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It may well be believed that the course of work given in this book has been proved by experience to be both interesting and instructive to all classes of students, as stated in the preface. The author has in his mind particularly the mixed classes in training colleges and medical schools, some of the students being beginners, while others have a considerable knowledge of elementary chemistry. For such classes the historical method is undoubtedly the best, and this book provides just what they need, and will moreover be found very valuable by teachers. It gives an account of classical experiments and theories often in the actual words of the original descriptions, and contains many illustrations of the apparatus used by early workers in the science. It is divided into two parts, the first dealing with the discovery of the facts of chemistry, while Part II. discusses chemical theories, beginning with a full treatment of the atomic theory. In both parts recent work is included; thus some account is given of Moseley's investigation of the high frequency spectra of the elements. Short summaries of each chapter are provided, and a bibliographical index is included, which gives in tabular form, with dates, lists of the works of the most prominent investigators. (C. N. 14/1/16)

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HISTORICAL INTRODUCTION TO CHEMISTRY

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HISTORICAL INTRODUCTION TO CHEMISTRY

BY

T. M. LOWRY, D.Sc., F.R.S.

MACMILLAN AND CO., LIMITED
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1915

HEMISTRY

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PREFACE

In the preparation of this volume the purpose has been to present an historical account of the more important facts and theories of chemistry, as these disclosed themselves to the original workers in this branch of science. No attempt has been made to write a formal History of Chemistry, either as a survey of the various periods into which the history of the science may be divided, or in the more usual biographical form. The material has been classified by subjects rather than by authors; but it will be found that under this system the work of individual experimenters is described quite as fully as in a biographical survey, whilst in the case of certain chemists, such as Priestley, Lavoisier and Gay-Lussac, it has been possible to include detailed descriptions of experimental work which could scarcely have found a place in a brief biography.

The Biographical Index provides a key to the work of each author as it is described in the text, and contains most of the essential items for an account in narrative form of the achievements of the great pioneers of chemistry.

In a few cases this index contains dates and titles of works not included in the text, as, for example, Cavendish's work on the density of the earth, and some of Faraday's physical experiments; but no attempt has been made either in the biographical index or in the text to record the later and more detailed developments of organic or of physical chemistry. Such a record would be out of place in a historical

introduction dealing with fundamental facts and problems; only the most incidental references will be found therefore to the work of Hofmann in organic chemistry, or of van t'Hoff in the various branches of physical chemistry. This limitation is of little importance, as the advanced student will find ample descriptions of the achievements and discoveries of these later workers in the two volumes of Memorial Lectures issued by the Chemical Society.

In compiling the present volume, the standard histories of Thomson and of Kopp have been invaluable as guides to the literature, but the whole story has been written afresh from the original sources. Almost without exception, every reference and quotation has been checked directly in the printed proofs against the original text; if, however, any errors should have survived, the author would be very grateful to anyone who would direct his attention to them. The few statements for which dates but no references are given are made on the authority of Kopp, but most of them refer only to incidental points. Much of the narrative, even when not enclosed between inverted commas, is in the actual words of the original descriptions, a feature which the present volume shares with the text-books of 100 years ago, but which has gradually disappeared as the early history of chemistry has become more and more a "twice-told tale."

In order to present the material in the most accessible form, quotations have been taken so far as possible from modern reprints, such as those of Scheele's *Essays*, or the *Alembic Club Reprints*, or from collected *Works* such as those of Lavoisier, Davy, and Stas. To guard against anachronism, full use has been made of contemporary translations of such works as Bergman's *Essays* and Berthollet's *Chemical Statics*; but as the object in view was to present a picture of the development of chemistry rather than a formal history, it was thought better not to introduce unnecessary confusion by using the name "nitric acid" when nitrogen peroxide was meant, nor to obtrude at every point the various names

by which oxygen and chlorine were described up to 1787 and 1810 respectively; but whenever some more familiar term has been introduced into the text, the alteration has been indicated by square brackets.

The detailed descriptions of classical experiments, which form a leading feature of the book, should be of value not only to the student but also to the teacher of chemistry, since they show not merely how the great facts of chemistry might have been discovered, but the actual course of the discoveries themselves. Such information has proved of real value in devising courses of instruction in elementary chemistry, and forms a sure guarantee against an incorrect or illogical sequence; from this point of view the book may be commended to those who are responsible for the training of teachers, as well as to students who intend to become teachers themselves. The historical method has also been found to provide a complete solution of the difficult problem of teaching mixed classes of students, some absolute beginners and others with a considerable knowledge of elementary text-books of chemistry. This problem is insistent in training colleges and in medical schools, and is probably but little less urgent in other departments of teaching. The material included in the present volume has been proved, by several years of actual practice, to provide a means of interesting and instructing both types of students. Even the laws of chemical combination acquire a new interest when presented in the picturesque imagery of Proust, or with some of the glow of Berzelius's early enthusiasm.

In contrast with most of the well-known histories of chemistry, the volume is provided with many illustrations, especially of the apparatus used by the earlier workers. It is unfortunate that large-scale copper-plate illustrations cannot be reduced in exact facsimile without destroying all their technical merits; but great care has been taken that the wood-blocks shall reproduce as faithfully as possible all the essential features of the original drawings. Thus,

Bunsen's burner (1866) has been removed, it is hoped finally, from Dumas's apparatus for the composition of water (1841), and the big spirit-lamp has been restored to its place; and Lavoisier's red-hot gun-barrel is again sealed with clay joints instead of with rubber. The temptation to reconstruct early apparatus (which has led to the association of the Bunsen burner with Lavoisier's work) has been resisted even in the pressing case of Cavendish's experiments on the composition of water, where the gap has been filled by reproducing the contemporary apparatus of Monge; only when the text and illustrations were complete was the discovery made that two of the globes used in these experiments are still preserved in the library of the Royal Institution. The single case in which a figure has been consciously modified is a small alteration in Priestley's blackboard and table (Fig. 19 *b*) with the view of making the most of the limited space available for reproduction.

An exact historical narrative, such as is here presented, could not have been written without free access to books and journals, many of which are rare and some almost inaccessible. I wish to express my indebtedness to Mr. A. H. White, of the Royal Society's Library, and to Mr. F. W. Clifford, the Librarian of the Chemical Society, for their invariable courtesy and helpfulness over a period of several years, as well as to the Institution of Electrical Engineers for access to their important collection of Volta's papers. I am indebted to the late Miss Freund for a quotation from a copy of Wenzel's *Theory of Affinity* in the library of the University of Bonn, to Prof. Victor Henri of Paris for some information in reference to early French publications, and to Prof. Ernst Cohen of Utrecht for a number of historical details. The early chapters of the book were written in collaboration with the late Mr. G. C. Donington, whose double qualification in History and Natural Science gave special value to his opinions and criticisms. I have also derived great benefit from the expert advice which Prof. R. A. Gregory

and Mr. A. T. Simmons have generously given to me through the whole period occupied by the compilation of the book. The proof-sheets have been read by Mr. W. A. Davis, by Dr. Merriman, by Lieut. Victor Steele and by Mr. H. S. Patterson, to whom I am grateful for much valuable help and criticism.

T. M. Lowry.

London:
August, 1915.

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HISTORICAL INTRODUCTION TO CHEMISTRY

PART I

ELEMENTS AND COMPOUNDS

CHAPTER I

RAW MATERIALS AND PRIMITIVE MANUFACTURES

THE study of Chemistry as a branch of natural knowledge may be said to begin with the work of the Honourable **Robert Boyle** (1627–1691). But, at the time when Boyle commenced his work, the most important chemical processes and many well-defined substances were already familiar, many of them having been used for practical purposes from very early times. Early chemical discoveries group themselves naturally into three periods:

1. **The Prehistoric and Ancient Period** culminated in the civilisations of Egypt, Greece, and Rome. During this period many of the raw materials, which it is the business of Chemistry to study, were collected, purified, and brought into common use in daily life; but only in a few cases were processes discovered for the preparation of new substances by the action of these raw materials on one another. Evidence as to the substances which were known during this period is derived mainly from casual references in the writings of ancient authors rather than from systematic works of a scientific character.

2. **The Earlier Alchemistic Period** extended from the early part of the Christian era to about 1500 A.D. During

this second period the search for the PHILOSOPHER'S STONE, a substance by which baser metals could be converted into gold, led to an exhaustive study of all available materials. Their actions upon one another were also studied, and the effect of heat upon them both separately and in mixtures of varying complexity. In this way, many new processes and compounds were discovered. The physician **Geber**, who lived in Spain at the close of the eighth century, was perhaps the greatest of the alchemists; the writings that have been attributed to him afford a clear picture of the progress which the science had made in the hands of the earlier alchemistic workers.

3. **The Later Alchemistic Period** extended roughly from 1500 to 1650 A.D. During this period the search for the philosopher's stone (then regarded as a means of healing all diseases) and for the equally imaginary ELIXIR OF LIFE gradually gave place to deliberate investigations of the action of drugs on the human body and to the preparation of new substances for use in medicine. The writings of **Glauber** (1603–1668) contain a description of many substances discovered during this period, and give a good idea of the state of knowledge at the time when Boyle laid the foundations of the modern science of Chemistry.

The following pages contain an account of some of the most important materials which became known during the earlier part of these three periods, but large groups of substances (including, for instance, the acids and alkalis) are reserved for separate treatment in subsequent chapters. The various materials may be classified conveniently under the following headings:

Soluble salts.—Among the substances in common use from very early times was the salt obtained by the evaporation by the sun's rays of sea-water collected in shallow pools along the sea-shore. The product was a mixture of several substances, remarkable for their sharp taste and

their solubility in water, and contained a large proportion of the substance now known as COMMON SALT (Fig. 1). The name SALT was applied subsequently to all similar solids. Thus Boyle defined a "salt" as being characterised by two qualities, that "it is easily dissoluble in water and that it affects the palate with a savour, whether good or evil" (see *Experiments and Notes about the Producibleness of Chymical Principles*, 1680, p. 3; *Works*, 1725, III. 365).

SODA (Latin *natrum*), known from the earliest times as a natural deposit on the shores of the soda-lakes of Egypt, was originally called "nitre"; it was employed as a cleansing agent and in the manufacture of glass, but was almost unknown in Western Europe until the eighteenth century, when it was prepared from the ash of marine plants. POTASH, or "pearl ash," a white solid closely resembling soda in many of its properties, probably received its name from the fact that it was obtained by extracting the white ash of burnt wood with water in earthenware pots. During the middle ages the chief source of potash was the "lees" or sediment of wine to which the name of TARTAR was given; this sediment was calcined, and the potash thus prepared, the "burnt lees of wine," was known as CALCINED TARTAR, or more simply as "tartar." These two substances, soda and potash, were known as ALKALIS, and were remarkable for

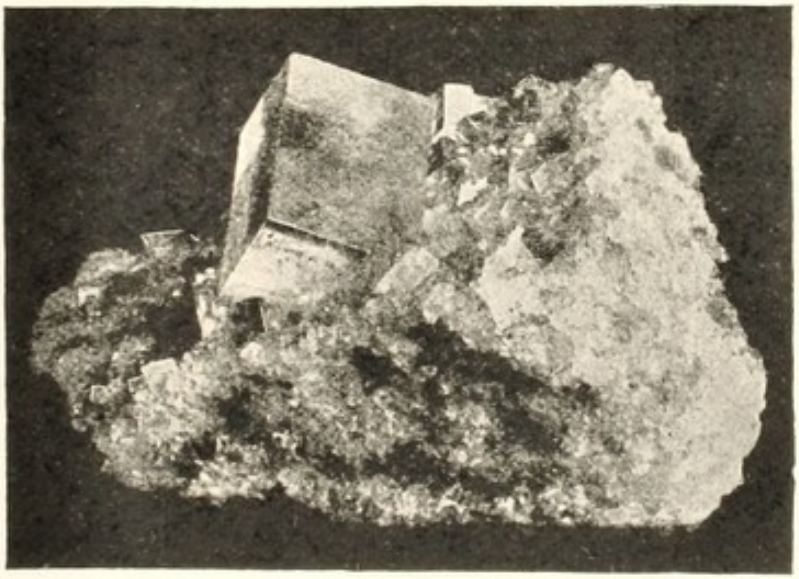


FIG. 1.—CUBIC CRYSTAL OF SALT.
British Museum (Natural History).

their power of effervescing when mixed with acids. This property served to distinguish the Egyptian nitre or soda from the common nitre or saltpetre described in the next paragraph. It is referred to in the proverb: "As he that taketh away a garment in cold weather, and as vinegar upon nitre, so is he that singeth songs to an heavy heart" (Prov., xxv. 20). In reference to this passage Robert Boyle,

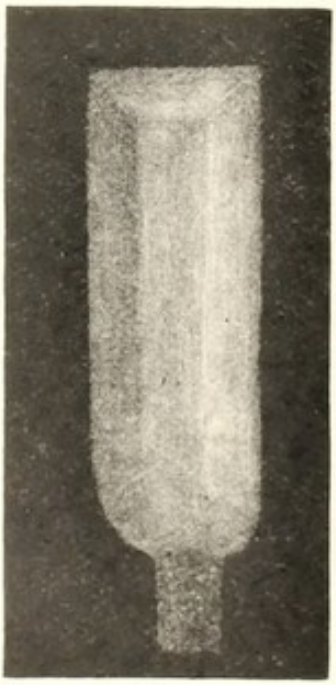


FIG. 2—CRYSTAL OF SALTPETRE. British Museum (Natural History).

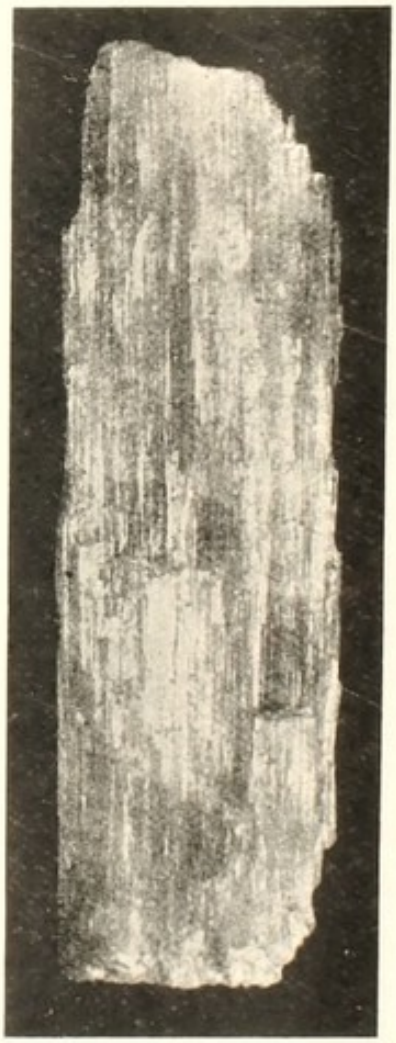


FIG. 3—SAL-AMMONIAC.

who had received a specimen of Egyptian "nitre" from Constantinople, wrote in 1680:—

"And here . . . . give me leave to take notice of a text of the holy Scripture, that has sometimes puzzled not only me, but far better Critics in the Hebrew tongue than I, ... where to illustrate Things very incongruous to one another

the disagreement of Vinegar and Nitre is mentioned, for supposing the words to be rightly translated . . . . it seems very hard to find what show of Antipathy there is between Vinegar, and the Saltpetre that is commonly sold in our shops for Nitre ; wherefore strongly presuming that Solomon . . . . made use of Egyptian Nitre . . . . when once I received the Nitre that I have mentioned, and saw it in signs of an Alcalizate nature, I quickly poured upon it some strong Vinegar, and found as I expected that there presently ensued a manifest conflict, with noise, and store of bubbles, with which Experiment I afterwards acquainted some Critics, and other learned men who were not ill-pleased with it" (*Experiments and Notes about the Producibleness of Chymical Principles*, 1680, p. 30 ; *Works*, 1725, III. 371).

FIG. 4—THE COLENSO DIAMOND
British Museum (Natural History).

SALTPETRE OR NITRE (Fig. 2), a salt-like substance formed by the decay of animal matter and found as an incrustation in the neighbourhood of stables, was introduced into Europe from the East. SAL-AMMONIAC (Fig. 3), a salt of similar origin, was manufactured by heating camel's dung ; it differed from other salt-like substances in that it could be vaporised completely by gentle heat. The name was first applied to a mixture of common salt and soda found near the temple of Jupiter Ammon in Upper Egypt, but was transferred by the early alchemists to the volatile salt just referred to.

Earths and rocks.—A number of other substances, which may be classed together as earths or rocks, were employed for various purposes. FULLER'S EARTH, a white, friable clay, was used as a cleansing agent prior to the manufacture of soap. CHALK, LIMESTONE, and MARBLE were employed

largely in their natural condition as building materials, but were also converted into lime by the action of heat and used in the preparation of mortar. SAND was used with soda in the manufacture of glass.

Many crystals and precious stones were also known and valued for personal adornment and for decorative purposes. Amongst the first to attract attention were probably EMERALD, TOPAZ, DIAMOND (Fig. 4), and QUARTZ (Fig. 5); the last

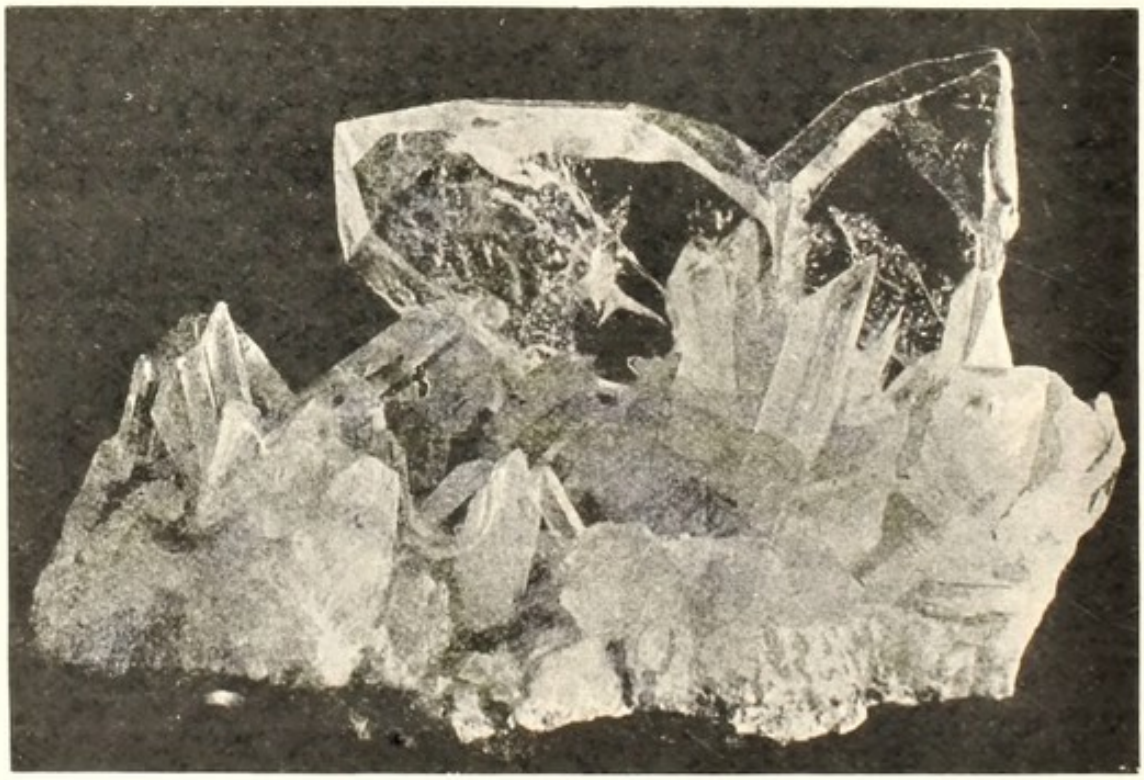


FIG. 5—CRYSTALS OF QUARTZ.
British Museum (Natural History)

substance, known also as ROCK-CRYSTAL, or CRYSTAL, gave its name to the whole of this class of substances.

Substances of organic origin.—Many of the substances known in ancient and mediæval times were formed by the agency of living organisms, either animals or plants. Among these may be mentioned SUGAR (in the form of honey), TURPENTINE, OILS, FATS, and WAXES (extracted from plants and from the bodies of animals), AMBER (a fossil resin), and PEARLS. WINE and VINEGAR were obtained by fermentation

from the juice of the grape and other fruits, whilst saltpetre and sal-ammoniac have been referred to already as products of the decay of animal matter.

