten iron left in the converter is then mixed with a suitable weight of

spiegeleisen (an alloy of iron, manganese and carbon) and thus converted into steel.

The removal of phosphorus is extremely important, since the presence of phosphorus in steel renders the metal very brittle. Use of a basic lining to the converter was suggested by THOMAS and GILCHRIST (1879) and was very successful, since it not only efficiently removes the phosphorus but also yields a by-product (the " basic slag ") which is an excellent

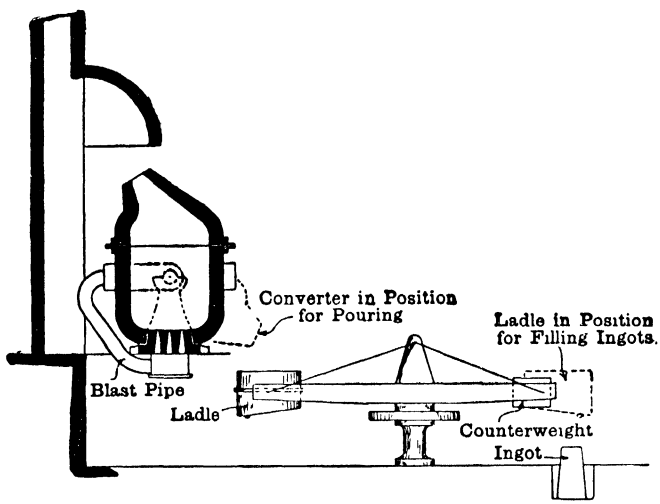


FIG. 120.—General Arrangement of Bessemer Plant.

fertilizer for grass-lands. The general arrangement of the plant is shown in Fig. 120.

(iii) *Siemens-Martin Process.*—Most of the steel manufactured at the present day is made by the Siemens-Martin process. A mixture of cast iron, scrap iron and hæmatite is placed on an open hearth and heated by producer-gas (p. 301) or by blast-furnace gases. The hearth is lined with calcined dolomite to remove phosphorus, as in the Bessemer process. By suitably adjusting the proportions of the cast iron and

hæmatite, the carbon content of the product may be regulated as desired ; the molten steel is run off when ready by tilting the hearth.

The properties of steel depend upon (*a*) its carbon content ; (*b*) its *temper*.

(*a*) *Carbon content.* This varies from 0·2 to 1·5 per cent. The hardness of steel increases as the percentage of carbon in it rises ; steel which contains but little carbon is called " mild steel."

(*b*) *Temper.* If steel is heated to a high temperature and then suddenly cooled by being plunged into water it becomes extremely hard and brittle and is known as *quenched steel.* When quenched steel is carefully heated it becomes less hard but tougher, the extent of the change depending on the length of the heating and on the temperature. A rough indication of the temperature of the heated steel is given by the colour of the film of oxide formed on the surface, which varies from yellow through brown to blue as the temperature rises. Steel treated in this way is said to be *tempered.* The temperature at which the film of oxide is pale yellow is 200–230° ; the blue colour is produced at 290–300°. Steel for cutting blades and tools is usually tempered yellow, while springs and chisels are generally tempered blue.

Various forms of steel, suitable for a large number of different purposes, are made by the admixture of small quantities of other elements, e.g. nickel, chromium, tungsten, vanadium, manganese, molybdenum, cobalt, titanium and silicon. Chromium produces a harder steel, nickel a more elastic, molybdenum a tougher, and so on. Details of these special steels may be found in the handbooks of metallurgy. Nickel steels, containing 1–5 per cent. of nickel and 0·25–0·45 per cent. of carbon, and nickel-chromium steels (1–4·5 per cent. nickel, 1–2 per cent. chromium) are used for propeller shafts, piston rods, crankshafts, steering gears, axles, brake rods, etc. Stainless steel contains about 12–15 per cent. chromium. Silicon steel, or silico-manganese steels (1–2 per cent. silicon, 0·4–1 per cent. manganese, 0·40–0·65 per cent carbon) are used especially for making springs. Manganese steels containing

12–14 per cent. manganese are used for tramways points and crossing-rails, as they are very hard and tough.

Properties.—Iron exists in four allotropic modifications, very similar to one another in general chemical properties. The form stable at ordinary temperatures is called α-iron or "ferrite"; at 766° this changes into β-iron, which is stable from 766° to 895°; at 895° β-iron changes into γ-iron and this is converted into δ-iron at 1,400°. Quenched steel is a solution of cementite (Fe_3C) in γ-iron; the various tempered steels consist of heterogeneous mixtures of α-iron, or "ferrite," with cementite.