Substances prepared by the action of fire.—Many other substances were prepared from natural materials by the action of fire. LIME, obtained in this manner from limestone or chalk, has been mentioned previously, but greater importance attaches to the use of fire as an agent for the preparation of metals. Two metals, GOLD and SILVER, are distributed somewhat widely in a native state, and were known from the earliest times. Native COPPER was also found and used.[1] MERCURY (Latin *hydrargyrum*, or liquid silver), which occurs in minute droplets in certain rocks, was known to the Greeks.

Other metals were obtained by smelting their ores, that is, by heating them with charcoal. Amongst these was TIN, obtained by smelting TINSTONE and valued highly as a means of hardening copper. The hard alloy of copper and tin is known as BRONZE. The stage of civilisation during which this alloy came into common use has been called the "Bronze Age," although the various European peoples learnt to use it for the manufacture of weapons and implements at widely different times. The smelting of IRON was a more difficult process, since a much higher temperature was required than in the case of tin or copper. The use of iron, therefore, follows that of bronze in the history of each race. Thus, the Greeks, as described in the Homeric poems, were accustomed to the use of bronze weapons and implements, but esteemed iron much more highly—a lump of iron being described as a valuable prize in a contest. The Romans had reached the "Iron Age" by early classical times. Four hundred years later, at the opening of the Christian era, the Germanic races still employed the earlier

[1] "A land whose stones are iron, and out of whose hills thou mayest dig brass" (Deut. viii. 9).

known metal, although the use of iron had superseded that of bronze partially amongst the Gauls and other Celtic races. LEAD was known to the Romans at the time of their conquest of Britain ; the mining of lead ores was carried on by them in Derbyshire and in other parts of the island.

Fire was also used as an agent in the purification of the so-called "noble metals," gold and silver, from baser impurities, such as tin and lead, the latter being converted into dross. The dross obtained by burning lead in order to separate it from the silver which it contained, received a special name, LITHARGE, that is, the stone (Greek, λίθος) obtained from silver (Greek, ἄργυρος) ; it was valued because it could be converted by gentle roasting into the scarlet paint known as MINIUM or RED LEAD.

FIG. 6—ARROWHEAD CRYSTALS OF MARCASITE
British Museum (Natural History).

Substances produced by weathering or decay.—New materials were also obtained by the natural processes of weathering or decay. SALTPETRE, WINE, and VINEGAR have been mentioned as examples of this kind, but special reference may be made to the green, glassy substance which is formed when the minerals MARCASITE and PYRITES (Figs. 6, 7, 8) are allowed to weather. The brilliant golden nodules of marcasite, which in England are often found as "thunderbolts," embedded in the chalk, decay and become "rusty" almost as easily as iron. When the rusty mass is extracted

with water, a soluble substance is dissolved out and separates in green crystals on allowing the washings to evaporate. The glassy appearance of the crystals won for the substance the name of VITRIOL (Latin *vitrum*, glass). It played a most important part in the early development of chemistry on account of

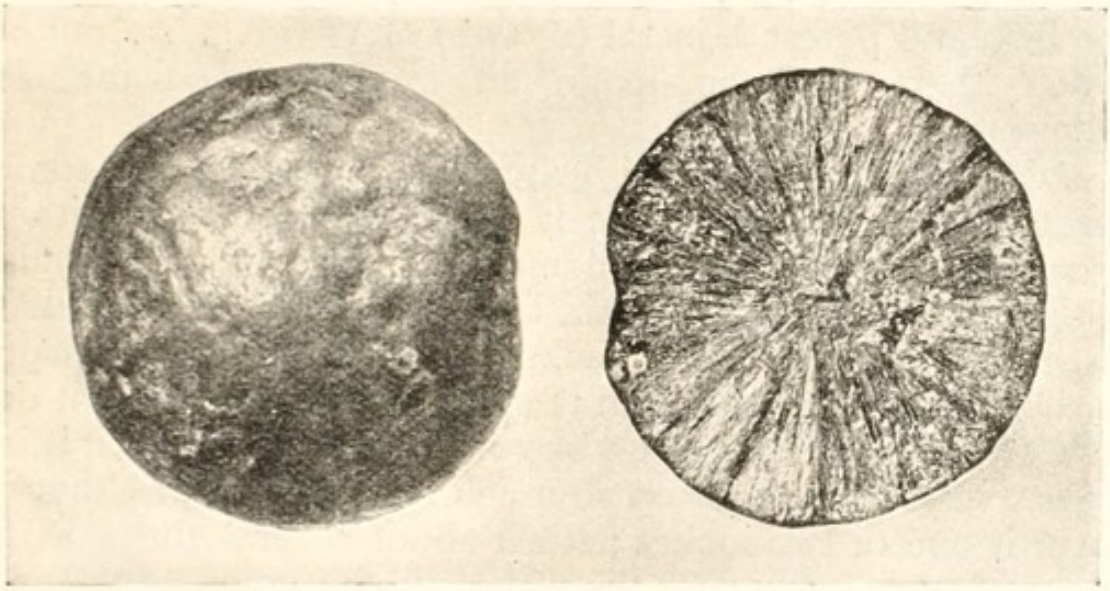


FIG. 7—NODULE OF MARCASITE AS DESCRIBED BY GLAUBER.

FIG. 8—STRIATED CUBES OF PYRITES.

Marcasite and iron pyrites both consist of disulphide of iron (FeS_2), but they differ in crystalline form. The crystals of iron pyrites are cubic whilst those of marcasite belong to the orthorhombic system.

the discovery of an oily product, OIL OF VITRIOL, to which it gave rise when strongly heated (see Chapter II). The following description of the way in which green vitriol was prepared from nodules of marcasite was written by Glauber about 1648 A.D., and translated into English in 1651 :—

"Commonly in all fat soils or clayey grounds, especially in the white, there is found a kind of stones, round or oval in form. . . . . Which if it is cleansed from the earth, and beaten to pieces, looks within of a fair yellow and in streaks, like a gold Marcasite, or a rich gold Ore, but there is no other taste to be perceived in it, than in another ordinary stone ;. . . . Now this stone is nothing else, but the best and purest Mineral (or Ore) of Vitriol, . . . out of which there may be made an excellent medicine, as followeth.

Take this Ore or Mineral beaten into pieces, and for some space of time, lay or expose it to the cool air, and within twenty or thirty days it will magnetically attract a certain saltish moisture out of the air, and grow heavy by it, and at last it falleth asunder to a black powder, which must remain further lying there still, until it grow whitish, and that it do taste sweet upon the tongue like vitriol. Afterward put it in a glass vessel, and pour on so much fair rainwater, as that it cover it one or two inches ; stir it about several times in a day, and after a few days the water will be coloured green, which you must pour off, and pour on more fair water, and proceed as before, stirring it often until that also come to be green : this must be repeated so often, until no water more will be coloured by standing upon it. Then let all the green waters which you poured off run through filtering paper, for to purify them ; and then in a glass-body [*i.e.*, a retort] cut off short let them evaporate till a skin appear at the top : then set it in a cold place, and there will shoot little green stones, which are nothing else but a pure vitriol : the remaining green water evaporate again, and let it shoot as before : and this evaporating and crystallising must be continued until no vitriol more will shoot" (*Philosophical Furnaces*, Part II. 1651, p. 71 ; *Works*, 1689, I. 21).

Summary and Supplement

Scientific Chemistry begins with **Robert Boyle** (1627–1691), but was preceded by three periods, namely :—

(1) An *Ancient Period*, extending up to the Christian era, in which many primitive manufactures were developed ;

(2) An *Earlier Alchemistic Period*, extending to about 1500 A.D., during which many substances were discovered in the attempt to convert base metals into gold ;

(3) A *Later Alchemistic Period*, extending to about 1650 A.D., in which new substances were prepared and tested for medicinal purposes.

Important substances known at a very early date include :

1. **Soluble Salts.**—
   Common Salt (Sodium chloride, NaCl).
   Washing Soda (Sodium carbonate, $Na_2CO_3,10H_2O$).
   Potash (Potassium carbonate, K_2CO_3).
   Saltpetre or Nitre (Potassium nitrate, KNO_3).
   Sal-ammoniac (Ammonium chloride, NH_4Cl).

2. **Earths and Rocks.**—
   Fuller's Earth.
   Chalk, Limestone, Marble (Calcium carbonate, $CaCO_3$).
   Sand, Quartz (Silicon dioxide, SiO_2).
   Emerald. Topaz. Diamond.

3. **Organic Products.**—
   Sugar. Turpentine. Oils, Fats and Waxes. Amber and Pearls. Wine and Vinegar. Saltpetre and Sal-ammoniac.

4. **Igneous Products.**—
   Lime from Limestone ($CaCO_3 \rightarrow CaO + CO_2$).
   Tin (*stannum*, Sn) from Tinstone
   ($SnO_2 + C \rightarrow Sn + CO_2$).
   Iron (*ferrum*, Fe) from Ironstone
   ($Fe_2O_3 + 3C \rightarrow 2Fe + 3CO$).
   Litharge from Lead ($2Pb + O_2 \rightarrow 2PbO$).

Also **Native Metals.**—
   Gold (*aurum*, Au).
   Silver (*argentum*, Ag).
   Copper (*cuprum*, Cu).
   Mercury (*hydrargyrum*, Hg).

5. **Products of Decay.**—Especially, Iron Pyrites (FeS_2)
   $\rightarrow$ Green Vitriol (Ferrous sulphate, $FeSO_4,7H_2O$)
   $\rightarrow$ Oil of Vitriol (Sulphuric acid, H_2SO_4).

CHAPTER II

THE ACIDS

A. Discovery of the Common Acids

Vegetable acids.—The earliest acids known were of vegetable origin, but until the middle of the eighteenth century scarcely any attempt was made to isolate them from the "sour" liquids in which they occur, or even to distinguish between various acids of similar origin. The most familiar of the vegetable acids was sour wine or VINEGAR, which was known to have a remarkable action upon soda (Chapter I. p. 4). Its power of dissolving chalky materials is illustrated by the story of Cleopatra and the pearls which she dissolved and drank in a cup of vinegar, as well as by Livy's fantastic story of the use of vinegar by Hannibal to dissolve away the limestone rocks of the Alps. DISTILLED VINEGAR was familiar to the alchemists from the time of Geber, and was frequently used as a solvent, but it was not until a much later period that the acid constituent, ACETIC ACID, was isolated in a pure state.

A large number of crystalline acids of animal and vegetable origin were, however, prepared at the close of the eighteenth century by the Swedish chemist, **Carl Wilhelm Scheele,** (1742–1786), whose work on these substances may be

regarded as the basis of the modern science of "Organic Chemistry." Amongst the acids discovered by Scheele were TARTARIC ACID prepared in 1770 from "tartar," in which it is present in combination with potash; BENZOIC ACID from benzoïn (1775); URIC ACID from bladder-stones (1776); LACTIC ACID from sour milk (1780); OXALIC ACID by the action of nitric acid on oils (1783); CITRIC ACID from lemon-juice (1784); and MALIC ACID from apples (1786).

Oil of vitriol, or sulphuric acid.—A great advance was made by the discovery in the early alchemistic period of powerful acids of mineral origin. The first of these to be prepared was undoubtedly oil of vitriol, which the writings of Geber (800 A.D.) describe as obtained by the distillation of alum. The acid can be prepared more easily by distilling green vitriol, as described in the writings of Basil Valentine and of Glauber, and it was from this method of preparation that the acid obtained the name OIL OF VITRIOL. The first stage of distillation results in the formation of clouds of steam: subsequently, dense white fumes are produced, which dissolve in the condensed steam to form oil of vitriol. When the white fumes are condensed separately, a strongly fuming liquid is produced which hisses violently when poured into water: this fuming liquid is often called NORDHAUSEN OIL OF VITRIOL from the name of the German town in which it used to be manufactured. The red, rusty residue remaining behind in the retort was known as COLCOTHAR, and is now sold as ROUGE. This method of making oil of vitriol is described by Basil Valentine as follows:—

"If you get such deep graduated and well prepared Mineral, called *Vitriol*, then pray to God for understanding and wisdom for your intention and after you have calcined it, put it into a well coated Retort, drive it gently at first, then increase the fire, there comes in the form of a white spirit of vitriol in the manner of a horrid fume, or wind, and cometh into the Receiver as long as it hath any such material in it." (*Last Will and Testament*, p. 158.)

The acid is now prepared by more direct methods from iron pyrites or from sulphur. The presence of sulphur in pyrites[1] and in oil of vitriol was known in Boyle's time, but the name SULPHURIC ACID by which the acid is now generally known was not adopted until 1787.

Aqua fortis or nitric acid.—A second acid of mineral origin was described by Geber as obtained by distilling a mixture of saltpetre with green vitriol and alum. At a later period Glauber showed that it could be prepared more easily, and in a much purer condition, by distilling a mixture of oil of vitriol and saltpetre from a glass retort heated gently in a bath of hot sand over a furnace. From its remarkable power of dissolving metals such as copper and silver, which were not readily acted on by oil of vitriol, it came to be known as AQUA FORTIS. In Boyle's time its acid properties, its volatility, and its origin from nitre were indicated by the name "acid spirit of nitre"; this was afterwards shortened to nitrous or NITRIC ACID, the last name being introduced by Lavoisier in 1787.

Aqua regia —By dissolving sal-ammoniac or salt in aqua fortis, Geber prepared a still more powerful acid which was capable of dissolving gold; it was therefore called AQUA REGIS, or AQUA REGIA.

Spirit of salt or muriatic acid.—The method of preparing spirit of salt by heating salt with oil of vitriol in a glass retort is due to Glauber. He had previously made it by throwing a mixture of salt, green vitriol, and alum upon the hot fuel of a charcoal fire and passing the fumes into a large glass globe. The action of oil of vitriol on salt produces a pungent fume which escapes into the air and is lost; but Glauber found that this fume condensed readily in a receiver half filled with water, giving an acid liquid which he described

[1] "Vitriols are produced from the stone . . . called Marchasite, and from it on the application of fire the flowers of common sulphur are elicited in considerable abundance" (John Mayow, *Medico-physical Works*, 1674; *Alembic Club Reprints*, XVII. 28).

as SPIRIT OF SALT; another common name for the acid is MURIATIC ACID (Latin, *murium*, brine). The gas itself was first isolated by Priestley, who showed that it could be collected quite readily over mercury.

Glauber also showed that the mixture of spirit of salt and aqua fortis, which is produced by distilling salt and saltpetre with oil of vitriol, was capable of dissolving gold and had the same properties as the aqua regia prepared by Geber's method.

B. PROPERTIES OF THE ACIDS.

Taste. Action on vegetable dyes.—The most conspicuous property possessed by all the above acids was their sour taste. To this may be added the fact that they were capable of changing the colour of various vegetable dyes. During the eighteenth century, SYRUP OF VIOLETS, which changes from violet to red on the addition of an acid, was largely used as a test or INDICATOR for these substances; at a later date "tournesol," or LITMUS, which changes from blue to red more easily than syrup of violets, and various artificial dyes, were used for this purpose.

When concentrated, the mineral acids were found to have very corrosive properties. Glauber describes the charring of a slip of wood and the ignition of turpentine and of spirit of wine as properties of the strongest oil of vitriol. Aqua fortis was equally corrosive, but both acids become harmless when sufficiently diluted. The diluted mineral acids were at one time employed in medicine and as substitutes for vinegar and lemon-juice in the preparation of food.

Action on alkalis and chalk.—When added to soda or potash all the acids were found to produce the violent effervescence that was first noticed in the action of vinegar on soda (p. 4). A similar "breaking out of air" took place when chalky materials were acted on by acids: in this action

the chalk was usually dissolved, but oil of vitriol gave a white solid which was proved by Margraaf, in 1750, to be identical with the mineral GYPSUM or SELENITE (Fig. 10, p. 19), from which "Plaster of Paris" is made by gentle burning. The origin and the nature of the "air" which is set free in these actions are discussed in Chapters IV. and VI.

Action of acids on metals.—The acids also had the property of corroding or dissolving metals. The poisonous green powder known as VERDIGRIS was prepared at a very early date by the action of vinegar on copper, and was used as a paint during the classical period. The mineral acids were found to act on metals in a much more powerful way; by the time of Geber (circ. 800 A.D.) methods had been discovered for dissolving all the metals that were known. The action of acids on metals was often accompanied (as in the case of soda and chalk) by the breaking out of a gas, but for many centuries no method was known by which these fugitive products could be collected. The important discoveries which were made when at last it was found possible to isolate and examine them are described in Chapter V.

C. Preparation of New Salts and Nomenclature of Salts

New salts.—One result of the discovery of the acids was to add very greatly to the number of "salts" which were known. When an acid acts on a metal, on chalk, or on an alkali, a solution is produced which no longer has the sour taste of the acid. These solutions contain a variety of salt-like substances, which can be isolated by evaporating either to dryness or until crystals begin to separate. In this way many beautiful and useful salts were obtained. At first a special name was given to each salt; but later a

system was devised in which each salt was named after the acid and the BASE (metal, alkali, or earth) from which it was derived, *e.g.*, nitrate of silver, sulphate of potash, muriate of lime. This system was initiated about the middle of the eighteenth century and completed by a group of French chemists in 1787 [1]; it led inevitably to the inclusion in the category of "salts" of many insoluble and tasteless substances. Selenite, for instance, when prepared by the action of oil of vitriol on lime or chalk, could scarcely be excluded from the category of salts merely because it was only slightly soluble in water; for the same reason it was necessary to regard as a salt the insoluble muriate of silver, which could scarcely be separated in an arbitrary way from the soluble muriates of copper and gold.

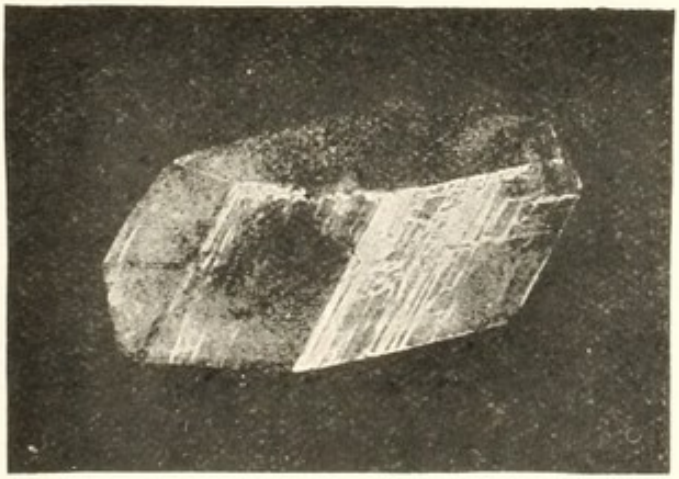


FIG. 9—CRYSTAL OF BLUE VITRIOL OR SULPHATE OF COPPER.

Some of the more important salts prepared with the help of the acids are described below.

Vitriols or sulphates.—The salts prepared by the action of oil of vitriol on metals were of a glassy crystalline character, which won for them the name of VITRIOLS.

"Out of all Metals there can be made a Vitriol or Chrystal (Chrystal and Vitriol is taken for one)." (Basil Valentine, *Last Will and Testament*, p. 157.)

This name was afterwards limited to crystals prepared from, or related to, oil of vitriol. The most important of these were GREEN VITRIOL, and BLUE VITRIOL (Fig. 9),

[1] The *Méthode de Nomenclature Chimique*, by MM. de Morveau, Lavoisier, Berthollet, and Fourcroy, was published in Paris in 1787, and translated into English in 1788 and 1796.

obtained by the weathering of different varieties of pyrites. The blue vitriol was of special interest because iron dipped into it became coated with copper, and seemed to have been transmuted into that metal. These two vitriols were prepared artificially by the action of oil of vitriol on plates of iron or copper, by Glauber, who writes as follows :—

"Take of your heavy oil . . . . as much as you please, put it into a glass body together with plates of copper or iron, set it in a warm sand, and let it boil until that the oil will dissolve no more of the metal, then pour off the liquor, filter it through brown paper, and put it into a low gourd glass and set it in sand, and let the phlegm evaporate until there appear a skin at the top, then let the fire go out, and the glass grow cold, then set it in a cold place, and within some days there will shoot fair Crystals ; if of Iron, greenish ; if of Copper, something bluish ; take them out and dry them upon filtering paper, the remaining liquor, which will not shoot into Vitriol, evaporate again in sand, and then let it shoot as before ; continue this proceeding, until all the solution (or filtered liquor) be turned to Vitriol" (*Philosophical Furnaces.* Part IV ; *Works*, I. 18).