Pure iron is a rather soft, lustrous, white, magnetic metal, with specific gravity 7·84, melting-point 1,500°, and boiling-point 2,450°. It dissolves in dilute sulphuric and hydrochloric acids with evolution of hydrogen; concentrated sulphuric acid dissolves it on heating, with formation of sulphur dioxide. It is dissolved by cold *dilute* nitric acid, forming ferrous nitrate and ammonium nitrate; *concentrated* nitric acid, however, renders it *passive*. In the "passive" state iron will not dissolve even in dilute acids; the phenomenon is supposed to be due to the formation of a coherent protective film of oxide on the surface of the metal, and is shown by certain other metals, e.g. chromium. Passivity is removed by heating the metal in hydrogen or by rubbing with sand-paper. Further information may be obtained from a paper by HEATHCOTE (*Jour. Soc. Chem. Ind.*, **26**, 899, 1907).

In moist atmospheric air ordinary iron rapidly rusts to a brown powder which has the composition $Fe_2O_3.H_2O$ or $2Fe_2O_3.3H_2O$. It is said that absolutely pure iron will not rust. The mechanism of rust-formation is a problem that has attracted the attention of a great number of chemists and cannot even yet be regarded as satisfactorily solved. It is probable that when ordinary iron rusts under normal atmospheric conditions *ferrous bicarbonate*, $Fe(HCO_3)_2$, is first formed; this dissolves in the water present and is oxidized by the dissolved oxygen in the water to a hydrated ferric oxide, with liberation of carbon dioxide. Other chemists regard the rusting of iron as essentially an electrochemical

phenomenon. On this theory, different bits of the piece of iron, varying in physical or chemical condition (e.g. local compression or strain, presence of small quantities of impurity) may act as the positive and negative plates of a battery when covered by air or impure water. Corrosion would then take place at those parts acting as negative poles, i.e. where the concentration of oxygen is least, as in cracks and crevices in the surface. It has been shown that the rate of corrosion is affected by many different factors, and the problem is an extremely complicated one. The student is recommended to read the following papers—

DUNSTAN, JOWETT, AND GOULDING, *Trans. Chem. Soc.*, **87**, 1,548 (1905); MOODY, *ibid.*, **89**, 720 (1906); WHITNEY, *Jour. Amer. Chem. Soc.*, **25**, 394 (1903); TILDEN, *Trans. Chem. Soc.*, **93**, 1,356 (1908); LAMBERT AND THOMSON, *ibid.*, **97**, 2,426 (1910); DUNSTAN AND HILL, *ibid.*, **99**, 1,835 (1910); LAMBERT, *ibid.*, **101**, 2,056 (1912); U. R. Evans, *The Corrosion of Metals* (London, Edward Arnold & Co., 1926).

Iron will combine directly with many non-metallic elements if heated with them; thus with sulphur it yields *ferrous sulphide*, in oxygen it burns brilliantly to *magnetic oxide of iron*, and with chlorine it gives *ferric chloride*. It does not form a hydride, but red-hot iron will allow hydrogen to pass freely through it.

COMPOUNDS OF IRON.—Iron forms three oxides and two series of salts—

FeO, ferrous oxide, to which correspond ferrous salts.

Fe_3O_4, ferroso-ferric oxide or magnetic oxide of iron. No corresponding salts.

Fe_2O_3, ferric oxide, to which correspond the ferric salts.

Solutions of ferrous salts contain the bivalent ion $F^{\cdot\cdot}$; those of ferric salts contain the tervalent ion $Fe^{\cdot\cdot\cdot}$. Ferrous salts are reducing agents since they are readily oxidized to the ferric state.

Ferrous oxide, FeO.

Ferrous oxide is obtained as a black powder by gently heating finely divided iron with nitrous oxide or by carefully reducing ferric oxide with hydrogen at 300°. Mixed with iron

it can be made by igniting ferrous oxalate in absence of air.

$$FeC_2O_4 = FeO + CO + CO_2.$$

It takes fire spontaneously in the air, burning with incandescence to ferric oxide, Fe_2O_3. It dissolves in acids, forming ferrous salts.

Ferrous hydroxide, $Fe(OH)_2$, is precipitated as a *white* gelatinous solid by addition of caustic soda solution to a solution of a ferrous salt in absence of air. It rapidly oxidizes in the air, forming first the *green* compound $Fe(OH)_2.2Fe(OH)_3$ and finally *brown* ferric hydroxide $Fe(OH)_3$.

Ferrous chloride, $FeCl_2$, is made in the anhydrous state by heating iron wire in a current of hydrochloric acid gas—

$$Fe + 2HCl = FeCl_2 + H_2.$$

It is a white crystalline solid and can be vapourized unchanged. Vapour density determinations show that the molecules are at first Fe_2Cl_4; on further heating these dissociate into $FeCl_2$—

$$Fe_2Cl_4 \rightleftharpoons 2FeCl_2.$$

The dissociation is complete at 1,500°.

The *tetrahydrate,* $FeCl_2.4H_2O$, is most conveniently made by dissolving iron in dilute hydrochloric acid and evaporating the solution. It forms pale-green crystals.

Ferrous sulphate, or green vitriol, $FeSO_4.7H_2O$, may be made by dissolving iron in dilute sulphuric acid and evaporating the solution to crystallization. Commercially it is made by exposing marcasite, FeS_2, to moist air—

$$2FeS_2 + 2H_2O + 7O_2 = 2FeSO_4 + 2H_2SO_4.$$

The anhydrous salt may be obtained as a white powder by cautiously heating the hydrate in absence of air.

Other hydrates are known, e.g. $FeSO_4.5H_2O$ and $FeSO_4.H_2O$. Ferrous sulphate crystals are slowly oxidized in the air and therefore in volumetric analysis it is more convenient to make a standard solution of ferrous iron from the double salt *ferrous ammonium sulphate,*

$$FeSO_4.(NH_4)_2SO_4.6H_2O,$$

which is much more stable.

When strongly heated ferrous sulphate decomposes, yielding oxides of sulphur, steam, and ferric oxide. If the gases are cooled in a receiver fuming sulphuric acid (pp. 468, 474) is formed.

The brown compound formed when nitric oxide dissolves in ferrous sulphate solution has been described previously (p. 363).

Ferrous sulphate is largely used in making ink, which consists of a mixture of a dark-blue dye with tannin and ferrous sulphate solution. When fresh, writing in such an ink is blue, but goes black gradually on exposure to air owing to the formation of an oxidized iron-tannin compound.

Ferrous sulphide, FeS, is made by heating iron and sulphur together or by adding sodium sulphide to ferrous sulphate solution—

$$FeSO_4 + Na_2S = FeS\downarrow + Na_2SO_4.$$

It is a black solid that melts at about 1,200° and can easily be cast in sticks. It is used for the preparation of sulphuretted hydrogen. The commercial substance always contains uncombined iron, to which it probably owes its black colour; it is said that the pure substance forms brownish-yellow crystals.

Ferrous carbonate, $FeCO_3$, occurs naturally as *spathic iron ore* and, mixed with clay, in *clay ironstone*. It comes down as a white precipitate on addition of sodium carbonate to ferrous sulphate solution; on exposure to air it oxidizes, becoming first green and then brown. It will dissolve if suspended in water through which a current of carbon dioxide is blown, owing to the formation of soluble *ferrous bicarbonate*—

$$FeCO_3 + H_2O + CO_2 = Fe(HCO_3)_2.$$

Like the normal carbonate, the bicarbonate is quickly oxidized in air.

Ferroso-ferric oxide, Fe_3O_4.

Ferroso-ferric oxide occurs naturally as *magnetite* or *loadstone*. It is formed when iron burns in air or oxygen, and when iron is heated in a current of steam—

$$3Fe + 4H_2O = Fe_3O_4 + 4H_2.$$

Chemically it behaves as a loose "molecular compound" of ferrous oxide and ferric oxide. The fused oxide is not

attacked by acids, oxygen, or chlorine and is therefore sometimes used for making anodes for electrolytic processes.

Ferric oxide, Fe_2O_3.

Ferric oxide occurs in the anhydrous state as the important mineral *hæmatite*, and in the hydrated state as *limonite*, $2Fe_2O_3 . 3H_2O$. It can be made by igniting ferric hydroxide or ferrous sulphate; prepared from the latter it is known as *jeweller's rouge* or *colcothar* and is used as a polishing powder and as a red pigment.

Ferric hydroxide, $Fe(OH)_3$, is formed as a reddish-brown precipitate by adding caustic alkali solution or ammonia to a solution of a ferric salt. It is a very weak base, and is soluble in acids, forming ferric salts. It is so weak a base that it will not form a carbonate; hence it is precipitated when a solution of sodium *carbonate* is added to a solution of a ferric salt.