These two vitriols were described by Lavoisier and his colleagues as SULPHATE OF IRON and SULPHATE OF COPPER, after the acid and metals from which they were derived.

GLAUBER'S SALT was prepared by the action of oil of vitriol on common salt. When this action was carried out in a glass retort, the salt was separated easily in a pure condition by crystallisation. Its discoverer attributed to it almost miraculous properties and called it "sal mirabile." It was afterwards prepared from oil of vitriol and soda, and was therefore called SULPHATE OF SODA. The corresponding salt prepared by the action of oil of vitriol on potash was known in Boyle's time as VITRIOLATED TARTAR, but in Lavoisier's system became SULPHATE OF POTASH.

GYPSUM or SELENITE (Fig. 10), which could be prepared

artificially from oil of vitriol and chalk or lime (p. 11), was called SULPHATE OF LIME. EPSOM SALTS, a purgative salt derived from mineral springs, was shown by Black in 1755 to contain a base MAGNESIA in combination with oil of vitriol; it was therefore called SULPHATE OF MAGNESIA.

Nitres or nitrates.—NITRE or SALTPETRE (Fig. 2, p. 4), for many centuries the only source from which nitric acid and the nitrates could be derived, was prepared artificially in 1674 by John Mayow, a friend and contemporary of Boyle, by recombining the nitric acid with potash; its systematic name was therefore NITRATE OF POTASH. A NITRATE OF SODA was prepared by Geber; enormous deposits of this salt have been discovered in the desert regions of Chile, and millions of tons are now exported every year for use in agriculture under the name of CHILE SALTPETRE.

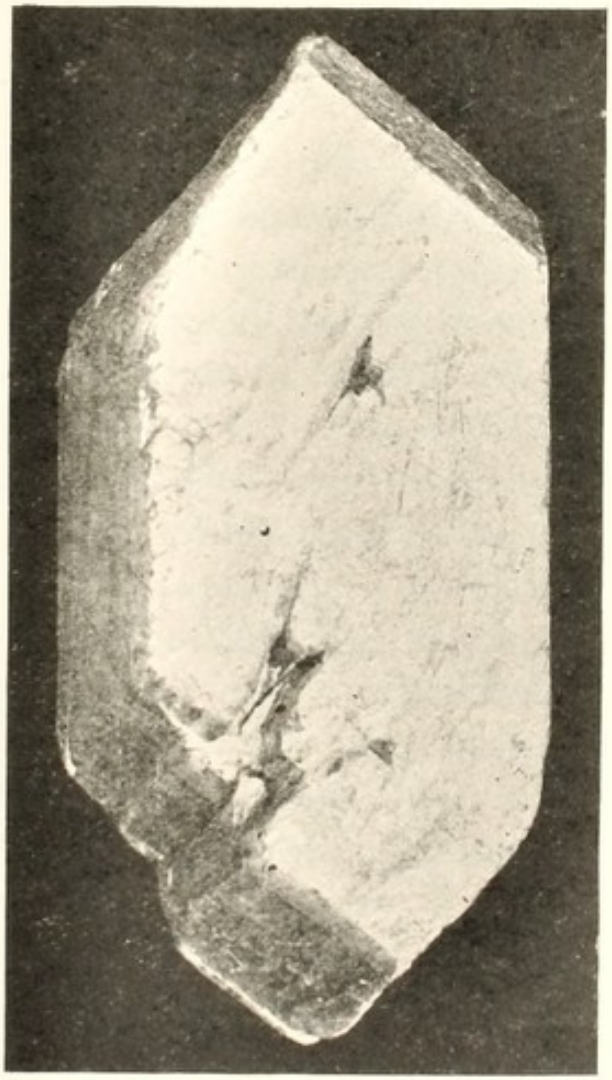


FIG. 10—LARGE CRYSTAL OF GYPSUM OR SELENITE (Sulphate of Lime).

The nitrates of the metals were well-known to the Alchemists. Geber describes LUNAR CAUSTIC, the NITRATE OF SILVER, as prepared in the form of "small fusible stones like crystal," by dissolving silver in aqua fortis and boiling away two-thirds of the water in a long-necked flask. The nitrates of lead, copper, iron, and mercury, were also prepared at an early date.

Muriates.—Glauber, who discovered the first efficient method of making spirit of salt or muriatic acid, prepared the MURIATES OF IRON, COPPER, GOLD, and other metals, by the action of spirit of salt, or of aqua regia upon the metals; he obtained them in the form of strong solutions which he described as "oil of Mars," "oil of Venus," etc., in accordance with the alchemistic system (which survives in the case of Mercury) of calling each of the common metals after a planet.

Common salt, which can be prepared artificially by recombining muriatic acid with soda, is a MURIATE OF SODA. The corresponding MURIATE OF POTASH, known as SAL SYLVII, or SYLVINE, was prepared by the action of muriatic acid on wood-ashes or potash. Extensive deposits of the salt have been found at Stassfurt in Germany; the mineral is used on a large scale as a fertiliser in agriculture, and is one of the chief sources from which potash is derived.

Black in 1755 prepared the MURIATE OF MAGNESIA, and compared its properties with those of MURIATE OF LIME.

Acetates.—Of the salts derived from organic acids the most important were the ACETATES prepared from vinegar, or acetic acid. The ACETATE OF SODA and ACETATE OF LIME prepared by the action of vinegar on soda and on chalk (as described on p. 15), were amongst the first salts to be prepared artificially. Mention may also be made of the ACETATE OF LEAD which Basil Valentine prepared from vinegar and litharge, and which acquired the name SUGAR OF LEAD on account of its sweet taste; also of the ACETATE OF COPPER, which he prepared by the action of vinegar on verdigris.

"There is extracted from calcined Saturn [*i.e.*, burnt lead or litharge] with distilled Vinegar a Crystalline Salt."

"Take some pounds of Verdigris, extract its Tincture with distilled Vinegar, let it shoot, then you have a glorious Vitriol." (Basil Valentine, *Last Will and Testament*, pp. 349 and 351.)

Black in 1755 prepared the ACETATE OF MAGNESIA, in addition to the muriate, nitrate, and sulphate, for comparison with the corresponding salts of lime.

Classification of salts.—The salts described above were prepared by the action of acids (1) on *metals* such as iron and copper; (2) on the *alkalis*, soda and potash; (3) on *earths* such as lime and magnesia. The distinction, which was at first made between these three classes of salts, was rendered of little value by the observation that the salts of metals could be prepared much more easily from the earthy calces which are formed when the metals are burnt: Glauber, for instance, showed that the muriate of copper was prepared easily by the action of muriatic acid on the calcined metal, although the metal itself was attacked but slowly. The distinction was broken down finally at the commencement of the nineteenth century by the discovery that the alkalis and earths were themselves calces of easily-burnt metals. When this had been proved the custom arose of describing all salts as derivatives of metals. Thus gypsum, which was called by Lavoisier "sulphate of lime," is now described as CALCIUM SULPHATE, and Glauber's salt is called SODIUM SULPHATE instead of "sulphate of soda." The older names are, however, still used in commerce and in pharmacy.

Strength of acids.—The fact that oil of vitriol could displace muriatic acid from common salt, and nitric acid from nitre, was recorded by Glauber. Attention was directed at first mainly to the liberated acid, but it was recognised soon that a soluble substance was left behind which contained the "fixed salt" (*i.e.*, the base or alkali) of the original substance in combination with the stronger vitriolic acid. Thus, when oil of vitriol acted upon common salt, the residue of Glauber's salt was found to be identical with sulphate of soda prepared by the action of oil of vitriol on soda; when nitre was used, the residue was a "vitriolated tartar" or

sulphate of potash identical with that prepared from oil of vitriol and "tartar" or potash.

These actions were studied carefully by **John Mayow**, a London Physician (1645–1697), who pointed out in 1674 that "although [acids] and [alkalis] pass into a neutral substance when they meet, yet they do not, as is generally supposed, entirely destroy each other," since when the conditions are suitable both the acid and the alkali may be recovered from the salt. Thus:—

"If oil of vitriol is poured upon nitre, which consists of an [alkali] and of a volatile [acid] (as was shown above), the fixed salt [*i.e.*, the base] of the nitre will soon leave its own acid and will enter into union with the acid of the vitriol, which is more concordant with it . . . . That the case is so, is clear, for if nitre mixed with oil of vitriol be distilled, the spirit, or [acid] of the nitre will pass under a mild heat into the receiving vessel, while yet in other circumstances that spirit will not be carried up except by a very vehement fire . . . . It is a corroboration of this view that the mass left in the retort after a distillation of this kind, closely resembles vitriolated tartar, and can be properly substituted for it." ("Of the combination of contrary salts," *Medico-physical Works*, A.C.R. XVII. 161—162.)

As oil of vitriol was found to liberate nitric acid from any nitrate and muriatic acid from any muriate, it was regarded as stronger than either of these acids, whilst vinegar was found by similar tests to be weaker than the three mineral acids. It is recognised now that this rough and ready method is not the best test of the strength of an acid, as it depends too largely on the readiness with which the various acids can be driven off in the form of vapour. But observations such as these were of great importance because they showed clearly that all salts possessed a dual structure; they thus prepared the way for the system of classifying salts which is described in the preceding paragraphs.

Summary and Supplement

A and B.—Discovery and Properties of the Acids.

Vegetable Acids include :—

Acetic acid, $C_2H_4O_2$, from Vinegar (known to Geber) ;
Tartaric acid, $C_4H_6O_6$, from Tartar (Scheele, 1770) ;
Benzoic acid, $C_7H_6O_2$, from Benzoïn (Scheele, 1775) ;
Uric acid, $C_5H_4N_4O_3$, from Bladder-stones (Scheele, 1776) ;
Lactic acid, $C_3H_6O_3$, from Sour Milk (Scheele, 1780) ;
Oxalic acid, $C_2H_2O_4$, from Oils (Scheele, 1783) ;
Citric acid, $C_6H_8O_7$, from Lemons (Scheele, 1784) ;
Malic acid, $C_4H_6O_5$, from Apples (Scheele, 1786).

Mineral Acids include :—

Oil of Vitriol, Vitriolic acid, or Sulphuric acid, H_2SO_4, prepared by distilling Alum (Geber) or Green Vitriol (Glauber).

Aqua Fortis, Acid Spirit of Nitre, or Nitric Acid, HNO_3, prepared by distilling Nitre and Alum (Geber) or Nitre and Oil of Vitriol (Glauber), $2KNO_3 + H_2SO_4 \rightarrow K_2SO_4 + 2HNO_3$.

Spirit of Salt, Muriatic acid, or Hydrochloric acid, HCl, prepared by heating Salt and Oil of Vitriol, and collected in water (Glauber), $2NaCl + H_2SO_4 \rightarrow Na_2SO_4 + 2HCl$.

Aqua Regia, a mixture of Aqua Fortis and Spirit of Salt prepared by adding Sal-ammoniac to Aqua Fortis (Geber), $NH_4Cl + HNO_3 \rightarrow NH_4NO_3 + HCl$, or by distilling a mixture of Nitre and Salt with Oil of Vitriol (Glauber).

The acids as a class possess the following properties, though some of them may be lacking in the case of individual acids :—

(*a*) *General Properties* : Sour taste ; acids turn syrup of violets red and redden blue litmus ; the mineral acids are corrosive when concentrated but harmless when dilute ;

(*b*) *Acids dissolve Alkalis and Chalk, liberating gas, e.g.*, "Vinegar upon Nitre (*i.e.*, soda)" and upon Chalk,

$$Na_2CO_3 + 2C_2H_4O_2 \rightarrow 2NaC_2H_3O_2 + H_2O + CO_2$$
$$CaCO_3 + 2C_2H_4O_2 \rightarrow Ca(C_2H_3O_2)_2 + H_2O + CO_2 ;$$

Oil of Vitriol with Soda gives "Glauber's salt," with Chalk gives "Gypsum" or "Selenite" (almost insoluble in water)

$$Na_2CO_3 + H_2SO_4 \rightarrow Na_2SO_4 + H_2O + CO_2$$
$$CaCO_3 + H_2SO_4 \rightarrow CaSO_4 + H_2O + CO_2 ;$$

(*c*) *Acids dissolve metals, e.g.*, Oil of Vitriol and Muriatic acid dissolve Iron ; Oil of Vitriol (concentrated) and Aqua Fortis dissolve also Copper, Mercury and Silver ; Aqua Regia dissolves Gold.

The action of acids and alkalis on vegetable tinctures such as the blue-fluorescent extract of "Lignum nephriticum," syrup of violets and cornflowers, and the purple juice of ripe privet-berries was described by Boyle (*Experiments on Colours*, 1663).

D. Salts.

Many salts can be prepared artificially by the action of Acids on Metals, Alkalis (Soda and Potash) and earths. Amongst the salts which were prepared and examined at an early date the following may be noted :—

(*a*) **Vitriols or Sulphates.**—*From Metals* : Green Vitriol, Sulphate of Iron, or Ferrous Sulphate, $FeSO_4, 7H_2O$; Blue Vitriol, Sulphate of Copper, or Copper Sulphate, $CuSO_4, 5H_2O$.

From Alkalis : Glauber's Salt, Sulphate of Soda, or Sodium Sulphate, $Na_2SO_4, 10H_2O$; Vitriolated Tartar, Sulphate of Potash, or Potassium Sulphate, K_2SO_4.

From Earths : Gypsum or Selenite, Sulphate of Lime, or Calcium Sulphate, $CaSO_4, 2H_2O$; Epsom Salts, Sulphate of Magnesia, or Magnesium Sulphate, $MgSO_4, 7H_2O$; Alum, Sulphate of Potash and Alumina, or Potassium Aluminium Sulphate, $KAl(SO_4)_2, 12H_2O$.

(*b*) **Nitres or Nitrates.**—Nitre or Saltpetre, Nitrate of Potash, or Potassium Nitrate KNO_3 ;

Chile Saltpetre, Nitrate of Soda, or Sodium Nitrate, $NaNO_3$;

Lunar Caustic, Nitrate of Silver, or Silver Nitrate, $AgNO_3$.

Also Nitrates of Lead, Copper, Iron and Mercury.

(*c*) **Muriates or Chlorides.**—Muriates or Chlorides of Iron ($FeCl_3$), Copper ($CuCl_2$), and Gold ($AuCl_3$). Common Salt Muriate of Soda, or Sodium Chloride, NaCl ;

Sylvine, Muriate of Potash, or Potassium Chloride, KCl ;

Muriate of Magnesia or Magnesium Chloride, $MgCl_2$;

Muriate of Lime or Calcium Chloride, $CaCl_2$.

(*a*) **Acetates.**—Sugar of Lead, Acetate of Lead, or Lead Acetate, $Pb(C_2H_3O_2)_2$;

Acetate of Copper or Copper Acetate, $Cu(C_2H_3O_2)_2$, pre-

pared from Verdigris or Basic Acetate of Copper, $Cu(C_2H_3O_2)_2+Cu(OH)_2$;
Acetate of Soda or Sodium Acetate, $NaC_2H_3O_2$;
Acetate of Lime or Calcium Acetate, $Ca(C_2H_3O_2)_2$;
Acetate of Magnesia, or Magnesium Acetate, $Mg(C_2H_3O_2)_2$.

Three systems of nomenclature are seen in the names given to the salts set out above :—(1) At first each salt received a special name, in many cases recalling the origin or properties of the salt. (2) The system of naming salts after the acid and the metal, alkali or earth from which they are derived was elaborated by de Morveau, Lavoisier, Berthollet, and Fourcroy in their *Méthode de Nomenclature Chimique*, published in 1787. (3) This system became obsolete when Davy, twenty years later, showed that the alkalis and earths contained metals ; it was then possible to name every salt after the acid and the metal from which it was derived and to abandon the use of the alkalis and earths in naming salts.

The idea that salts still contained the acid and alkali from which they were derived was put forward by **John Mayow** in his *Medico-Physical Works* published in 1674 ; he showed that Ammonia could be displaced from its Salts by Potash, $2NH_4Cl+K_2CO_3 \rightarrow 2KCl+(NH_4)_2CO_3$ and Aqua Fortis by Oil of Vitriol, $2KNO_3 + H_2SO_4 \rightarrow K_2SO_4 + 2HNO_3$, and was impressed with the idea of the unequal "concordance" of the two acids with the alkali, an idea that is essentially the same as that of the unequal strengths of different acids. **Rouelle,** to whom we owe the terms *base* (*Mem. Acad.*, 1754, 572) and *water of crystallisation* (*ibid.*, 1744, 356) described how neutral salts had been restricted at first to "salts formed by the union of acids with alkalis, which are soluble in water, and imprint on the tongue a saline taste. . . . The number of neutral salts was at first very small, scarcely any were known but sea salt and nitre ; but the number was soon increased, above all by the work of Glauber. Others have since been added of which the bases are the volatile alkali and an absorbent earth. Finally there have been added salts formed by the union of acids with metallic substances" (*Mem. Acad.*, 1754, 572). He himself, in 1744, had defined as a neutral salt, "a salt formed by the union of an acid with any substance whatever, which serves as a base for it and imparts to it a concrete or solid form" (*ibid.*, 573).

CHAPTER III

THE BURNING OF METALS AND THE DISCOVERY OF OXYGEN

A. The Burning of Metals.

Jean Rey (1630) shows that lead and tin increase in weight when burnt—It has been known from very early times that the metals, except gold and silver, are, by heating, gradually changed to powders of various colours. These powders were called CALCES from the resemblance which they showed to lime (Latin, *calx*), and the process of burning was called CALCINATION. A casual examination showed that the calx was a lighter material than the metal from which it was formed; it was, therefore, natural to suppose that the burning of the metal had resulted in a loss of weight, just as is obviously the case when wood or coal is burnt. The fact "that tin and lead increase in weight when they are calcined," was therefore "observed with astonishment" by those who first put the matter to the test of experiment.

The Essays of **Jean Rey** (1630), a French Doctor of Medicine, "On an Enquiry into the cause wherefore Tin and Lead increase in weight on Calcination" (Alembic Club Reprints, No. XI), contain an account of one of the earliest chemical researches of which a clear record has been preserved. He records that Brun, an apothecary of Bergerac, "having placed two pounds six ounces of fine English tin in an iron vessel and heated it strongly on an open furnace

for the space of six hours with continual agitation and without adding anything to it, he recovered two pounds thirteen ounces of a white calx; which filled him with amazement, and with a desire to know whence the seven ounces of surplus had come" (A. C. R. XI. 36).

It had been suggested that the gain in weight was due to soot or vapour from the furnace condensing on the tin, or to the disintegration of the iron vessel; Rey showed that these explanations were unlikely, and concluded (on the basis of argument rather than of experiment)

"That this increase in weight comes from the air, which in the vessel has been rendered denser, heavier, and in some measure adhesive, by the vehement and long-continued heat of the furnace: which air mixes with the calx (frequent agitation aiding) and becomes attached to its most minute particles: not otherwise than water makes heavier sand which you throw into it and agitate, by moistening it and adhering to the smallest of its grains" (A. C. R. XI. 36).

Rey supported his argument by quoting an experiment of Hamerus Poppius, who had calcined a cone of antimony on a marble slab by means of a burning mirror, and had found the weight to be augmented instead of diminished, in spite of the copious exhalation of vapours and fumes (A. C. R. XI. 49); in this case at least, the gain in weight could not be attributed to contamination of the metal by the furnace or vessel, and must surely be due to the condensation of air. A similar explanation was given in the case of lead, of which it had been recorded that "it is a remarkable thing that lead on calcination increases in weight by eight or ten pounds per cent" (A. C. R. XI. 41).

Robert Boyle (1673) confirms Rey's statement that metals gain in weight on calcination.—Jean Rey himself does not appear to have made any experiments on the gain in weight of tin and lead. But the fact that metals gain in weight when calcined was confirmed forty-three years later

by the careful experiments of Robert Boyle on the calcination of copper and iron, as well as of tin and lead. Boyle's observations showed a gain of :—

30 to 49	grains	on	480	grains	of copper [1]
60	,,	,,	480	,,	,, tin
66	,,	,,	240	,,	,, iron
7	,,	,,	480	,,	,, lead (in spite of loss)

whilst silver showed a gain of only 2 grains on 212.

Boyle's experiments were carried out as follows :—

"Into a very shallow crucible, we put an ounce of copper-plates, and set it in a cupelling furnace, where it was kept for two hours ; and then being taken out, we weighed the copper, which had not been melted (having first blown off all the ashes), and found it had gained thirty grains."

A similar experiment with an ounce of copper filings gave an increase of 49 grains.

"Upon a good cupel, we put an ounce of English tin, of the better sort ; and having placed it in the furnace, under a muffler, though it presently melted, yet it did not forsake its place, but remain upon the concave surface of the cupel, till, at the end of about two hours, it appeared to have been well-calcined ; and then being taken out, and weighed by itself, the ounce of metal was found to have gained no less than one dram."

"An ounce of lead was put upon a cupel, made of calcined hartshorn, and placed under a muffler, after the cupel was first made hot, and then weighed. This lead did not enter the cupel, but was turned into a kind of litharge on the top of it, and broke the cupel, whereby some part of the latter was lost in the furnace ; yet the rest, together with the litharge, weighed seven grains more than the lead and heated cupel, when they were put in."

"Four drams of the filings of steel, being kept two hours

[1] 20 grains = 1 scruple
3 scruples = 1 dram
8 drams = 1 ounce.

on a cupel, under a muffler, acquired one dram, six grains and a quarter, increase of weight."

"A piece of refined silver, being put upon a cupel under a muffler, and kept there for an hour and a half, was taken out, and weighed again; and as before it weighed three drams, thirty-two grains and a quarter, it now weighed in the same scales, three drams, thirty-four grains and a quarter" (*Works*, 1725, II. 389–390).

Boyle calcines tin in sealed flasks.—Although Boyle was convinced that metals really gained in weight when burnt, he regarded these experiments as unsatisfactory because the metals were exposed to the smoke and dust of the furnace. To get over this difficulty he heated the metals between two crucibles cemented together with clay, and finally (in the case of the more fusible metals) made use of glass flasks, the necks of which were loosely stoppered, drawn out to a fine point, or sealed up altogether. Boyle's experiments on the calcination of tin in sealed flasks are of special interest as having provided the basis for Lavoisier's experiments on the same subject.

"To prevent all suspicion of any increase of weight, in the metals, arising from smoke, or saline particles, getting in at the mouth of the vessel, I made the experiment in glasses, hermetically sealed, as follows. Eight ounces of good tin, carefully weighed, we hermetically sealed up in a new, small retort, with a long neck, by which it was held in the hand near a charcoal fire, that kept the metal in fusion; being now and then shaken for almost half an hour; in which time, it seemed to have acquired, on the surface, such a dark colour, as argued a beginning calcination; and it both emitted fumes that played up and down, and also, afforded two or three drops of liquor, in the neck of the retort. The glass was, at length, laid on quick coals, where the metal continued above a quarter of an hour longer in fusion; but, before the time was come, that I intended, to suffer it to cool, in order to its removal, it suddenly broke into a great multitude of pieces, and with a noise, like the report of a gun."

In order to reduce the risk of explosion the flask was next heated before sealing.

"Two ounces of filings of tin, were carefully weighed, and put into a little retort, whose neck was afterwards drawn slender to a very small apex; then the glass was placed on kindled coals, which drove out fumes at a small orifice of the neck, for a pretty while. Afterwards, the glass, being sealed at the apex, was kept in the fire for above two hours; and then being taken off, was broken at the same apex: whereupon I heard the external air rush in, because, when the retort was sealed, the air, within it, was highly rarefied. Then the body of the glass being broken, the tin was taken out, consisting of a lump, about which there appeared some grey calx, and some very small globules, which seemed to have been filings melted into that form. The whole weighed two ounces, and twelve grains" (*Works*, II. 393–394).

"Fire and flame weighed in a balance" by Robert Boyle.—Although the observations on calcination which are described under this title[1] (*Works*, 1725, II. 388) agreed closely with those quoted by Jean Rey, Boyle gave a different explanation of the gain in weight, which he attributed to the absorption of heat instead of to the condensation of air. Boyle's failure to recognise the essential part played by air in combustion may be attributed to his observations "Of the strangely difficult Propagation of Actual Flame in Vacuo Boyliano" (*New Experiments, touching the Relation betwixt Flame and Air*, London, 1672; compare *Works*, 1725, II. 517) in which he found that various substances including sulphur, gunpowder, and fulminating gold, could be fired, although with difficulty, by contact with hot iron in a vessel from which much of the air had been removed by means of an air-pump.

Boyle's opinion forms the basis of the "Phlogiston" theory of Becher and Stahl.—Boyle's view that fire and flame were material things which could be "weighed in a

[1] The title of the original tract is "New Experiments to make the Parts of Fire and Flame stable and ponderable." London, 1673.

balance" appeared again in a modified form in the THEORY OF PHLOGISTON which dominated the science of chemistry during the next hundred years, but was finally overthrown by the work of Lavoisier from 1770 to 1787. This theory was elaborated by two German philosophers, **John Joachim Becher** (1635–1682), and **George Ernest Stahl** (1660-1734), who sought to explain the phenomena of combustion as due to a fire-element, or principle of inflammability, to which Stahl gave the name PHLOGISTON. It was supposed that phlogiston was present in all combustible substances; the largest proportion was contained in soot, which was thought to be almost pure phlogiston, since it left only the smallest residue of ash when burnt. In the smelting of metals the phlogiston of the fuel combined with the ore to produce the metal; when the metal was burnt it parted with the phlogiston it had taken from the fuel and was converted into an incombustible calx, or ash. It will be noticed that whilst Boyle regarded the calx as a compound of the metal with igneous particles from the fire, thus

$$Metal + Fire = Calx,$$

Stahl regarded the calx as a simple substance, and the metal as a compound of the calx with phlogiston, thus,

$$Calx + Phlogiston = Metal.$$
$$Metal - Phlogiston = Calx.$$

As the calx is heavier than the metal from which it is derived it was clear that the phlogiston which escaped during calcination must have a negative weight; this curious conclusion, although not much considered at first, led ultimately to the destruction of the theory.

In Stahl's opinion, air was required in combustion merely to absorb the phlogiston set free by the burning substance; air which had become exhausted by combustion was thought to be saturated with phlogiston, and was called PHLOGISTICATED AIR.

Hooke (1665) & Mayow (1674) suggest that air contains an active principle similar to nitre.—The air, to which Jean Rey had attributed the gain in weight of lead and tin during calcination, was regarded by Boyle as having little or nothing to do with this change. It was, therefore, left to his contemporaries, Robert Hooke and John Mayow, to follow up the clue which Rey had provided and to demonstrate the part which air plays, not only in the burning of metals, but in other cases of combustion.

Robert Hooke, in his "Micrographia" (1665), called attention to the close resemblance between the action of nitre, or saltpetre, and of air in various cases of burning. He regarded air as a solvent for the burning substance, and attributed its activity to the presence in it of a substance similar to (or even identical with) melted saltpetre, but in a very attenuated condition.

The similarity between air and nitre also formed the basis of the theory of combustion put forward by **John Mayow** in his "Medico-Physical Works" (*Alembic Club Reprints*, No. XVII.), published in 1674. He showed, as Boyle had done, that air was not needed for the burning of gunpowder, since damp gunpowder would continue to burn when the tube in which it was contained was plunged under water (A. C. R. XVII. 9). There was, therefore, something in the nitre which would take the place of air in enabling charcoal and sulphur to burn. To this common principle, present in air and in nitre, he gave the name SPIRITUS NITRO-ÆREUS or NITRO-ÆRIAL SPIRIT (A. C. R. XVII. 1).

Mayow (1674) proves that air is absorbed during combustion.—Hitherto no attempt had been made to collect and examine gases. When substances were distilled the volatile products were condensed in a cold receiver, in which water was sometimes placed, but gases and vapours which were not condensed in this way had always been lost. To Mayow belongs the credit of intro-

ducing into chemistry the method of collecting gases in flasks or bottles inverted over water, and of studying

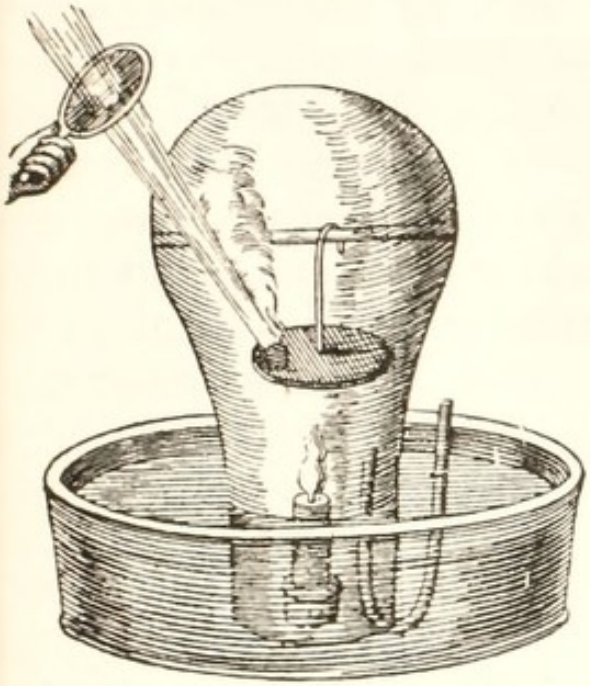


FIG. 11.

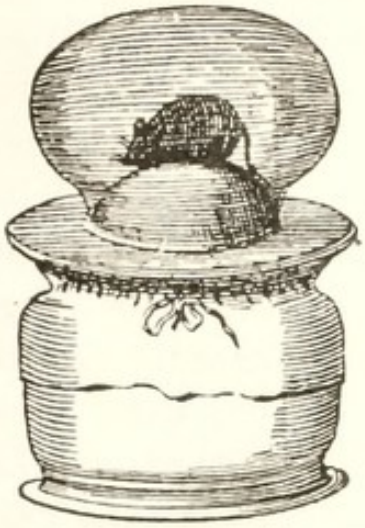


FIG. 12.

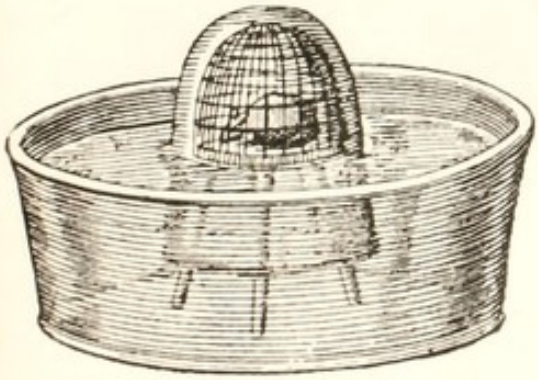


FIG. 13.

FIG. 14.

MAYOW'S APPARATUS.

Fig. 11 shows a candle burning in a glass vessel inverted over water, and also a piece of camphor being fired by a burning-glass.
Fig. 12 shows the diminution of the volume of air by a mouse breathing in it; a stretched bladder is sucked inwards as the air diminishes.
Fig. 13 shows the same experiment carried out with air contained in a glass vessel inverted over water.
Fig. 14 shows the apparatus used to collect gases prepared artificially by the action of acids on iron.

changes of volume in the gas by noticing the position of the water in the glass vessel. Mayow's apparatus is shown in Figs. 11, 12, 13 and 14 (A.C.R. XVII. Plate 5). With

this apparatus he showed that a decrease in the volume of air occurred when a candle was burned in an inverted flask, or when camphor was fired in it by means of a burning glass (Fig. 11): this decrease he attributed to the disappearance of the nitre-air during burning. He also showed that a decrease in the volume of air was caused by a mouse breathing in it (Figs. 12 and 13), and that the mouse died almost immediately if placed in a jar of air in which a flame was burning: the nitre-air used in burning was therefore also necessary for breathing, and was used up in just the same way as by a burning candle.

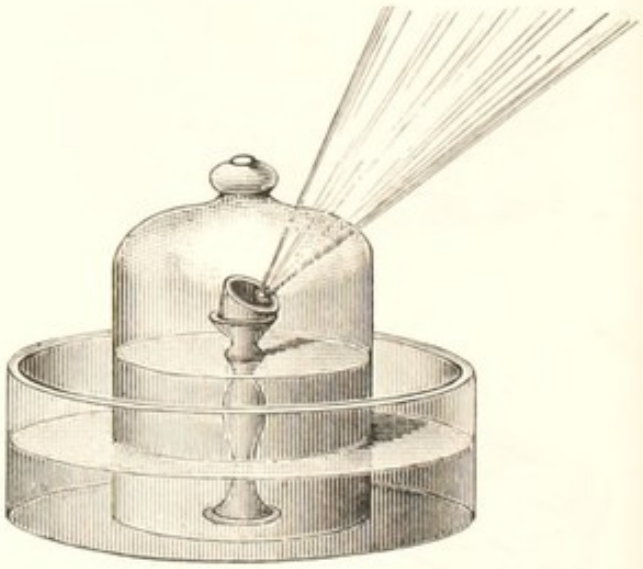


FIG. 15 — LAVOISIER'S APPARATUS FOR CALCINING LEAD AND TIN IN AIR OVER WATER OR MERCURY.

Lavoisier (1774) proves that the gain in weight when tin is calcined is due to absorption of air. — The overthrow of the phlogiston theory and the establishment of the theory of combustion, were the work of a French nobleman, **Antoine Laurent Lavoisier** (1743–1794). Lavoisier met with an untimely death during the French Revolution, but himself brought about a revolution in the science of chemistry, so complete as almost to justify the dictum of a fellow countryman, "Chemistry is a French science. Its founder was Lavoisier of immortal memory."[1] His experiments on combustion

[1] This is the opening passage of Wurtz's *Atomic Theory*. A contrary opinion was expressed by Brande, Professor of Chemistry in the Royal Institution, who wrote in 1819: "It is, I think, among our own countrymen that we discover the fathers of chemical philosophy: for Bacon, Boyle, Hooke, and Newton, present unequivocal claims to that distinctive title" (*Manual of Chemistry*, p. xviii.).

were carried out with a full knowledge of the work of his predecessors, and were modelled largely upon the work of Mayow and Boyle.

By means of a burning-glass 33 inches in diameter, Lavoisier calcined lead and tin in air enclosed in a glass vessel inverted over water or mercury[1] (Fig. 15), and found that "the volume of air diminished by about a twentieth as a result of the calcination, and that the weight of the metal is increased by an amount almost equal to that of the air destroyed or absorbed." He concluded "that a portion of the air . . . . combined with the metals during their calcination, and that the increase in weight of the metallic calces was due to this cause" ("Memoir on the Calcination of Tin in Closed Vessels," 1774, *Works*, II. 105.) Thus in contrast to the current view that

$$Metal = Calx + Phlogiston$$

Lavoisier reverted to the suggestion of Jean Rey that

$$Metal + Air = Calx,$$

the metal being regarded as a simple substance and the calx as a compound.

Lavoisier calcines tin in a sealed flask.—In order to test the view that the gain in weight of metals during calcination was due to the absorption of air, Lavoisier, in 1774, repeated Boyle's experiment of heating lead and tin in sealed glass vessels. But, unlike Boyle, he carried out the critical experiment of weighing the sealed retort both before and after heating. In making these experiments Lavoisier had the advantage of using a balance, more sensitive than any that had been constructed previously, with which he was able to detect changes in weight of $\frac{1}{100}$ of a grain.

The experiment was carried out as follows: Eight ounces of tin were weighed into a retort of 43 cubic inches capacity, heated to drive out part of the air, sealed up and again weighed. The tin was then heated in the sealed retort for

[1] Compare Priestley, *Experiments on Air*, I. 136.

an hour and a quarter, until the surface of the molten metal ceased to tarnish and a considerable quantity of a *black*[1] calx had collected. In spite of the calcination that had taken place the sealed retort had only changed in weight by the loss of a quarter of a grain. If, therefore, the metal had gained in weight "it was necessary to look for the cause in the interior of the retort" (*Works*, II. 112).

The retort was then broken into halves by cracking it with a hot coal, and the whole was weighed again. A comparison with the first weighing of the tin and retort showed a gain of 3·13 grains; further weighings showed that the tin in the retort had gained 3·12 grains, whilst the retort itself had not changed in weight. Lavoisier was able to calculate that the weight of air which he had sealed up in the retort was $15\frac{1}{3}$ grains, and therefore concluded that one-fifth of this air had been absorbed by the tin.

In a second experiment 20 ounces of tin were heated during two and a-half hours in a large retort of 250 cubic inches capacity. After allowing air to enter through a small crack, the retort and its contents were found to be 10·06 grains heavier than when they were first weighed: the tin had gained in weight by 10·00 grains or $\frac{1}{8}$ to $\frac{1}{9}$ of the weight of air in the retort. The agreement between these two figures could not be predicted, as the cracked retort did not contain ordinary air; but it is referred to below as evidence that the ordinary air entering the retort had almost the same density as the portion which had been absorbed by the tin.

Lavoisier's figures are given on p. 37.

Lavoisier concluded:

"1. That only a limited quantity of tin can be calcined in a given quantity of air.

[1] When tin is heated in an excess of air, a *white* calx is produced.

LAVOISIER'S EXPERIMENTS ON HEATING TIN IN A SEALED RETORT.

	First Experiment.	Second Experiment
	Grains.	Grains.
Weight of tin + retort	4608 + 3026·50 = 7634·50	4608 + 7395·75 = 12003·75
,, ,, ,, heated and sealed	... ... = 7628·87	... ... = 11968·88
Air driven out	... ... = 5·63	... ... = 34·87
Weight of sealed retort after long heating	... ... = 7628·60	... ... = 11967·88
Loss by calcination	... ... = 0·27	... ... = 1·00
Weight after breaking open	... ... = 7637·63	... ... = 12013·81
Total gain in weight	7637·63 - 7634·50 = 3·13	... ... = 10·06
Gain in weight of calcined tin	4611·12 - 4608 = 3·12	4618·00 - 4608 = 10·00
Loss ,, ,, retort	3026·50 - 3026·50 = Nil	7395·75 - 7395·62 = 0·13

"2. That the quantity of tin calcined is greater in a large retort than in a small one. . . .

"3. That the sealed retorts, weighed before and after the calcination of a portion of the tin which they contain, show no difference in weight, proving that the gain in weight of the metal does not come from the fire nor from anything outside the flask.

"4. . . . That in the calcination of tin, the gain in weight of the metal is almost exactly equal to the weight of the quantity of air admitted, proving that the part of the air which combines with the metal during calcination has almost the same density as that of atmospheric air" (*Works*, II. 118–119).

Having thus shown that air was made up of two parts, one of which was absorbed by tin, whilst the other was not acted on, Lavoisier set himself to obtain separately the part of the air which combines with metals and enables substances to burn. He was able to imagine what the properties of this gas must be: it must support combustion, and probably substances would burn in it with great ease. He tried to obtain it from metallic calces in which he knew it was present, but was unable to set it free by any of the methods at his disposal. The recovery of this lost air, which Lavoisier required to complete the proof of his theory of combustion, was, however, accomplished within a few months by the independent work of Priestley in England and of Scheele in Sweden.

B. The Discovery of Oxygen.[1]

Priestley (1774) discovers a gas richer than common air.—The facts which Lavoisier required in order to complete the proof of his theory of combustion were supplied

[1] The discovery of oxygen followed that of most of the gases described in Chapter V. It is described here in order to complete the story of the calcination of metals.

almost immediately by **Joseph Priestley** (1733—1804), a nonconformist pastor of Leeds, who was at this time making a large number of experiments with the object of finding out what "airs," or gases, were formed when various substances were heated. Having procured a new burning glass twelve inches in diameter, Priestley "proceeded with great alacrity to examine, by the help of it, what kind of air a great variety of substances, natural and factitious, would yield, putting them into vessels . . . . filled with quicksilver, and kept inverted in a bason of the same." (*Experiments and Observations on Different Kinds of Air*, 1774, II. 28; A.C.R. VII. 8.)