Ferric chloride, $FeCl_3$, is formed as a black scaly crystalline solid by heating iron in a stream of chlorine. It can be vapourized unchanged, and vapour density determinations show that at 445° the molecules are Fe_2Cl_6. On further heating dissociation takes place, first into $2FeCl_3$ and finally into ferrous chloride and chlorine.

$$Fe_2Cl_6 \rightleftharpoons 2FeCl_3 \rightleftharpoons 2FeCl_2 + Cl_2.$$

Ferric chloride forms many hydrates, all of which are yellow in colour—

$FeCl_3 . 6H_2O$ (ordinary "ferric chloride crystals").
$FeCl_3 . 3\frac{1}{2}H_2O$. $FeCl_3 . 2\frac{1}{2}H_2O$. $FeCl_3 . 2H_2O$.

Aqueous solutions of ferric chloride are strongly acid, owing to hydrolysis. Ferric hydroxide is a weak base and is therefore formed from the hydroxyl ions of the water and the ferric ions of the ferric chloride. Each hydroxyl ion removed in this way leaves a free hydrogen ion in solution and hence the solution becomes acid—

(i) $H_2O \rightleftharpoons H^{\cdot} + OH'$.
(ii) $FeCl_3 \rightleftharpoons Fe^{\cdot\cdot\cdot} + 3Cl'$.
(iii) $Fe^{\cdot\cdot\cdot} + 3OH' \rightleftharpoons Fe(OH)_3$.

Or

$$FeCl_3 + 3H_2O = Fe(OH)_3 + 3HCl.$$
Un-ionized. Ionized.

If a solution of ferric chloride is dialysed the hydrochloric acid passes through the membrane and a colloidal solution of ferric hydroxide is left in the dialyser. This solution is used in medicine under the name of " dialysed iron."

Ferric sulphate, $Fe_2(SO_4)_3$ is usually met with in the form of its double salt with ammonium sulphate, *ferric alum*, $(NH_4)_2SO_4.Fe_2(SO_4)_3.24H_2O$. This salt is isomorphous with ordinary potash alum and generally has a pale violet colour. *Potassium ferric alum*, $K_2SO_4.Fe_2(SO_4)_3.24H_2O$, is very similar.

Ferric sulphate is formed by heating ferrous sulphate with a mixture of sulphuric and nitric acids—

$$6FeSO_4 + 3H_2SO_4 + 2HNO_3 = 3Fe_2(SO_4)_3 + 4H_2O + 2NO.$$

The anhydrous salt is a white or yellowish powder.

Ferric sulphide, Fe_2S_3, is a black substance that may be made by passing sulphuretted hydrogen through a suspension of ferric hydroxide in water—

$$2Fe(OH)_3 + 3H_2S = Fe_2S_3 + 3H_2O,$$

or by adding a solution of a ferric salt to an excess of ammonium sulphide solution. In presence of excess of sulphuretted hydrogen it is converted into iron disulphide, FeS_2.

Iron disulphide, FeS_2, exists naturally in two different crystalline forms, *iron pyrites* and *marcasite*. Marcasite is much more readily oxidized by moist air than is pyrites.

Iron carbonyls.—When iron is heated in carbon monoxide it forms a compound, $Fe(CO)_5$, known as *iron pentacarbonyl*. This is a yellow liquid boiling at 103° and freezing at —21°. In the presence of light it gradually decomposes into another carbonyl of iron, $Fe_2(CO)_9$—

$$2Fe(CO)_5 = Fe_2(CO)_9 + CO.$$

Iron tetracarbonyl, $Fe(CO)_4$, is also known.

All the carbonyls of iron are decomposed at a fairly high temperature into iron and carbon monoxide.

Organic Compounds of Iron.—Iron forms many important organic compounds, the chief of which are *potassium ferrocyanide*, $K_4Fe(CN)_6$, *potassium ferricyanide*, $K_3Fe(CN)_6$, and *sodium nitroprusside*, $Na_2Fe(NO)(CN)_5$. For the preparation and properties of these compounds, see p. 215, and text-books of organic chemistry. Consult also FENTON'S *Notes on Qualitative Analysis* for the use of ferrous salts as catalysts in certain organic preparations, and for the detection of iron.