With this apparatus, on the 1st of August, 1774, Priestley endeavoured to extract air from "mercurius calcinatus per se," the RED CALX OF MERCURY prepared by heating the metal gently in air. Having "found that by means of this lens, air was expelled from it very readily," Priestley proceeded to examine the product, and discovered to his great astonishment that "a candle burned in this air with a remarkably vigorous flame . . . . and a piece of red-hot wood sparkled in it, exactly like paper dipped in a solution of nitre, and it consumed very fast" (A.C.R. VII. 10). He placed a mouse in a vessel filled with the gas where "it remained perfectly at its ease another full half hour," twice as long as it would have lived in ordinary air (A.C.R. VII. 17). Later he had the curiosity to breathe the gas himself, and fancied that his "breast felt peculiarly light and easy for some time afterwards" (A.C.R. VII. 54). Priestley also obtained the gas by heating other substances, including red-lead, a red powder formed by gently roasting white lead, or litharge, and capable, like the mercury calx, of being decomposed when heated more strongly.

The only explanation which Priestley could give of his discovery of a gas better and richer than air was that

ordinary air must contain some phlogiston, and that in this new gas he had, for the first time, obtained air free from phlogiston. He therefore described it as DEPHLOGISTICATED AIR, and attributed its superior power of supporting combustion, to the fact that it was capable of receiving more phlogiston from burning substances, and could therefore maintain a flame for a longer period than ordinary air.

Lavoisier makes quantitative experiments on the calcination of mercury.—In October of the same year Priestley, when on a visit to Paris, informed Lavoisier of his experiments. Lavoisier concluded that the new gas was the active part of the air which he had tried without success to separate. In November, 1774, he repeated Priestley's experiments, and in the spring of the following year read before the Academy of Sciences at Paris a memoir "On the Nature of the Principle which Combines with the Metals during their Calcination and Increases their Weight" (*Works*, II. 122). In this memoir he described as VITAL AIR or EMINENTLY RESPIRABLE AIR the gas obtained by heating the red calx of mercury, and confirmed Priestley's observations as to its properties, but without making any reference to the source from which he had obtained his first information as to the behaviour of the calx.

In his "Elementary Treatise on Chemistry," published in 1789, Lavoisier described a series of experiments on the calcination of mercury (*Works*, I. 35–38) which display to the full his genius for exact and careful measurements. In order to study the part that air played in the formation of the red calx, he placed four ounces of pure mercury in a retort, the neck of which was bent so that it passed up into a bell-jar of air inverted over mercury (Fig. 16). The total volume of air thus enclosed in the retort and the bell-jar amounted to 50 cubic inches. He then heated the retort, and observed the formation of a red scale on the

surface of the mercury contained in it. At the end of twelve days, when further heating did not cause the formation of any more of the red scale, the retort was allowed to cool. The mercury rose in the bell-jar and the total volume of air was found to have been reduced to 42 or 43 cubic inches, a loss of 7 or 8 cubic inches. The calx on the mercury was collected and found to weigh 45 grains. "The air which remained after this operation, and which had been reduced to five-sixths of its volume by the calcination of the mercury, was no longer fit for respiration nor combustion; since animals introduced into it perished in a few moments, and lights were extinguished in it at once, as if they had been plunged into water" (*loc. cit.* p. 37).

As the mercury calx (unlike the black calx from the tin) could be decomposed by heating it, Lavoisier transferred the 45 grains to a small retort and obtained from its decomposition 41½ grains of mercury, and 7 to 8 cubic inches of gas, which was "much more fit than atmospheric air to support respiration and combustion," since "a candle plunged into it, gave out a dazzling light; charcoal, instead of burning quietly as in ordinary air, burnt with a flame . . . . and a brightness of light which the eye could scarcely bear" (*loc. cit.* pp. 37–38).

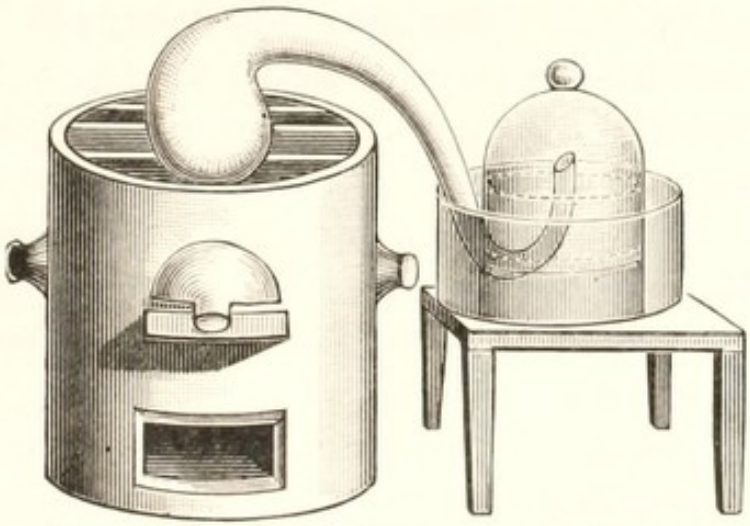


FIG. 16—LAVOISIER'S APPARATUS FOR HEATING MERCURY IN A LIMITED VOLUME OF AIR. No illustration is given of the retort used afterwards to decompose the calx.

From these experiments it was clear that the whole of the 7 or 8 cubic inches of air absorbed in the first experiment had been liberated in an intensely active form in

the second. A further experiment showed that a mixture of 8 cubic inches of the respirable air with 42 cubic inches of non-respirable air behaved in all respects like ordinary air. There was, therefore, no doubt that the air which disappeared during calcination had actually combined with the mercury, and had been released from it by heating it more strongly.

In order to complete the proof it was only necessary to show that the loss in weight of the calx (45 grains), when reconverted into mercury ($41\frac{1}{2}$ grains), was equal to the weight of the gas which had been liberated: a knowledge of the density of the active gas showed that the quantity collected would weigh $3\frac{1}{2}$ to 4 grains, agreeing closely with the loss of $3\frac{1}{2}$ grains already recorded.

Lavoisier completes his "oxygen" theory of combustion.—Lavoisier's proof was now complete: he had shown that the calcination of a metal meant the combination of the metal with an active constituent of the air, which in the case of mercury could be recovered from the calx by heating it: the calx was, therefore, a *compound*, and the combustible metal a simpler substance. The same constituent of the air was required for the burning of fuel and for respiration, two processes which differed from the burning of metals mainly in giving rise to gaseous instead of solid products (see Chapter VI).

Lavoisier showed that the same constituent of air was also concerned in the burning of sulphur and of phosphorus; but the products of combustion differed completely from the metallic calces, dissolving readily in water and producing acid solutions. Lavoisier regarded his active gas as an essential constituent of these and of all other acids. He therefore selected for it the name OXYGEN or "acid-producer" (compare German, *sauerstoff*), deriving it "from the Greek words ὀξὺς, *acid*, and γείνομαι, *I beget*, on account of the property of this principle, the basis of vital air, to

change a great many of the substances with which it unites into the state of acid, or rather because it appears to be a principle necessary to acidity" (*Chemical Nomenclature*, p. 24; compare *Works*, II. 249, where the name "oxygen" is first used) This name has been retained to the present day in spite of the discovery (see Chapter XII) of acids in which no oxygen is present. The compounds in which oxygen was present were described as OXIDES; under this title were included, not only the acid oxides of sulphur and phosphorus, but also the basic calces derived from the metals.

By making use of the discovery of oxygen, Lavoisier had been able to explain all the main facts on which the phlogiston theory was based; the phlogiston theory was therefore no longer necessary, and gradually ceased to be used. Lavoisier's theory was completed in the year 1777. It won its first converts nearly ten years later, when it was accepted by de Morveau, Fourcroy, and Berthollet. The "System of Chemical Nomenclature" which they issued in 1787 was one of the first manifestoes of the new faith.

Scheele's discovery of oxygen.—The separation of the gases of the atmosphere was accomplished independently by the Swedish chemist Scheele in a research, "On Air and Fire" (A. C. R. VIII), completed about the same time as Priestley's work, but not published until 1777, and not known either to Priestley or to Lavoisier at the time when they were carrying out their experiments.

Scheele's experiments led him to the belief that common air consisted of two gases, one of which could be removed by various substances. Thus when damp iron filings rusted in air, in a tightly closed bottle which was afterwards opened under water, about a quarter of the air was found to be absorbed. Similar results were obtained when phosphorus was burnt in a thin flask tightly corked, or when it was simply allowed to stand for six weeks in a closed flask until it ceased to glow. The part of the air remaining at the

close of these experiments was slightly less dense than ordinary air, and did not allow a candle to burn in it, or even the smallest spark to continue glowing. This inactive portion of the air was separated by no fewer than sixteen different methods, but the recovery of the "lost air," as Scheele called it, was a problem of much greater difficulty. Scheele actually obtained it from a variety of substances, amongst which was nitric acid, thus confirming the view of Hooke and Mayow as to the close relationship existing between nitre and air. He found that it could be prepared most readily either from nitre (saltpetre) or from common RED PRECIPITATE (obtained by dissolving mercury in nitric acid and heating the residue until the product became red) which he proved to be identical with calcined mercury (red oxide of mercury).

Having separated this PURE FIRE-AIR Scheele repeated the experiments which he had carried out with ordinary air and proved that the substances which diminished the volume of ordinary air when left or burnt in it, were capable of absorbing "fire-air" entirely. For example, phosphorus, heated in a closed flask filled with "fire-air," burnt with remarkable brilliancy; on allowing the flask to cool and opening it under water, it was found that water entered the bottle and filled it almost completely. Scheele showed that his "fire-air" (Lavoisier's "oxygen") was slightly denser than air, and soluble in water. He also proved it to be essential to the breathing of animals, and the growth of plants. By mixing it with $3\frac{1}{2}$ times its volume of "foul air," left after burning phosphorus in a closed vessel, there was obtained a gas which in every respect resembled common air. Scheele rightly concluded that common air is a mixture of "fire-air" with about four times its volume of "foul air."

Azote.—The residue left after removing the oxygen from air was described by Priestley as "phlogisticated air," by

Scheele as "foul air" (*Air and Fire*, p. 54), whilst Lavoisier usually called it the "atmospheric mofette"; the French chemists in 1787 (*Chemical Nomenclature*, p. 26) described it as AZOTE, "from the Greek privative α and ζωή, *life*," in order to indicate its inability to support life. It was shown by Cavendish to consist mainly of a gas, present in nitre, to which Chaptal gave the name NITROGEN. (See Chapter X.)

SUMMARY AND SUPPLEMENT.

Jean Rey, in 1630, "On an enquiry into the cause wherefore tin and lead increase in weight on calcination," concluded that the gain in weight on calcining tin, lead, and antimony must be due to condensation of air.

Robert Boyle, in 1673, in an essay entitled "New Experiments to make Fire and Flame stable and ponderable," proved that copper, iron, tin and lead gained in weight when burned, but attributed this to the absorption of igneous particles. This materialistic view of the nature of fire was elaborated in the "phlogiston theory" of Becher and Stahl; they assumed that combustion and calcination involved an escape of phlogiston, whilst in smelting an ore, or calx, the addition of phlogiston from the fuel revivified the metal.

Robert Hooke, in 1665, in his "Micrographia," and **John Mayow**, in 1674, in his "Medico-physical Essays," suggested that air must contain an active principle similar to nitre; Mayow described this as "spiritus nitro-aereus," or "nitro-aerial spirit." Mayow showed that damp gunpowder would continue to burn under water. He made experiments with air trapped over water, and showed that the volume of air was diminished by the burning of a candle or of camphor, as well as by the breathing of a mouse.

Antoine Laurent Lavoisier, in 1774, "Memoir on the Calcination of Tin in Closed Vessels," showed that a similar decrease of volume took place when lead and tin were heated by a burning-glass in air confined over water or mercury. He repeated the experiments in which Boyle had calcined tin in sealed glass flasks, but proved that no change in weight took place until the flask was opened; as the flask did not change in

weight, the gain in weight of the tin must have been accompanied by the disappearance of an equal weight of air. When the flask was opened a quantity of air rushed in, the weight of which was almost equal to that gained by the tin ; this showed that the part of the air absorbed by the tin (about $\frac{1}{5}$) did not differ greatly in density from the air outside.

Joseph Priestley, in 1774, isolated the active part of the air by heating the red calx of mercury, and showed that it was a brilliant supporter of combustion and maintained respiration much longer than ordinary air. He regarded it as air minus phlogiston, and called it "dephlogisticated air." **Lavoisier** then carried out quantitative experiments on the calcination of mercury, in which he showed that the volume of gas set free when the calx was heated was identical with the volume of air absorbed in its preparation, whilst the weight of the gas set free was equal to the loss in weight of the calx when reconverted into metal.

Since sulphur and phosphorus were converted into acids by combination with the active part of the air, Lavoisier gave to it the name *oxygen*, *i.e.*, acid-producer, the same idea being implied in the expressive German name, *sauerstoff*.

Oxygen was also prepared independently about 1774 by **Carl Wilhelm Scheele**, who obtained it first by heating nitric acid and nitre. He proved in many ways that air was a mixture of an active and an inactive constituent, and showed that ordinary air could be reproduced by adding "fire-air," or oxygen, to the "foul air" remaining after rusting or burning had taken place in it.

The chemical changes described in this chapter may be represented by the following equations :—

Calcination of tin . $Sn + O_2 = \underset{\text{(Stannic oxide.)}}{SnO_2}$ (white calx).

$2Sn + O_2 = \underset{\text{(Stannous oxide.)}}{2SnO}$ (black calx).

" " *lead* . $2Pb + O_2 = \underset{\text{(Litharge.)}}{2PbO}$ (yellow calx).

" " *copper*. $2Cu + O_2 = \underset{\text{(Cupric oxide.)}}{2CuO}$ (black calx).

Calcination of iron . $3Fe + 2O_2 = \underset{\text{(Magnetic oxide of iron.)}}{Fe_3O_4}$ (blue-black scale or calx.)

Preparation of red oxide of mercury—

(*a*) "Mercurius calcinatus per se"

$$2Hg + O_2 = 2HgO.$$

(*b*) "Red precipitate"

$$3Hg + 8HNO_3 = \underset{\text{(Mercuric nitrate.)}}{3Hg(NO_3)_2} + \underset{\text{(Nitric oxide.)}}{2NO} + 4H_2O.$$

$$2Hg(NO_3)_2 = \underset{\text{(Mercuric oxide.)}}{2HgO} + \underset{\text{(Nitrogen peroxide.)}}{4NO_2} + O_2.$$

Decomposition of red oxide of mercury—

$$2HgO = 2Hg + O_2.$$

„ „ *nitric acid—*

$$4HNO_3 = 2H_2O + 4NO_2 + O_2.$$

„ „ *nitre—*

$$\underset{\text{(Potassium nitrate.)}}{2KNO_3} = \underset{\text{(Potassium nitrite.)}}{2KNO_2} + O_2.$$

Red lead contains more oxygen than litharge, but has not a definite composition, and cannot be represented by any exact formula. Its preparation and decomposition may be shown thus—

$$2PbO + xO_2 = 2PbO_{1+x},$$
$$2PbO_{1+x} = 2PbO + xO_2,$$

where x is a fraction which is always less than 0·5.

CHAPTER IV

CHALK, LIME, AND THE ALKALIS

A. Chalk and Lime

The burning of chalk to lime.—The changes wrought by the action of fire have been described (Chapter I, p. 7) as leading at an early period to the preparation of tin from tinstone, iron from ironstone, and so forth. In addition to these metallic ores, a number of rocks were known which were converted by burning into a caustic substance, known as LIME, which was used in the preparation of mortar. **Joseph Black** (1728–1799), an Edinburgh physican who afterwards occupied the chairs of chemistry at Glasgow and at Edinburgh, was one of the first to make a careful study of these substances. He regarded chalk as the typical source of lime, and included in the calcareous class of substances "all those that are converted into a perfect quick-lime in a strong fire, such as limestone, marble, chalk" and "those spars and marls which effervesce with aqua fortis" (A.C.R. I. 10).

The substance formed by heating chalk has remarkable properties. When brought into contact with the skin, it produces blisters and wounds resembling those caused by fire. Hence it was known as a *caustic*. This property has long been used for removing the hairs from hides in the manufacture of leather. The lime drawn from the kilns is

described as QUICKLIME because it becomes hot and steamy when water is poured upon it; the soft powder formed when the hard lumps of quicklime are wetted with water, or are left exposed to the air, is known as SLAKED LIME. Slaked lime dissolves easily in acids and to a slight extent in water; the solution in water is known as LIME-WATER.

At the time when Black began his investigations, it was generally believed that the caustic properties of lime were due to the absorption of igneous particles from the fire in which it had been burnt; this view, like the phlogiston theory of calcination, was found to be untenable as soon as exact quantitative measurements were made. Black's experiments were described in a paper "Experiments upon Magnesia Alba, Quick-lime and some other Alkaline Substances" (A. C. R. No. I.) published in 1755. They were of importance on account of his success in solving the problem of the relationship between chalk and lime, and also because of the stimulus that they gave to exact quantitative work. The principal points of this investigation are set out in the following paragraphs.

Chalk loses in weight when burnt to lime owing to the escape of fixed air.—Black found that "a piece of perfect quick-lime made from two drams of chalk . . . weighed one dram and eight grains" (A. C. R. I. 28), *i.e.*, 120 grains of chalk gave 68 grains of lime, a loss in weight of 52 grains, or nearly 44%. This large loss in weight could only be due to the escape of a gas, since nothing but a little water could be condensed, when chalk was burnt to lime in a retort.

"That the calcareous earths really lose a large quantity of air when they are burnt to quick-lime, seems sufficiently proved by an experiment of Mr. Margraaf. . . He subjected eight ounces of [chalk] to distillation in an earthen retort, finishing his processs with the most violent fire of a reverberatory, and caught in the receiver only two drams of

water, which by its smell and properties shewed itself to be slightly alkaline" (A. C. R. I. 23).

Black had himself carried out the experiment of heating magnesia (a compound resembling chalk, but more easily decomposed by heat), and had "found only five drams of a whitish water in the receiver," although the three ounces (24 drams) of magnesia in the retort "had lost more than the half of its weight" (A. C. R. I. 15).

From these experiments it was clear that the burning of chalk to lime resulted in the escape of an invisible gas; to this gas Black applied the name FIXED AIR. He regarded chalk as "a peculiar acrid earth rendered mild by its union with fixed air." According to his view:—

"When the calcareous earths are exposed to the action of a violent fire, and are thereby converted into quick-lime, they suffer no other change in their composition than the loss of a small quantity of water and of their fixed air. The remarkable acrimony which we perceive in them after this process, was not supposed to proceed from any additional matter received in the fire, but seemed to be an essential property of the pure earth" (A. C. R. I. 22).

The contrast between Black's theory and that which it replaced may be expressed by the equations:

Old theory: *Limestone* + *phlogiston* = *lime*.
New theory: *Limestone* − *fixed air* = *lime*.

Lime combines with water and with fixed air.—In the process of slaking, lime combines vigorously with water to form slaked lime; but in presence of fixed air it releases the water, recombines with the fixed air and is reconverted into chalk. Black writes:—

"A calcareous earth deprived of its air, or in the state of quick-lime, greedily absorbs a considerable quantity of water, becomes soluble in that fluid, and is then said to be slaked: but as soon as it meets with fixed air it is supposed to quit

the water and join itself to the air, for which it has a superior attraction, and is therefore restored to its first state of mildness and insolubility in water" (A. C. R. I. 24).

The conversion of soluble lime into insoluble chalk was thus a test for the presence of fixed air. The test was most sensitive when lime-water was used, because the chalk could then be seen immediately. But in all important cases Black preferred to rely on quantitative experiments in which the chalk, after burning to lime, was recovered in such a way as to show that the original weight of chalk had been reproduced.

Fixed air is present in common air and in air dissolved by water.—By noticing its action upon lime, Black was able to show that a small quantity of fixed air was dissolved in ordinary water, since :—

"When slaked lime is mixed with water, the fixed air in the water is attracted by the lime, and saturates a small portion of it, which then becomes again incapable of dissolution, but part of the remaining slaked lime is dissolved and composes lime-water" (A. C. R. I. 24).

The presence of fixed air in common air was also shown by its action on lime-water, for :—

"If this fluid be exposed to the open air, the particles of quick-lime which are nearest the surface gradually attract the particles of fixed air which float in the atmosphere. But at the same time that a particle of lime is thus saturated with air, it is also restored to its native state of mildness and insolubility; and as the whole of this change must happen at the surface, the whole of the lime is successively collected there under its original form of an insipid calcareous earth, called the cream or crusts of lime-water" (A. C. R. I. 24).

The fixed air forms, however, only a small proportion both of ordinary air and of the air which is dissolved in water, for (1) "lime-water, which soon attracts air, and forms

a crust when exposed in open and shallow vessels, may be preserved, for any time, in bottles which are but slightly corked, or closed in such a manner as would allow free access to elastic air, were a vacuum formed in the bottle," and (2) under an exhausted receiver the same quantity of air escapes from common water, and from water from which the fixed air has been removed by the addition of lime (A. C. R. I. 30).

Fixed air is liberated from chalk by the action of acids.—Although Black was able to show that the loss of weight in burning chalk to lime was due to the escape of an invisible gas, it did not occur to him to attempt to collect the gas, or even to render it visible by causing it to bubble through water. But no special methods were needed to render obvious the "violent breaking out of air" which takes place when chalk is acted on by acids, nor the absence of this effervescence when well-burnt quick-lime is substituted for chalk. Remembering that

Chalk = lime + fixed air,

the contrast between the action of acids in the two cases was sufficient to suggest that the gas so easily set free by acids must be the same as the fixed air which escapes when chalk is burnt to lime.

It is remarkable that Black did not attempt to test the gas by passing it into lime-water,[1] but apparatus such as is now used for this purpose had not yet been devised, and the systematic study of gases did not begin until nearly twenty years later.

A very satisfactory proof of the identity of the two gases was, however, obtained by showing (1) that the weight of gas which escapes is the same, whether the chalk is decomposed by acids or by heating it in a furnace; and (2) that the same weight of acid is required to dissolve the chalk

[1] See footnote, p. 385, for Black's use of lime-water as a test for fixed air.

before and after burning it to lime. In the first experiment Black saturated 120 grains of chalk with diluted spirit of salt in a long-necked Florentine flask, and found a loss in weight of 48 grains, as compared with 52 grains when an equal weight of chalk was burnt to lime. In the second experiment he found that 120 grains of unburnt chalk were dissolved by 421 grains of diluted spirit of salt, whilst the same quantity of chalk, burnt to quick-lime and slaked with an ounce of water, required 414 grains of the acid, but dissolved "without any sensible effervescence or loss of weight" (A. C. R. I. 28).

Fixed air is present in mild alkalis such as soda and potash.—It had been known from early times that the mild alkalis resembled chalk in that they effervesced when acted on by acids. This property was regarded as a chief characteristic of the alkalis,—an idea that is preserved in the use of the word "kali" to describe a mixture of sugar with a mild alkali and a solid acid, which gives an effervescent drink when added to water. As in the case of the action of acids on chalk, Black did not test the gas by passing it into lime-water, but he obtained an even more satisfactory proof of the presence of fixed air in the alkalis by showing that they could reconvert lime into chalk quantitatively. This process had the advantage that it rendered the use of an acid quite unnecessary in proving the composition of the alkalis.

"A piece of perfect quick-lime made from two drams of chalk, and which weighed one dram and eight grains, was reduced to a very fine powder, and thrown into a filtrated mixture of an ounce of a fixed alkaline salt, and two ounces of water. After a slight digestion, the powder being well washed and dried, weighed one dram fifty-eight grains.[1] It was similar in every trial to a fine powder of ordinary

[1] *i.e.* One hundred and twenty grains of chalk gave 68 grains of lime from which 118 grains of chalk were recovered by the action of an alkali.

chalk, and was therefore saturated with air which must have been furnished by the alkali" (A. C. R. I. 28).

B. The Alkalis.

Mild alkalis are made caustic by the removal of fixed air.—The preparation of CAUSTIC ALKALIS by the action of caustic lime on the MILD ALKALIS, soda and potash, was described by Geber. The caustic liquid[1] thus prepared was used from an early period in the manufacture of soap by the action of the hot alkali on fat; it was, therefore, generally called a "soap lye." Its caustic properties had been attributed to lime dissolved in it; but Black was not able to prepare from it any trace either of chalk or of gypsum; he therefore concluded that "the acrimony of the caustic alkali does not depend on any part of the lime adhering to it" (A. C. R. I. 26).

On the other hand, Black found that a mild alkali made caustic by lime was acted on by acids "without the least effervescence or diminution of weight" (A. C. R. I. 32) nor did it produce more than a slight cloudiness with lime-water. The caustic alkali, when properly prepared, was thus free both from lime and from fixed air.

The action of lime in rendering the alkali caustic was therefore due, not to its ability to dissolve in the liquid or to impart to it some fiery principle which it had acquired in the lime-kiln, but on the contrary to its property of removing from the alkali the fixed air which had rendered it mild.

Caustic alkalis are rendered mild by exposure to air.—Black found that after a fortnight's exposure to the air in an open shallow vessel his caustic alkali "became entirely mild, effervesced as violently with acids, and had the same effect upon lime water as a solution of an ordinary alkali"

[1] "A very hellish spirit, in which great mysteries lie hid" (Basil Valentine, *Last Will and Testament*, p. 302).

(A. C. R. I. 32). The caustic alkali therefore resembled slaked lime in its power of absorbing fixed air from the atmosphere, but differed from it in its much greater solubility in water.

On account of their great solubility the caustic alkalis had not been isolated previously. Black attempted to separate them by evaporating the caustic lye in an earthenware bowl, but found that the inside of the bowl became corroded and pitted with holes. By using a silver dish, however, he succeeded in evaporating all the water, and obtained the caustic potash as a fused mass which solidified on cooling, but dissolved again on adding a small quantity of water (A. C. R. I. 33).

At a later date, strong solutions of the caustic alkalis were used in order to absorb (and so to collect and weigh) fixed air from various sources, the greater concentration of the solutions enabling them to take up much more fixed air than in the case of lime-water; but Black, at that date, did not understand the manipulation of gases, and had no opportunity of making use of this valuable quality.

The alkalies are not easily decomposed by heat.—From the above observations it was clear that the relationship between the mild and caustic alkalis was much the same as that between chalk and slaked lime. Soda and potash were closely analogous to chalk, from which they differed chiefly in being soluble in water; whilst caustic soda and caustic potash were similar to slaked lime, but differed from it in their extraordinary solubility in water.

As potash parts with its fixed air so readily when mixed with lime, it seemed probable "that alkalis might be entirely deprived of their air, or rendered perfectly caustic, by a fire somewhat weaker than that which is sufficient to produce the same change" in chalk (A. C. R. I. 37). This was found not to be the case: potash was "exposed, for several hours, in a covered crucible," to the action of a

strong fire, black lead being added to soak up the potash and so prevent it from corroding the vessel; the potash was found to "lose a part of its air, and acquire a degree of causticity," but this was only slight, and it was not found possible to convert the alkalis into a perfect caustic by the action of heat alone. Black points out, however, that "the alkali newly obtained from the ashes of vegetables is generally of the more acrid kind" (A. C. R. I. 39) owing to its partial conversion into a caustic alkali during calcination.

The caustic alkalis, prepared in the form of solutions, evidently correspond with slaked lime rather than with quick-lime. But they are even less easily decomposed by heat than the mild alkalis; the form of the alkali corresponding with quick-lime is therefore very difficult to prepare, and was not discovered until Davy (Chapter XII) had succeeded in isolating from the alkalis the very refractory metals which they contain.

Sal volatile is a mild alkali: spirit of hartshorn is a caustic alkali.—It had long been known that sal ammoniac, the volatile salt described in Chapter I, could be converted into a volatile alkali, SAL VOLATILE, by heating it with soda or potash. This volatile alkali resembled the fixed alkalis in that it effervesced when acted upon by acids. In this action the volatile alkali was reconverted into a salt; for instance, sal ammoniac could be formed from sal volatile and spirit of salt. These facts were used by Mayow in 1674 to prove that the alkali as well as the acid still exists in the salt prepared by mixing them.

"Although [acids] and alkalis pass into a neutral substance when they meet, yet they do not, as is generally supposed, entirely destroy each other. For example, when the acid spirit of salt is coagulated with a volatile [alkali] . . . . although the mixed salts seem to be destroyed, yet they may be separated from each other with

their forces unimpaired, as takes place when sal ammoniac . . . . is distilled with salt of tartar [*i.e.*, potash] (A. C. R. XVII. 160).

When sal ammoniac is acted on by lime a pungent gas is liberated, to which, at a comparatively late date, the name of AMMONIA was given. During the alchemistic period this pungent vapour was (like spirit of salt) known only in the form of a solution which was called the VOLATILE SPIRIT OF SAL AMMONIAC. It was also prepared by distilling horn, and was therefore known as SPIRIT OF HARTSHORN.[1] Priestley, who was the first to collect spirit of salt as a gas over mercury, was also the first to collect ammonia in the gaseous state (see Chapter V).

Black showed that the "mild spirit of sal ammoniac" (described above as sal volatile) could be rendered caustic by removing its fixed air with the help of magnesia; it then "emitted a most intolerably pungent smell," effervesced only slightly with acids, and produced only a turbidity when mixed with lime-water. It was therefore evident that the pungent gas was a caustic alkali which could be rendered mild by union with fixed air. Final proof of these facts was supplied when Priestley showed that gaseous ammonia could be combined with fixed air to produce solid sal volatile, whilst with gaseous spirit of salt it united to form sal ammoniac.

C. Preparation of New Earths.

Earths can be prepared from salts by the action of alkalis.—At the close of Chapter II it was shown how the

[1] "Of the spirit and oil of Harts-horn.—Take Harts-horn, cut it with a saw into pieces, of the bigness of a finger, and cast in one at a time into the aforesaid distilling vessel, and when the spirits are settled, then another, and continue this until you have spirits enough: and the vessel being filled with the pieces that were cast in, take them out with the tongs, and cast in others, and do this as often as is needful."—(Glauber, *Philosophical Furnaces*, Part II.; *Works*, I. 51)

discovery of the acids led to the preparation of a number of new salts. It may now be pointed out how the alkalis were used from a very early period to prepare earths, or bases, from the salts in which they were combined. Thus it was found that gold, which could not be converted into a calx by heating, was transformed into an earth by dissolving it in aqua regia and precipitating again with an alkali. This earth was decomposed when heated, leaving behind a residue of "revivified" metal. By precisely similar methods, silver (which likewise resisted calcination) was converted into an earth from which the metal could be recovered by the action of heat. At a much later date these unstable earths were used by Scheele for the preparation of oxygen. The earth prepared by precipitating gold from its solutions by means of the volatile alkali, exploded violently when heated, and was called AURUM FULMINANS or FULMINATING GOLD ; its composition is discussed in Chapter XII.

These actions were studied by Mayow, who suggested that the metallic earth was precipitated because the acid had left it in order to combine with the stronger alkali, just as in the action of oil of vitriol on nitre the alkali of the nitre left it in order to combine with the stronger acid of the vitriol.

Preparation of magnesia from Epsom salts.—The paper "On Magnesia Alba," in which Black's experiments on chalk and lime are described, derived its name from a white earth, prepared by the action of alkalis on a variety of saline liquids, and used as a mild aperient. It was first made from MOTHER OF NITRE, the mother liquor left after crystallising out saltpetre ; it was here present in combination with nitric acid, which could be removed either "by the addition of an alkali which attracted the acid to itself" or "by exposing the compound to a strong fire in which the acid was dissipated" (A.C.R. I. 6). Black prepared it from "the bitter saline liquor called BITTERN, which remains in the

pans after the evaporation of sea-water," but he "afterwards made use of a salt called EPSOM SALT, which is separated from bittern by crystallisation, and is evidently composed of magnesia and the vitriolic acid" (A. C. R. I. 7).

The magnesia prepared with the help of an alkali effervesced with acids in just the same way as chalk, but gave rise to a totally different series of salts; in particular it was dissolved by oil of vitriol, reproducing the Epsom salt from which it had been prepared, instead of giving a sparingly soluble residue of gypsum.

Like chalk, it was decomposed by heat, its weight decreasing to a remarkable extent. The product resembled lime in dissolving without effervescence in acids, but differed from it in that it could not be slaked, and was not soluble in water.

"An ounce [480 grains] of magnesia was exposed in a crucible for about an hour to such a heat as is sufficient to melt copper. When taken out, it weighed three drams and one scruple [200 grains], or had lost 7/12 of its former weight."

"I repeated, with the *magnesia* prepared in this manner, most of those experiments I had already made upon it before calcination, and the result was as follows:

"It dissolves in all acids, and with these composes salts exactly similar to those described in the first set of experiments: but what is particularly to be remarked, it is dissolved without any the least degree of effervescence" (A. C. R. I. 14).

This decomposition could be effected in a *glass* retort, but although the magnesia "lost more than the half of its weight," only 5 drams of water could be collected from 24 drams of the earth.

"We may, therefore, safely conclude, that the volatile matter lost in the calcination of magnesia, is mostly air; and hence the calcined magnesia does not emit air, or make an effervescence, when mixed with acids."

The work upon "magnesia" was of special importance because it provided Black with the knowledge which enabled him to solve the more difficult problem of the relationship between chalk and lime.

Preparation of an earth from alum.—Black also made use of the alkalis in order to separate from alum an earth to which the name of ALUMINA was afterwards given. This earth is present in the alum as a vitriol, or sulphate. It does not combine with fixed air, and this gas is therefore set free when the alum is precipitated by means of a mild alkali.

Preparation of earths from salts by heat.—A second method of preparing earths from salts, which was practised from the earliest period of alchemy, depended on dissipating the acid of the salt by heat. When salts were thrown into a charcoal fire, or were distilled from a retort, it was often found that an acid vapour escaped, leaving behind an earthy residue to which the name of CAPUT MORTUUM was given. Amongst the salts distilled in this way were green vitriol and alum, both used in the preparation of oil of vitriol; the residue of "colcothar" from the green vitriol was a red-brown earth somewhat resembling rust; the alum left behind a whitish residue of alumina. The nitrates were also frequently decomposed, as for instance, in the preparation of "red precipitate" by heating nitrate of mercury. Black prepared magnesia in this way from mother of nitre; and Boyle in 1680 (*Works*, 1725, III, 372) prepared an alkali from sea-salt by converting it into a nitrate and igniting this with charcoal. As a further illustration, it will be shown in a later chapter that fixed air may be regarded as an acid, and the decomposition of chalk by heat as that of a salt into acid and base.

The method of decomposing salts by heat, although very simple, was not always available. Some salts were not changed in the fire; others (such as sal-ammoniac and salt) were dissipated without leaving any residue: in the case of

silver and gold the residue left on heating a salt often consisted of the revivified metal. In cases such as these the base of the salt could only be separated with the help of an alkali.

Summary and Supplement

A. Chalk and Lime

Joseph Black (1728–1799), in his "Experiments upon Magnesia Alba, Quick-lime, and some other Alcaline Substances," read in June 1755, showed

(1) That chalk loses in weight by about 44 per cent. when burnt to lime.

(2) That, as nothing but a trace of water could be condensed by cooling the vapour (Margraaf), this loss in weight must be due to the escape of gas, to which he gave the name **fixed air.**

(3) That lime combines with water to form slaked lime, but releases it when it re-combines with fixed air to form chalk.

(4) That fixed air is present in small quantities in common air and in air dissolved in water.

(5) That fixed air is liberated from chalk by the action of acids ; apart from this liberation of gas, the action of acids upon chalk and lime is identical both qualitatively and quantitatively.

These changes may be represented by the following equations :

Burning of chalk, $CaCO_3 \rightarrow CaO + CO_2$

chalk → lime + fixed air

(Calcium carbonate.) (Calcium oxide.) (Carbon dioxide.)

Slaking of lime, $CaO + OH_2 \rightarrow Ca(OH)_2$

lime + water → slaked lime

(Calcium hydroxide.)

Action of fixed air on slaked lime—

$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + OH_2$

slaked lime + fixed air → chalk + water

Action of acids on chalk, slaked lime, and quicklime—

1. *Oil of vitriol*

$CaCO_3 + H_2SO_4 \rightarrow CaSO_4 + H_2O + CO_2$

$Ca(OH)_2 + H_2SO_4 \rightarrow CaSO_4 + 2H_2O$

$CaO + H_2SO_4 \rightarrow CaSO_4 + H_2O$

In each case, if dilute acid is used, solid *gypsum* or *selenite*, $CaSO_4,2H_2O$, is produced.

2. *Muriatic acid*
$$\begin{cases} CaCO_3 + 2HCl \rightarrow CaCl_2 + H_2O + CO_2 \\ Ca(OH)_2 + 2HCl \rightarrow CaCl_2 + 2H_2O \\ CaO + 2HCl \rightarrow CaCl_2 + H_2O \end{cases}$$

In each case a solution of *muriate of lime* (calcium chloride, $CaCl_2$) is produced.

B. THE ALKALIS

Boyle recognised an alkali by the facts that "it had a fiery taste upon the tongue," that it would "make an ebullition with acid spirits and precipitate diverse spirits made with them" and would "turn syrup of violets green" (*Producibleness of Chymical Principles*, 1680, pp. 35 and 37; *Works*, 1725, III. 372–373).

Black's observations on the alkalis are set out with modern equations in the following paragraphs:

1. *Mild alkalis* contain fixed air since they are able to re-convert lime into chalk—

K_2CO_3	+	$Ca(OH)_2$	→	$2KOH$	+	$CaCO_3$
potash	+	slaked lime	→	caustic potash	+	chalk
(Potassium carbonate.)		(Calcium hydroxide.)		(Potassium hydroxide.)		(Calcium carbonate.)

2. The *caustic alkali* which is produced in this action contains neither lime nor fixed air. It is very corrosive, but can be separated by evaporating in a silver dish.

3. The caustic alkali absorbs fixed air from the atmosphere, and is rendered mild thereby—

$$2KOH + CO_2 \rightarrow K_2CO_2 + H_2O.$$

4. The caustic alkalis, unlike the mild alkalis, do not effervesce with acids, *e.g.*—

KOH	+	HCl	→	KCl	+	H_2O
caustic potash	+	muriatic acid	→	sal sylvii	+	water

K_2CO_3	+	$2HCl$	→	CO_2	+	$2KCl$	+	H_2O
potash	+	muriatic acid	→	fixed air	+	sal sylvii	+	water

5. *Sal volatile* is a mild alkali, which can be rendered caustic by means of lime—

$(NH_3)_2CO_2$	+	CaO	→	$2NH_3$	+	$CaCO_3$
sal volatile	+	lime	→	ammonia	+	chalk
(Ammonium carbamate.)						

C. PREPARATION OF EARTHS.

Black prepared *magnesia alba* (magnesium carbonate, $MgCO_3$) by the action of alkalis on—

1. *Mother of nitre* (containing magnesium nitrate),

$$Mg(NO_3)_2 + K_2CO_3 \rightarrow MgCO_3 + 2KNO_3$$

2. *Bittern* (containing magnesium chloride),

$$MgCl_2 + K_2CO_3 \rightarrow MgCO_3 + 2KCl.$$

3. *Epsom salts* (magnesium sulphate),

$$MgSO_4 + K_2CO_3 \rightarrow MgCO_3 + K_2SO_4.$$

This magnesia is easily decomposed by heat, liberating fixed air and losing more than half its weight,

$$MgCO_3 \rightarrow MgO + CO_2.$$

It effervesces with acids, but after it has been burnt it dissolves without effervescence,

$$MgCO_3 + H_2SO_4 \rightarrow MgSO_4 + H_2O + CO_2$$
$$MgO + H_2SO_4 \rightarrow MgSO_4 + H_2O$$

Magnesia, free from fixed air, was also prepared by igniting the nitrate,

$$2Mg(NO_3)_2 \rightarrow 2MgO + 4NO_2 + O_2.$$

CHAPTER V

THE STUDY OF GASES

A. Fixed Air and Inflammable Air

Van Helmont recognises the existence of gases differing from ordinary air.—The fact that metals, insoluble in most liquids, are dissolved by acids, was known and used from very early times. The liberation of gases during this process must have been noticed from the first, but it was not until the latter part of the seventeenth century that any attempt was made to collect and examine these volatile products. **Van Helmont** (1577–1644), to whom we owe the name of "gas," recognised the existence of a poisonous GAS SYLVESTRE, *i.e.* "wood-gas," which possessed the power of extinguishing a lighted candle; he detected it in the air of a cavern, in the fumes from a charcoal fire, and as a product of the fermentation of wine and beer; he also recognised what he thought to be the same gas as a product of the action of nitric acid on silver, and of distilled vinegar on chalk. In contrast to this, he found in the large intestine, and as a product of the fermentation of dung, an inflammable gas to which he applied the name GAS PINGUE. The names used by van Helmont were applied broadly to two types of gas, analogous with the "choke-damp" and "fire-damp" of miners; no attempt was made to distinguish

between one inflammable gas and another, or between one poisonous gas and another.