Estimation of Iron.—*Ferrous* iron is usually estimated by addition of sulphuric acid and titration with standard potassium permanganate or potassium dichromate. *Ferric* iron may be estimated by reduction to the ferrous state (e.g. with zinc and acid), followed by titration with permanganate, or preferably by direct titration with standard titanous chloride, using ammonium thiocyanate as indicator. See BERRY, *Volumetric Analysis*, and KNECHT and HIBBERD, *New Reduction Methods in Volumetric Analysis*.

Titration of ferrous sulphate with (i) Permanganate—

$$10FeSO_4 + 8H_2SO_4 + 2KMnO_4 = K_2SO_4 + 2MnSO_4 + 5Fe_2(SO_4)_3 + 8H_2O.$$

(i.e. 316 grams $KMnO_4 \equiv 560$ grams Fe). *Indicator:* None. *End-point:* Permanent pink colour.

(ii) Dichromate—

$$6FeSO_4 + 7H_2SO_4 + K_2Cr_2O_7 = K_2SO_4 + Cr_2(SO_4)_3 + 3Fe_2(SO_4)_3 + 7H_2O.$$

(i.e. 293·4 grams $K_2Cr_2O_7 \equiv 336$ grams Fe). *Indicator:* Potassium ferricyanide solution, externally, on white tile. *End-point:* Red-brown colouration.

Titration of ferric chloride with titanous chloride—

$$FeCl_3 + TiCl_3 = FeCl_2 + TiCl_4.$$

The titanous chloride solution is standardized against a standard ferric solution. *Indicator:* Ammonium (or potassium) thiocyanate. *End-point:* Blood-red colour vanishes.

Cobalt

Group in Periodic System: VIII; *Symbol:* Co; *Valency:* 2 and 3; *Atomic Weight:* 58·94; *Melting-Point:* 1450°; *Specific Gravity:* 8·8.

Occurrence.—It is said that the word *cobalt* is etymologically connected with *kobold*, the name given to certain gnomes who lived in copper mines in the Hartz Mountains and took a spiteful glee in deceiving men by exposing ores which looked like copper ores but from which no copper could be extracted. These ores are now known by the name of *smaltine* ($CoAs_2$) and *cobaltine* ($CoAs_2 . CoS_2$), and are obtained at the present day chiefly from North America (Ontario, etc.). The word *kibaltu* occurs among the names of other minerals on an ancient Assyrian tablet dealing with glass-making, but it is uncertain whether the word refers to a cobalt ore or not.

Extraction.—The cobalt ores are first roasted in a current of air, which removes the arsenic and leaves the cobalt in the form of oxide. This is then reduced with charcoal or hydrogen. As the cobalt ores are seldom pure, special methods of separation are generally necessary.

Properties.—Cobalt is a silvery metal with a reddish lustre. Its specific gravity is 8·8, and it melts at about 1450°. It is unchanged on exposure to air at ordinary temperatures, but oxidizes gradually when heated. It is readily soluble in nitric acid but dissolves only very slowly in hydrochloric or sulphuric acids. It is magnetic but much less so than iron, although it retains its magnetic properties up to a temperature of over 1,000° C. Finely divided cobalt has the power of absorbing many times its own volume of hydrogen.

Compounds of Cobalt.—Cobalt forms two main oxides and two corresponding series of salts.

Cobaltous oxide, CoO, is a greenish-brown powder obtained by gently heating cobaltous hydroxide or carbonate out of contact with air. Cobaltous salts are pink in solution or when they contain water of crystallization, but the anhydrous salts are blue.

Cobaltous chloride, $CoCl_2.6H_2O$, is obtained by dissolving cobaltous oxide or carbonate, or the metal itself, in dilute hydrochloric acid. On evaporating the solution, red crystals of cobaltous chloride hexahydrate separate out. Other hydrates are known. The anhydrous salt is blue, and this fact has been made use of in the preparation of "invisible" or "sympathetic" ink. When a dilute solution of cobaltous chloride is used for writing, the characters are invisible, but on heating the paper over a lamp or before the fire the hydrated salt loses its water of crystallization and the blue anhydrous salt is formed, the characters becoming apparent at once. If the paper be now breathed on, or exposed to damp air, the writing fades again. Paper soaked in cobaltous chloride solution and then dried is sometimes used as a rough weather-glass, as when the air is very hot and dry the paper goes blue, becoming pink again on the approach of rain; the paper may also be used for showing the transpiration from the under surface of dorsiventral leaves.