Gases collected over water by Mayow (1674).—A few years later, about 1674, the familiar method of collecting gases over water was described by John Mayow, who used it both for investigating the reduction in volume of air during burning and breathing, and for examining gases prepared artificially.[1] For the latter purpose Mayow used a flask inverted in a trough filled with diluted oil of vitriol (Fig. 14, p. 33). The gas was produced by the action of the acid on two or three iron spheres in the neck of the flask. When nitric acid was used, much of the gas dissolved in the liquid, and repeated action of the acid on the metal was needed to fill the flask with gas. With oil of vitriol no such contraction occurred. Mayow proved that these gases possessed the same elastic properties as air,[2] and that, when added to a limited volume of ordinary air, they did not in any degree prolong the life of a mouse confined in it ; but no other tests were made, and Mayow could not be certain "whether air of this kind is really common air or not" (A. C. R. XVII. 113).

Cavendish prepares "Factitious Air" (1766).—Nearly one hundred years intervened between the experiments of Mayow and the appearance in the *Philosophical Transactions of the Royal Society* for 1766 of a remarkable series of three papers by the Honourable **Henry Cavendish** (1731–1810) entitled "Experiments on Factitious Air." Black had already investigated the part played by "fixed air" in the burning of chalk to lime, and in other related processes. But although he showed that fixed air was present in the atmosphere, he did not attempt to collect or

[1] As described by Boyle in 1660 (*Works*, 1725, II. 432).

[2] Boyle's tract "Touching the Spring of Air and its Effects" (1660) had recently appeared, so that this point was of special interest at the time (see Chapter XV. p. 320).

handle it. It was therefore left to Cavendish to make the first careful examination of those gases whose existence had been vaguely recognised during the preceding one hundred and fifty years. Cavendish writes:

"By factitious air, I mean in general any kind of air which is contained in other bodies in an unelastic state, and is produced from thence by art."

"By fixed air, I mean that particular species of factitious air, which is separated from alkaline substances by solution in acids or by calcination; and to which Dr. Black has given that name in his treatise on quick-lime (*Phil. Trans.*, 1766, **56**, 141).

Describing next the action of acids on metals he writes:

"I know of only three metallic substances, namely, zinc, iron and tin, that generate inflammable air[1] by solution in acids; and those only by solution in the diluted vitriolic acid, or spirit of salt."

"Zinc dissolves with great rapidity in both these acids; and, unless they are very much diluted, generates considerable heat. One ounce of zinc produces about 356 ounce measures of air[2]: the quantity seems just the same whichever of these acids it is dissolved in. Iron dissolves readily in the diluted vitriolic acid, but not near so readily as zinc. One ounce of iron wire produces about 412 ounce measures of air: the quantity was just the same, whether the oil of vitriol was diluted with $1\frac{1}{2}$, or 7 times its weight of water: so that the quantity of air seems not at all to depend on the strength of the acid" (*ibid.*, p. 144).

Inflammable air was also obtained by the action of spirit of salt on iron, but the quantity was not measured. One ounce of tinfoil dissolved in strong spirit of salt yielded 202 ounce measures of inflammable air; the same gas was also produced slowly by the action of vitriol on tin.

[1] The name "inflammable air" is here used for the first time.

[2] The "ounce-measure" as used by Cavendish was the volume occupied by an ounce of water.

The identification of inflammable air and fixed air by Cavendish.—To Cavendish belongs the credit of introducing the method of identifying gases by careful measurements of their physical properties. For this purpose he measured the density of inflammable air and of fixed air from various sources; in the case of fixed air the solubility in water was also found. The densities were measured by filling a bladder with the gas, and finding the change in weight when the bladder was emptied. If the gas was heavier than ordinary air the bladder became lighter when emptied, but if the gas was lighter than air a gain in weight was observed. In either case the density of the gas was calculated from the known weight of the bladder-full of air, and the change of weight on emptying the bladder.

In the case of inflammable air a *gain* of weight was observed amounting in four experiments to $40\frac{3}{4}$, $40\frac{1}{2}$, $41\frac{1}{2}$ and 41 grains, when using 80 ounce-measures of gas prepared by the action of zinc on vitriolic acid and on spirit of salt, of iron on oil of vitriol, and of tin on spirit of salt respectively. The gas produced by the four methods was therefore the same; as air was 800 times lighter than water, 80 ounce-measures of common air weighed 80×480[1] $\div 800 =$ 48 grains; the same volume of inflammable air weighed $48 - 41 = 7$ grains; this gas was therefore $48 \div 7 = 6{\cdot}9$ times lighter than common air or $80 \times 480 \div 7 = 5490$ times lighter than water.[2]

In the case of fixed air there was a *loss* in weight of 34 grains on a volume of 100 ounces; the air weighed $100 \times 480 \div 800 = 60$ grains; the fixed air weighed $60 + 34 =$ 94 grains; it was therefore $1\frac{57}{100}$ times heavier than air or 511 times lighter than water.[2] The values for fixed air were trustworthy; those for inflammable air were un-

[1] 480 grains = 1 ounce.

[2] The correct values are: for inflammable air, 14·4 and 11600; for fixed air, 1·53 and 530.

trustworthy, because they depended so largely on an exact knowledge of the density of the common air displaced by the bladder, *e.g.*, taking the density of common air as being 850 (instead of 800) times less than that of water, Cavendish found inflammable air to be "9,200 times lighter than water, or $10\frac{8}{10}$ lighter than common air."

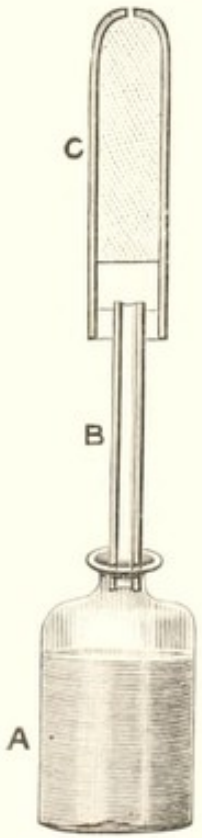


FIG. 17 — CAVENDISH'S APPARATUS FOR FINDING THE WEIGHT AND DENSITY OF GASES.

Cavendish devises a new method of weighing gases.—In order to overcome this difficulty Cavendish devised a method of weighing directly the gas liberated by the action of acids on a known weight of metal or chalk. If the volume of the gas had been determined in a separate experiment the density could easily be calculated. Cavendish writes:

"I endeavoured to find the weight of the air discharged from a given quantity of zinc by solution in the vitriolic acid in the manner represented in Fig. 17. *A* is a bottle filled near full with oil of vitriol diluted with about six times its weight of water: *B* is a glass-tube fitted into its mouth and secured with lute:[1] *C* is a glass cylinder fastened on the end of the tube, and secured also with lute. The cylinder has a small tube at its upper end to let the inflammable air escape, and is filled with dry pearl-ashes[2] in coarse powder. The whole apparatus together with the zinc, which was intended to be put in, and the lute which was to be used in securing the tube to the neck of the bottle, were first weighed carefully; its weight was 11930 grains. The zinc was then put in, and the tube put in its place. By this

[1] "The lute used for this purpose . . . . is composed of almond powder, made into a paste with glue, and beat a good deal with a heavy hammer. This is the strongest and most convenient lute I know of" (*loc. cit.*, p. 143, footnote).

[2] *I.e.*, potash.

means the inflammable air was made to pass through the dry pearl-ashes; whereby it must have been pretty effectively deprived of any acid or watery vapours that could have ascended along with it (*Phil. Trans.* 1766, **56**, 153).

The loss in weight was $11\frac{3}{4}$ grains, but one grain of this was due to the displacement of the common air in the bottle by inflammable air; the true weight of the inflammable air was therefore $10\frac{3}{4}$ grains.

The weight of zinc used in this experiment was 254 grains. A previous experiment (p. 66) had shown that one grain of zinc gave 356 grain-measures of inflammable air. The volume from 254 grains would therefore be $254 \times 356 = 90424$ grain-measures of gas.

By combining the two experiments it was seen that $10\frac{3}{4}$ grains of the gas occupied the same volume as 90424 grains of water. The gas was therefore 8410 times lighter than water, or $10\frac{1}{2}$ times lighter than common air.

Cavendish determines the weight of fixed air set free by the action of acids on chalk and the alkalis.—The same method was applied to find the weight of fixed air liberated by acids from various substances, blotting-paper being substituted for the pearl-ashes because the greater weight of gas demanded less careful drying. Cavendish found that:

1000 parts of marble lost 407 parts of fixed air.
1000 parts of sal volatile lost 528 to 538 parts of fixed air.
1000 parts of pearl-ashes lost 284 to 287 parts of fixed air.
1000 parts of a crystalline salt obtained by saturating pearl-ashes with fixed air lost 423 parts of fixed air.

The quantity of acid required to liberate the fixed air from each substance was also measured, and compared with the weight of fixed air set free. It was found that the acid which liberated 100 parts of fixed air from marble set free 109 parts from pearl-ashes, 217 from sal volatile, and 211 parts from the crystals prepared by the action of fixed

air on potash; the two latter compounds thus contained twice as much fixed air, relatively to their neutralising power, as the two former.

Cavendish measures the solubility of fixed air.—In the case of fixed air, its solubility in water was measured and used to identify the gas. Cavendish states that:

"Water when the thermometer is about 55° will absorb rather more than an equal bulk." "Water heated to the boiling point is so far from absorbing air, that it parts with what it has already absorbed" (*Phil. Trans.*, 1766, **56**, 163).

The gas was also lost by exposure to air.

By measuring the solubility, as well as the density, Cavendish was able to prove that the gas set free during fermentation was identical with fixed air prepared from chalk and the alkalis.

In his investigation of fixed air Cavendish introduced the method of storing over mercury the gas which he had collected by the displacement of water from an inverted bottle. This use of mercury in place of water for manipulating soluble gases proved to be of very great value in Priestley's experiments a few years later.

B. Gases Derived From Nitric Acid.

Priestley's work on gases.—Whilst Cavendish was the first to make accurate measurements of the physical properties of gases, the discovery of their chemical properties was mainly the work of Priestley. The state of knowledge when Priestley began his work upon gases is described in the following paragraphs:

"Van Helmont, and other chymists who succeeded him, were acquainted with the property of some *vapours* to suffocate, and extinguish flame, and of others to be ignited . . . But they had no idea that the substances (if, indeed, they knew that they were *substances*, and not merely *properties*, and *affections* of bodies which produced those effects) were

capable of being separately exhibited in the form of a *permanently elastic vapour*, not condensible by cold, to which I give the name of *air*, any more than the thing that constitutes *smell*. In fact they knew nothing at all of any air besides *common air*, and therefore they applied the term to no other substances whatever.

"Mr. Boyle was, I believe, the first who discovered that what we now call *fixed air*, and also *inflammable air*, are really *elastic fluids*, capable of being exhibited in a state unmixed with common air . . . .

"Besides these two kinds of factitious air, that which I call *nitrous air* obtruded itself upon Dr. Hales; but even he had no idea of there being more than *one kind of air*, loaded with different vapours; and was far from imagining that they differed from one another so very essentially as they are now known to do. And though Mr. Boyle, Dr. Hales, and others, could not but be acquainted with the effluvium of *spirit* of salt, and also of *volatile alkali*, they could have no idea that the substance which had those powers was capable of being separated from common air, and of being exhibited free from moisture, in the form of a permanently elastic vapour, to appearance exactly like that which constitutes the common atmosphere . . . .

"Even Mr. Cavendish, whose experiments relating to air immediately preceded my own, appears not to have had so much as a suspicion of this kind. For he relates an experiment of his, on the solution of copper in the marine acid, as inexplicable, except on the hypothesis of there being a kind of *air that lost its elasticity by the contact of water*, which admits of the easiest solution imaginable, on the supposition of the spirit of salt emitting a vapour, which though capable of being confined by quicksilver, and of being by that means exhibited in the form of air, was instantly absorbed by water, which would thereupon become possessed of all the properties of common spirit of salt.

"In fact, none of the chymists appear to have had the least idea of its being even possible to separate the acid or alkaline principles from the water with which they are always found combined; and therefore, though they did suppose them capable of further *concentration*, they still

considered a certain portion of water as absolutely *essential* to them; and consequently all the experiments that have hitherto been made on the affinities of the acids, and alkalis are, in fact, nothing more than the affinities of compound substances, consisting of *acids* or *alkali*, and *water*. I have been so particular in stating these historical facts, for the sake of those chymists who can see nothing *new* in my experiments on the several acids and alkali, *divested of water*, and exhibited *in the form of air*" (*Experiments on Air*, 1777, Vol. III. pp. 325 *et seq.*).

Priestley (1772) prepares and examines nitrous air.—The gas which Mayow prepared by the action of iron on nitric acid was dismissed by Cavendish with the remark that iron, zinc and tin, "dissolve readily in the acid and generate air; but the air is not at all inflammable." Priestley, however, after examining fixed air and inflammable air, proceeded to make a detailed study of this action. By dissolving various metals (amongst them brass, iron, copper, tin, silver, mercury) in nitric acid, Priestley collected over water a colourless gas, which he named NITROUS AIR. (*Experiments on Air*, 1774, I. 109). The gas was noxious to animals, and extinguished a lighted taper. But it differed from fixed air in that it did not precipitate lime-water and was only slightly soluble in common water; water, he says, "absorbs one-tenth of its bulk of nitrous air." The gas is, however, freely soluble in a solution of green vitriol in water, which can be made to "absorb more than ten times its bulk of nitrous air, without any sensible approach to saturation." (*Experiments and Observations*, 1779, IV. 48); this fact was afterwards used by Humboldt and by Davy to test the purity of different samples. The solution in which the gas has been absorbed "becomes of a very dark colour; but becomes green again on being exposed to the open air" (*Experiments on Air*, 1777, III. Preface p. xxxiii). Davy showed that the green colour could be restored and pure nitrous air recovered by gently heating the solution (*Works*, III. 99).

Priestley studies the combination of nitrous air with common air and with oxygen.—The most remarkable property of nitrous air was that of combining with common air to form brown NITROUS FUMES[1] which dissolved at once in water. Priestley made a careful study of this action and showed that the diminution of volume occasioned by the addition of an equal volume of nitrous air could be used to measure the goodness of common air. Speaking of nitrous air he says:

"One of the most conspicuous properties of this kind of air is the great diminution of any quantity of common air with which it is mixed, attended with a turbid red, or deep orange colour, and a considerable heat. . . . ."

"The diminution of a mixture of this and common air is not an equal diminution of both the kinds . . . but of about one-fifth of the common air, and as much of the nitrous air as is necessary to produce that effect; which, as I have found by many trials, is about one-half as much as the original quantity of common air. . . ."

"If, after this full saturation of common air with nitrous air, more nitrous air be put to it, it makes an addition equal to its own bulk, without producing the least redness, or any other visible effect. . . ."

"It is exceedingly remarkable that this effervescence and diminution, occasioned by the mixture of nitrous air, is peculiar to common air, or *air fit for respiration*; and, as far as I can judge, from a great number of observations, is at least very nearly, if not exactly, in proportion to its fitness for this purpose; so that by this means the goodness of air may be distinguished much more accurately than it can be done by putting mice, or any other animals, to breathe in it" (*Experiments on Air*, 1774,[2] I. 110–115).

[1] These fumes were generally regarded as the vapour of nitric acid; Priestley described them as "nitrous acid vapour," Davy (1800) as "nitrous acid gas," Gay-Lussac in 1809 as "nitric acid" and in 1816 as "nitrous acid"; in order to avoid confusion, the term "nitrous fumes" is used in the succeeding pages. The name "nitrogen peroxide" was not introduced until about 1850.

[2] The first part of Vol. I., published in 1774, describes experiments carried out in 1772.

Priestley tests the goodness of common air by mixing it with nitrous air.—Priestley's method of testing air was described in detail a few years later as follows :—

"I first provide a phial, containing about half an ounce of water, which I call *the air-measure*. This I fill with air by having first filled it with water, and placed it over the opening of the funnel in my shelf, and when it is filled I slide it along the shelf, always observing that there be a little more air than I want. The phial being thus exactly filled with the air which I am about to examine, and care being taken that it be not warmed by holding in the hand, &c. I empty it into a jar about an inch and a half in diameter, and then introduce to it the same measure of nitrous air, and let them continue together about two minutes. I choose to have an overplus of nitrous air, that I may be sure to have phlogiston enough to saturate all the common air. If I find the diminution with these measures to be very considerable, I introduce another measure of nitrous air ; but the purest dephlogisticated air will not, I believe, require more than two equal measures of nitrous air."

"Sometimes I leave the common and nitrous air in the jar all night, or a whole day ; but always take care that, whatever kinds of air I be comparing together, they remain the same space of time before I proceed to note the degree of diminution."

"When the preceding part of the process is over, I transfer the air into a glass tube, about three feet long, and one-third of an inch wide, carefully graduated according to the air measure, and divided into *tenths* and *hundredth parts ;* so that one of the latter will be about a sixth or an eighth of an inch. Then immersing the tube in a trough of water, so that the water in the inside of the tube shall be on a level with the water on the outside, I observe the space occupied by them both, and express the result in *measures* and *decimal parts of a measure*, according to the graduation of the tube" (*Experiments and Observations*, 1779, IV. Introduction, pp. xxx.—xxxii.).

Using this method, Priestley in 1772 thought he perceived

a slight inferiority in the air of his study as compared with that outside, and in a sample of air from York as compared with that of Leeds.

Two years later he discovered the gas, richer than common air, to which Lavoisier gave the name oxygen. On adding nitrous air to the gas prepared from red precipitate or from mercury calx, he found that it was about five times "as good as the best common air" he had ever tested.

It was soon recognised that the diminution of volume of common air was due to the absorption of oxygen, but the variations which Priestley thought he had found in the behaviour of different samples were proved to be due to experimental errors. The careful experiments made by Cavendish in 1783 showed that the composition of air is remarkably constant, the value found for 100 volumes of air being:

Diminution by nitrous air	(oxygen)	20·84 volumes.
Residue	(azote)	79·16 volumes.

The graduated glass tube which Priestley used for measuring the goodness of air is still known as a EUDIOMETER (Greek εὐ, *good*, μέτρον, *a measure;* see Priestley, *Experiments on Air*, 1777, III. 379 and 380).

Priestley (1777) describes the properties of nitrous fumes.—On account of their solubility and corrosive properties, the brown nitrous fumes produced by combination of nitrous air with oxygen, or by the action of strong nitric acid on metals, could not be collected by the methods which Priestley employed for other gases. He was, therefore, obliged to collect the gas by displacing the air from narrow-necked flasks provided with glass stoppers. This gas, as Priestley prepared it by the action of nitric acid upon bismuth, was obviously contaminated both with nitrous air and with common air. He writes:

"Being disappointed, as has been seen, in my expecta-

tions of confining the nitrous acid vapour by *animal oils*, it occurred to me, that, in lieu of this, it might not be wholly without its use, if I could shut up this vapour in dry glass phials, with ground stopples. And though, in this method of procuring it, by the solution of bismuth, or other things with which it unites most rapidly, there is necessarily a mixture of *nitrous air*, it is inconsiderable in proportion to the quantity of pure nitrous vapour itself. And although a mixture of *common air* also would necessarily remain in the phial, it could only serve to dilute the acid vapour, and could not materially alter the properties of it. Also, if the mouths of the phials were small, they might be opened, and various substances admitted to the vapour, without much loss of the acid ; especially as all acid vapours, I had reason to think, were heavier than common air" (*Experiments on Air*, 1777, III. 184).