An interesting observation is that a solution of cobaltous chloride goes blue (*a*) on heating, if sufficiently concentrated; (*b*) on addition of strong hydrochloric acid; (*c*) on addition of strong sulphuric acid; and (*d*) on addition of alcohol. These facts may be explained by assuming a diminution in the ionization of the salt brought about under the above conditions; it is considered that the *cobaltous ion* is pink, while the un-ionized molecules $CoCl_2$ are blue. It is possible, however, that a complex anion of a deep blue colour is formed; certainly cobalt forms many complex compounds, the colours of which are very varied.

Cobaltous sulphide is the black precipitate obtained in Group IV of the Analysis Tables.

Cobaltous carbonate is a pink substance precipitated when sodium carbonate solution is added to a solution of cobaltous chloride. Solutions of cobaltous salts yield a precipitate of red *cobaltous hydroxide* when treated with caustic potash solution. The precipitate is soluble in ammonia.

Cobalt silicate is deep blue in colour and is used in the

preparation of blue glass, enamel and porcelain. The paint "cobalt blue" is the powdered silicate.

Cobaltic oxide, Co_2O_3, is obtained as a black powder by carefully heating cobaltous nitrate; further heating results in the formation of *cobalto-cobaltic oxide*, Co_3O_4. Co_2O_3 may also be formed by adding bleaching-powder solution to a solution of cobaltous chloride. It dissolves in acids, but the cobaltic salts so formed are unstable and readily decompose, forming cobaltous salts with liberation of oxygen, etc.

Complex Compounds of Cobalt.—Cobalt forms a great number of complex compounds, which have recently become of importance in connection with the work of WERNER and others on valency. The compounds formed by cobalt salts and ammonia are called the *cobaltammines*; several series of these are known, and they are classified, according to their colour, as *roseocobalt ammines*, *purpureo-*, *xantho-*, *croceo-*, and *flavo*-cobalt ammines, etc. Preparation of some of these salts is an interesting occupation for spare moments in the laboratory.

Potassium cobalticyanide, $K_3Co(CN)_6$, is a pale yellow crystalline solid, resembling potassium ferricyanide, $K_3Fe(CN)_6$, with which indeed it is isomorphous. *Potassium cobalto-cyanide*, $K_4Co(CN)_6$, is also known.

Potassium cobaltinitrite, $K_3Co(NO_2)_6 . 1\frac{1}{2}H_2O$, is obtained as a yellow precipitate by adding potassium nitrite to a solution of a cobaltous salt containing a little acetic acid. It is slightly soluble in water. Nickel does not form an analogous compound, so the two metals may be separated in this way.

NICKEL

Group in Periodic System: VIII; *Symbol:* Ni; *Valency:* 2 and 3; *Atomic Weight:* 58·68; *Melting Point:* 1452°; *Specific Gravity:* 8·9.

History.—Certain minerals that resembled copper ore but from which no copper was obtainable were called by the mediæval German miners *kupfernickel* or "false copper." From these minerals KRONSTEDT in 1751 obtained *nickel*. It

is to BERGMANN, however (1774), that we owe the first accurate description of nickel and its compounds.

Occurrence.—Nickel occurs in small quantities native, in meteorites, but is chiefly found as *kupfernickel*, NiAs. *smaltine* $(Ni,Fe,Co)As_2$, *nickel glance*, NiAsS, *nickel blende*, NiS, *pentlandite* (Cu,Fe,Ni)S, and *garnierite*, a silicate of magnesium and nickel of complex composition. The chief deposits are at Sudbury (Ontario) and New Caledonia.

Extraction.—Nickel is chiefly extracted by MOND'S carbonyl process. The ores are first roasted, when the sulphur is converted into sulphur dioxide and the nickel and other metals left as oxides. These are then heated in a stream of water-gas ($CO + H_2$), which reduces the nickel oxide to nickel; the temperature, however, is adjusted so that the iron oxide is not reduced.

The product is then placed in a tower (the "volatilizer") and heated to a temperature of 80–100° in a current of carbon monoxide. This combines with the nickel to form a volatile substance, *nickel carbonyl*, $Ni(CO)_4$, which is passed into another tower at a higher temperature (180°), where it is decomposed into nickel and carbon monoxide. The carbon monoxide is led off and used again.

$$Ni + 4CO \rightleftharpoons Ni(CO)_4.$$

The nickel so produced is of a high degree of purity (about 99·8 per cent.). It can be further purified, if necessary, by electrolysis.

Properties.—Nickel is a greyish metal that can be polished till it looks like silver. Its specific gravity is 8·9 and its melting-point 1,500°. It is stable in dry air and tarnishes only slowly in moist air; it is therefore used for *nickel-plating* other metals, on which it may be deposited by electrolysis. In chromium-plating, it is used to deposit the chromium on an underlying coating of nickel. In general and magnetic properties nickel resembles cobalt.

It is a constituent of many alloys, used for coinage, etc. *Nickel-steel* is steel containing varying amounts of nickel (usually about 10 per cent. by weight) and is used for armour-

plates on account of its extraordinary toughness, which renders it less likely to develop serious cracks when struck by shells.

Nickel is also widely employed as a catalyst in both pure and applied chemistry and in industry (see p. 185, etc.).

COMPOUNDS OF NICKEL.

Nickel forms at least two oxides, NiO and Ni_2O_3. The former is basic and gives rise to the nickel salts, in which nickel is bivalent. The nickel ion $Ni^{\cdot\cdot}$ is green, as are most nickel compounds.

Nickel carbonyl, the compound used in the extraction of the metal, is a colourless liquid boiling at 43° C. It has the formula $Ni(CO)_4$, as shown by vapour density determinations. On strongly heating it explodes, forming nickel, carbon, and carbon monoxide. It burns in air with a smoky flame.

Nickel may be detected in margarine, fats, etc., where it is liable to occur occasionally (see hydrogen, p. 185), by means of *dimethylglyoxime*, $\begin{matrix} CH_3\text{---}C = N.OH \\ | \\ CH_3\text{—}C = N.OH \end{matrix}$, with which it gives a scarlet precipitate. (See FENTON'S *Notes on Qualitative Analysis*.)

QUESTIONS

1. What do you know of the history of iron?
2. Describe the metallurgy of iron.
3. What is steel? How is it made?
4. How would you prepare the anhydrous chlorides of iron? What are their properties?
5. Write a general account of the compounds of cobalt.
6. How is nickel extracted from its ores?
7. How far do iron, nickel and cobalt resemble one another?

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ANSWERS TO NUMERICAL EXAMPLES

CHAPTER II

5. Pentoxide—1 g. phosphorus combined with 1·29 g. oxygen.
Tetroxide—1 g. „ „ „ 1·032 g. „
Trioxide— 1 g. „ „ „ ·7742 g. „
Weights of oxygen are in ratio 5 : 4 : 3.

6. Stannous—1 g. tin combined with ·2695 g. sulphur.
Stannic— 1 g. „ „ ·5392 g. „
Weights of sulphur in ratio 1 : 2 (approx.).

7. (i) 1 g. vanadium combined with 1·389 g. chlorine.
(ii) 1 g. „ „ „ 2·083 g. „
(iii) 1 g. „ „ „ 2·778 g. „
Weights of chlorine in ratio 2 : 3 : 4.

8. Ferrous—1 g. iron combined with 1·72 g. "sulphate group."
Ferric 1 g. „ „ „ 2·58 g. „
Weights of "sulphate-group" in ratio 2 : 3.

9. Suboxide— 1 g. oxygen combined with 25·9 g. lead.
Monoxide— 1 g. „ „ „ 12·95 g. „
Sesquioxide—1 g. „ „ „ 8·668 g. „
Peroxide— 1 g. „ „ „ 6 475 g. „
Weights of lead in ratio 12 : 6 : 4 : 3.

10. Aurous—1 g. gold combined with ·18 g. chlorine.
Auric—1 g. „ „ „ ·54 g. „
Weights of gold in ratio 1 : 3.

CHAPTER III

No. 2. 87·8.
No. 3. 45·4.
No. 4. 27·7.
No. 5. 64·3 c.c.

CHAPTER IV

No. 1. 2024·7 c.c.s.
No. 2. 2·70 litres.
No. 3. 651·5° C.
No. 4. 164 c.c.s.
No. 5. 21·4 c.c.

CHAPTER VI

No. 7. 31·78.
No. 8. 32·68.
No. 9. 31·7.
No. 10. 24·38.
No. 11. 58 68.
No. 12. 200 6; MI_2.

CHAPTER VII

No. 5. CoAsS.
No. 6. Mg_2SiO_4.
No. 7. $PtN_2H_6Cl_4$.
No. 8. $C_3H_4Br_2$.
No. 9. $C_{26}H_{42}NO_4Na$.

CHAPTER IX

No. 2. 52·3.
No. 5. 22,000 calories.

CHAPTER X

No. 3. 94·6.

CHAPTER XI

No. 6. 593 mm.
No. 7. 181½ atmospheres.
No. 8. 4·07 per cent.
No. 9. 200.
No. 10. 58·2° C., 5·9 atmospheres.
No. 11. 4 atmospheres.
No. 12. 180.
No. 13. 57·72.
No. 14. 49·8°.
No. 15. 40 00° C.
No. 16. 1 882 gms.
No. 17. 173·5.

CHAPTER XII

No. 4. 3·067 gr. mols. acid.
0·067 gr. mols. alcohol.
0·933 gr. mols. ester and water.

CHAPTER XIII

No. 10. 0·913.
No. 11. 0·805.
No. 12. —0·016° C.

CHAPTER XXVI

P. 413. No. 7. 8·93 litres.
No. 12. 41·5% ozone by volume.
No. 13. 0·207% ozone by volume.

P. 426. No. 6. 29 gms. per litre.
No. 7. 1·57 „ „ „
No. 8. 13·87 „ „ „

TABLE OF ATOMIC NUMBERS AND ATOMIC WEIGHTS

Element.	Symbol.	Atomic Number.	Atomic Weight.
Aluminium	Al	13	27·0
Antimony	Sb	51	121·8
Argon	A	18	39·94
Arsenic	As	33	74·96
Barium	Ba	56	137·37
Beryllium	Be	4	9·0
Bismuth	Bi	83	209·0
Boron	B	5	10·82
Bromine	Br	35	79·92
Cadmium	Cd	48	112·40
Caesium	Cs	55	132·81
Calcium	Ca	20	40·07
Carbon	C	6	12·00
Cerium	Ce	58	140·25
Chlorine	Cl	17	35·46
Chromium	Cr	24	52·01
Cobalt	Co	27	58·94
Copper	Cu	29	63·57
Dysprosium	Dy	66	162·5
Erbium	Er	68	167·7
Europium	Eu	63	152·0
Fluorine	F	9	19·0
Gadolinium	Gd	64	157·3
Gallium	Ga	31	69·9
Germanium	Ge	32	72·6
Gold	Au	79	197·2
Hafnium	Hf	72	178·6
Helium	He	2	4·00
Holmium	Ho	67	163·5
Hydrogen	H	1	1·008
Indium	In	49	114·8
Iodine	I	53	126·93
Iridium	Ir	77	193·1
Iron	Fe	26	55·84
Krypton	Kr	36	82·92
Lanthanum	La	57	139·0
Lead	Pb	82	207·20
Lithium	Li	3	6·94
Lutecium	Lu	71	175·0
Magnesium	Mg	12	24·32
Manganese	Mn	25	54·93
Masurium	Ma	43	
Mercury	Hg	80	200·6
Molybdenum	Mo	42	96·0
Neodymium	Nd	60	144·3
Neon	Ne	10	20·2
Nickel	Ni	28	58·68
Niobium	Nb	41	93·1
Radon	Rn	86	222·5
Nitrogen	N	7	14·01
Osmium	Os	76	190·9
Oxygen	O	8	16·00 [standard]
Palladium	Pd	46	106·7
Phosphorus	P	15	31·02
Platinum	Pt	78	195·2
Potassium	K	19	39·1
Praseodymium	Pr	59	140·9
Radium	Ra	88	225·97
Rhenium	Re	75	188·7
Rhodium	Rh	45	102·9
Rubidium	Rb	37	85·45
Ruthenium	Ru	44	101·7
Samarium	Sa	62	150·4
Scandium	Sc	21	44·1
Selenium	Se	34	79·2
Silicon	Si	14	28·3
Silver	Ag	47	107·88
Sodium	Na	11	23·00
Strontium	Sr	38	87·63
Sulphur	S	16	32·06
Tantalum	Ta	73	181·0
Tellurium	Te	52	127·5
Terbium	Tb	65	159·2
Thallium	Tl	81	204·0
Thorium	Th	60	232·4
Thulium	Tm	69	168·5
Tin	Sn	50	118·7
Titanium	Ti	22	47·9
Tungsten	W	74	184·0
Uranium	U	92	238·14
Vanadium	V	23	51·0
Xenon	Xe	54	130·2
Ytterbium	Yb	70	173·5
Yttrium	Yt	39	89·0
Zinc	Zn	30	65·38
Zirconium	Zr	40	91·22