The most conspicuous quality of the nitrous fumes is their brown colour, by which their presence is disclosed in many operations in which nitric acid takes part. The colour is permanent, and has the remarkable property of becoming much intensified by heating. This observation interested Priestley so much that he was in the habit of carrying a bottle of the gas in his pocket in order to show its curious behaviour to his friends. Priestley writes :

"The change of colour given to this vapour by heat is not a little remarkable, for it is altogether independent of gravity or condensation. In order to make some experiments of this kind to proper advantage, I procured a glass tube, three feet long, and about an inch wide, closed at one end, and fitted with a ground stopple at the other. This tube I easily filled with red vapour, in consequence of its being much heavier than common air ; and closing the open end with the stopple, observed, that that part of the tube which I held in my hand was manifestly of a deeper colour than any other part of the tube. On this I held one end of it to the fire, and found that that end grew most intensely red, three or four times more so than the rest of the tube. The direction in which the tube was

held made no difference with respect to the red part of it; the part that was hottest being always of the deepest colour, whether it was held upwards or downwards; so that whether the heated vapour ascended or descended, it did not retain its colour in the smallest degree, after it had been opposite to the heated part of the glass.

"That this extraordinary redness was not occasioned by the vapour being more *rarefied* in that particular place, appeared by the whole tube assuming the same deep red colour when the whole length of it was made equally hot: for the vapour being closely confined, the density of it within the tube must necessarily have continued the same in all the variations of heat or cold. This redness, therefore, must be the proper effect of *heat*, on the phlogiston, as I should imagine, of the vapour. Repeating this experiment very often, with the same tube, and the same vapour, it became alternately of a deeper or lighter colour, according as it was kept hot or cold, without any sensible change, except that which depended upon this single circumstance. This is really a striking experiment, and especially when the tube contains first so much vapour as to be nearly transparent when it is cold; so that the heat alone gives it all the colour that it acquires.

"In order to observe the *utmost effect of heat* on this vapour, I placed the closed end of the tube near the fire, and bringing it gradually nearer and nearer, observed that the colour deepened uniformly with the increase of heat, till, the glass actually melting, the compressed vapour burst its way out" (*Experiments on Air*, 1777, III. 186–188).

Priestley (1772) discovers "diminished nitrous air" or "laughing gas."—One of the agents used by Priestley for "phlogisticating" or deoxidising common air was a mixture of iron filings and brimstone, or sometimes iron filings alone. The action of this agent on nitrous air gave rise to a new gas possessing remarkable properties. Priestley describes this discovery as follows:

"The diminution of common air by a mixture of nitrous air, is not so extraordinary as the diminution which nitrous

air is subject to from a mixture of iron filings and brimstone, made into a paste with water. This mixture, as I have already observed, diminishes common air between one-fifth and one-fourth, but has no such effect upon any kind of air that has been diminished, and rendered noxious by any other process; but when it is put to a quantity of nitrous air, it diminishes it so much, that no more than one-fourth of the original quantity will be left."

"Nitrous air thus diminished has not so strong a smell as nitrous air itself, but smells like common air in which the same mixture has stood" (*Experiments on Air*, 1774, I. 118–119).

Priestley was astonished to find that an agent which he had employed previously to remove all the goodness from common air, had actually converted the inert nitrous air into a DIMINISHED NITROUS AIR "with properties which, at the time of my first publication on this subject, I should not have hesitated to pronounce impossible, *viz.* air in which a candle burns quite naturally and freely, and which is yet in the highest degree noxious to animals, insomuch that they die the moment they are put into it" (*ibid.*, p. 215).

As "diminished nitrous air" is soluble in cold water, it was best prepared over mercury; the gas was then almost like oxygen in its power of supporting combustion. On the other hand, long contact with iron over water destroyed this property, the diminished nitrous air being either absorbed or wholly deoxidised. Priestley found that:

"A candle burned with an enlarged flame . . . in nitrous air, which had been in contact with iron in quicksilver, about six months.

"Water being admitted to the remainder of this air, it began to be absorbed as usual.

"Nitrous air, which had been confined above a year in contact with iron, standing in water, was, in all respects like phlogisticated common air: it neither diminished common

air, nor was diminished by nitrous air, and extinguished a candle" (*Experiments on Air*, 1775, II. 177).

The action of nitric acid on metals gives rise to nitrous fumes, nitrous air, and diminished nitrous air.—In the action of nitric acid on metals, diminished nitrous air is often formed, especially if weak acid be used; being soluble in cold water, but expelled by heat, the gas may be set free by warming cold nitric acid in which iron, zinc, or tin has been dissolved.

"The solution of iron in spirit of nitre is known to produce nitrous air; but when all the nitrous air is produced in this manner, without foreign heat, if a candle be applied to the solution, more air will be procured; and this will be possessed of the peculiar kind of inflammability above mentioned.

"I have also procured this kind of air in a direct process by the solution of *zinc* and *tin*."

"When . . . I used only a very weak spirit of nitre in the solution of zinc . . . I got no other than this kind of air in which a candle burned with an enlarged flame; and the air was of the very same kind from the beginning to the end of the process" ("Of Nitrous Air in which a Candle Burns," *Experiments on Air*, 1777, III., pp. 133, 134, 139).

Berthollet (1785) prepares "diminished nitrous air" or "laughing gas" by heating nitrate of ammonia.—Berthollet discovered in 1785 that when nitrate of ammonia is heated to about 150°C., it is decomposed into water and "diminished nitrous air." This method of preparation was used in the year 1799 by Sir **Humphry Davy** (1778-1829), who found that the pure gas made by this method had the following properties:

a. A candle burnt in it with a brilliant flame, and crackling noise.

b. Phosphorus introduced into it in a state of inflammation, burnt with infinitely greater vividness than before.

c. Sulphur introduced into it when burning with a feeble blue flame, was instantly extinguished; but when in a state of active inflammation . . . it burnt with a beautiful and vivid rose-coloured flame.

d. Inflamed charcoal . . . burnt with much greater vividness than in the atmosphere.

e. To some fine twisted iron wire a small piece of cork was affixed: this was inflamed, and the whole introduced into a jar of the air. The iron burned with great vividness, and threw out bright sparks as in oxygen.

f. 30 measures of it exposed to water previously boiled, was rapidly absorbed; when the diminution was complete, rather more than a measure remained.

g. Pure water saturated with it, gave it out again on ebullition, and the gas thus produced retained all its former properties.

h. It was absorbed by red-cabbage juice; but no alteration of colour took place.

i. Its taste was distinctly sweet, and its odour slight, but agreeable.

j. It underwent no diminution when mingled with oxygen or nitrous gas (Davy's *Works*, III. 54).

Davy (1799) uses "laughing gas" as an anæsthetic.—Although the gas had been credited with the most deadly properties, and with the power of producing plague and other contagious diseases, Davy found from personal experiments in the spring of 1799 that it could be breathed without harm, and had indeed remarkable stimulating and exhilarating qualities. Robert Southey, one of many friends who submitted themselves to the action of the new intoxicant, describes his feelings as follows:

"My first definite sensation was a dizziness, a fullness in the head, such as to induce a fear of falling. This was momentary. When I took the bag from my mouth, I immediately laughed. The laugh was involuntary, but highly pleasurable, accompanied by a thrill all through me; and a tingling in my toes and fingers, a sensation perfectly new and delightful" (*Works*, III. 301).

Effects such as these gave to the gas the popular name of "laughing gas." Its permanent utility as an anæsthetic in dentistry is forshadowed in Davy's own experience:

"The power of the immediate operation of the gas in removing intense physical pain, I had a very good opportunity of asertaining.

"In cutting one of the unlucky teeth called dentes sapientiæ, I experienced an extensive inflammation of the gum, accompanied with great pain, which equally destroyed the power of repose, and of consistent action.

"On the day when inflammation was most troublesome, I breathed three large doses of nitrous oxide. The pain always diminished after the first four or five inspirations; the thrilling came on as usual, and uneasiness was for a few minutes swallowed up in pleasure. As the former state of mind however returned, the state of organ returned with it; and I once imagined that the pain was more severe after the experiment than before" (*Works*, III. 276).

C. Acid Air and Alkaline Air.

Cavendish (1766) collects "marine acid air."—From the time of Glauber it had been customary to prepare muriatic acid by distilling into water the pungent gas produced by the action of strong oil of vitriol on common salt (Chap. II, p. 14). The gas was first collected by Cavendish in "an experiment with design to see, whether copper produced any inflammable air by solution in spirit of salt." He found that he "could not procure any inflammable air thereby," but, on the application of heat, he was able to drive off a considerable quantity of gas which had the peculiar property of "losing its elasticity when in contact with water." The gas set free in the bottle containing the copper and acid (Fig. 18) was at first separated from the water in the receiver by a "barrier of common air," but as soon as this was removed the dissolution of the gas proceeded

rapidly, so that the water in the receiver "rushed violently into the bottle and filled it almost entirely full" (*Phil. Trans.* 1766, **56**, 157–158).

Priestley (1772) isolates "marine acid air."—By making use of mercury instead of water, Priestley had no difficulty in obtaining this ACID AIR in a permanent form. He showed that it could be driven off by heating spirit of salt alone, the presence of copper being unnecessary. Its peculiar behaviour depended entirely on its extreme solubility in water, which he found to absorb 576 times its volume of the gas.[1] Spirit of salt was, indeed, merely a solution of acid air in perhaps twice its weight of water. Priestley also prepared the gas by the action of oil of vitriol on salt, a more efficient method which had the advantage of producing a dry gas. He found that "acid air, extinguishes flame, and is much heavier than common air" (*Experiments on Air*, 1774, I. 143–147).

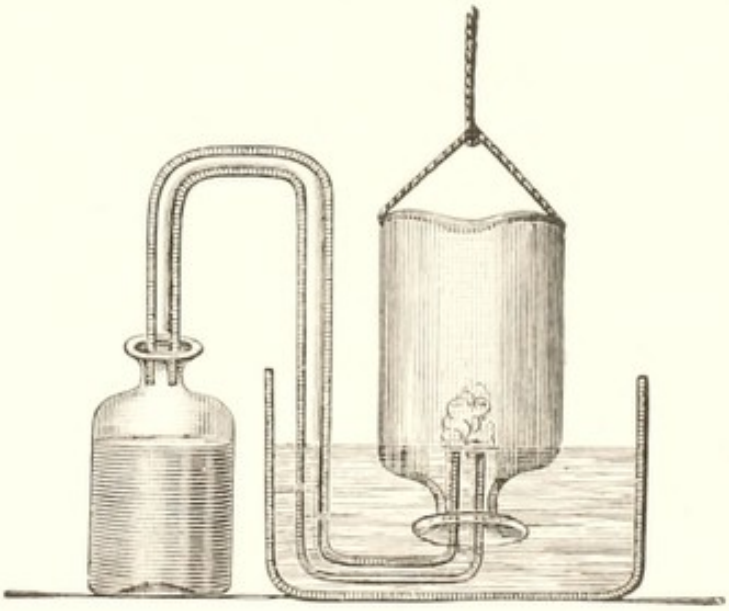


FIG. 18.—APPARATUS USED BY CAVENDISH TO PREPARE A GAS WHICH "LOST ITS ELASTICITY BY CONTACT WITH WATER."

Priestley isolates "alkaline air."—Encouraged by his success in separating an elastic air from spirit of salt, Priestley next endeavoured to collect an ALKALINE AIR from the "volatile spirit of sal-ammoniac." In this he was successful: the gas which was set free by heating the

[1] Two and a-half grains of water dissolved three ounce-measures of the gas.

volatile spirit remained permanently elastic when collected over mercury, but collapsed immediately when brought into contact with water. Priestley found that alkaline air was only a little less soluble than acid air, one volume of water dissolving 336 volumes of the gas.[1] It also differed from acid air in being lighter instead of heavier than common air. He found that the gas (to which the name of ammonia was given by Bergman in 1782), could be prepared directly by heating crystals of sal-ammoniac with slaked lime in a gun barrel: by passing the product into water he obtained a very strong "spirit" from which he could expel the alkaline air as required (*Experiments on Air*, 1774, I. 163–169).

Priestley prepares sal-ammoniac by mixing alkaline air with acid air.—Thinking that gases possessed of such opposite properties were likely to combine together to form a neutral substance, possibly identical with common air, Priestley brought together vessels containing alkaline air and acid air. To his great astonishment he obtained a solid product which he identified as sal-ammoniac; this volatile salt was therefore a compound formed by the union of alkaline air with acid air.

"Having satisfied myself with respect to the relation that alkaline air bears to water, I was impatient to find what would be the consequence of mixing this new air with the other kinds with which I was acquainted before, and especially with *acid* air; having a notion that these two airs, being of opposite natures, might compose a *neutral air*, and perhaps the very same thing with common air. But the moment that these two kinds of air came into contact, a beautiful white cloud was formed, and presently filled the whole vessel in which they were contained. At the same time the quantity of air began to diminish, and, at length, when the cloud was subsided, there appeared to be formed a solid *white salt*, which was found to be the common

[1] One and a-quarter grains of water dissolved seven-eighths ounce-measures of gas.

sal-ammoniac, or the marine acid united to the volatile alkali" (*Experiments on Air*, 1774, I. 169–170).

Sal-volatile formed by the union of alkaline air with fixed air.—On mixing alkaline air with fixed air Priestley again obtained a solid product which he identified as the volatile alkali "sal-volatile."

"*Fixed air* admitted to alkaline air formed long and slender crystals, which crossed one another and covered the sides of the vessel in the form of net-work. These crystals must be the same thing with the volatile alkalis which chemists get in a solid form, by the distillation of sal-ammoniac with fixed alkaline salts" (*Experiments on Air*, 1774, I. 171).

Apparatus for experiments on gases. — The first apparatus used for experiments on gases, as distinguished from condensible vapours, was that of **Mayow**, Figs. 11, 12, 13, 16. It should be noticed that, in preparing gases artificially by the action of acids on iron, Mayow was not able to collect the gas over water, but was obliged to fill the whole apparatus (Fig. 14, p. 33) with acid.

This disadvantage was removed by **Stephen Hales** (1677—1761), botanist, chemist, and Vicar of Teddington, who was one of the first to separate the GENERATOR from the RECEIVER of the gas. His *Vegetable Statics* (1727) is chiefly concerned with hydrostatic experiments on the pressure of the sap in plants. But the sixth chapter, occupying nearly one-third of the book, deals with "an attempt to analyse the Air by means of a great variety of chymio-statical experiments, which shew in how great a proportion Air is wrought into the composition of animal, vegetable, and mineral Substances, and withal how readily it resumes its former elastick state, when in the dissolution of those Substances it is disengaged from them."

In order to measure the volume of gas set free by heating animal, vegetable, and mineral substances, Hales used a

glass retort *r* (Fig. 19*a*) luted securely to a gauge *ab*, standing in a trough of water *xx*. The gauge was made from a long-necked flask, pierced at the bottom to admit a syphon-tube *y*, by means of which air could be drawn out and water sucked up as far as *z*. The fall or rise of the level of the water in the gauge, after heating the contents of the retort, showed how much air had been liberated or absorbed.

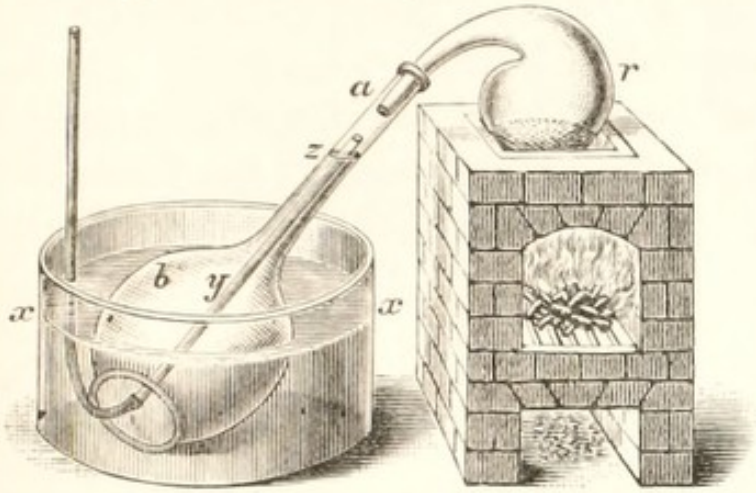


FIG. 19—(*a*) HALES'S APPARATUS FOR MEASURING THE VOLUME OF GAS SET FREE BY HEATING ANIMAL, VEGETABLE, AND MINERAL SUBSTANCES.

This apparatus had the disadvantage that the joint at *a* was liable to leak, especially when an iron retort had to be used for stronger heating, or when the gas had to be kept for several days before its volume became constant.

These difficulties were overcome in a second form of the apparatus (Fig. 19*b*). This consisted of a retort *rr* made from an iron gun-

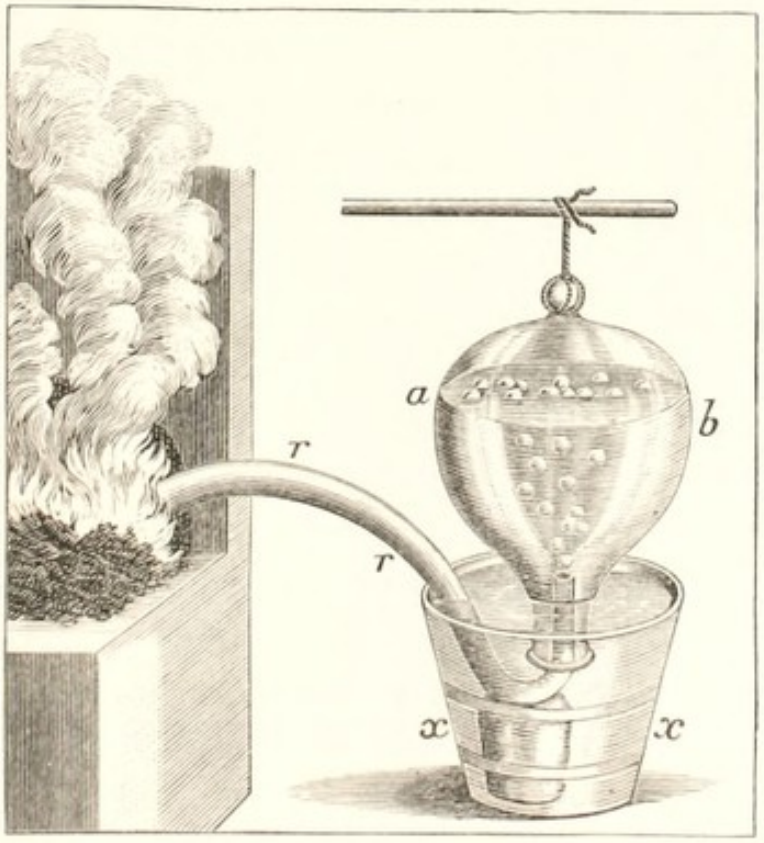


FIG. 19—(*b*) HALES'S APPARATUS (Improved design).

barrel, with a lead syphon attached to the end. The gas was carried by the syphon through a vessel of water *xx* into an inverted flask *ab*, where it could be stored for any length of time without risk of leakage.

The great importance of this new design will be realised on comparing it with the apparatus used by Cavendish (Fig. 18), by Lavoisier (Figs. 16, 21, 25), and by Priestley (Fig. 20).

Priestley's apparatus.—The apparatus which Priestley used for manipulating gases is described at the beginning of the first volume of his *Experiments on Air* and illustrated by two plates (numbered and lettered consecutively) which are reproduced in Fig. 20.[1]

The most important feature was the *trough*, often called a PNEUMATIC TROUGH, shown with all its accessories at 1 in the first plate. The original trough *a* was of earthenware, about eight inches deep, with thin flat stones, *bb*, just below the surface; afterwards a large wooden trough was used with a *shelf* fixed an inch from the top. The various gases were stored in cylindrical *jars*, *cc*, which could be immersed in the trough, or stood on the shelf, or lifted out in dishes as at 2 2 2. *Mice* were stored as at 3 in a receiver standing on a perforated tin plate and provided with a perforated cover held down by weights; in order to test the goodness of a sample of air, a mouse was held by the back of the neck and passed through the water into a tall *beer-glass*, *d*, of two or three ounces capacity, in which a mouse could usually live from twenty to thirty minutes. The *tapering cork*, 4, was used to close or open a small bottle inside a jar of air, whilst the *wire stand*, 5, served to support small dishes as at *f*. The *funnel*, 6, was used to pour gases from a vessel with a wide neck into a vessel with a narrow neck,

[1] In the second plate, the blackboard has been moved and the table altered a little in order to reproduce on as large a scale as possible.

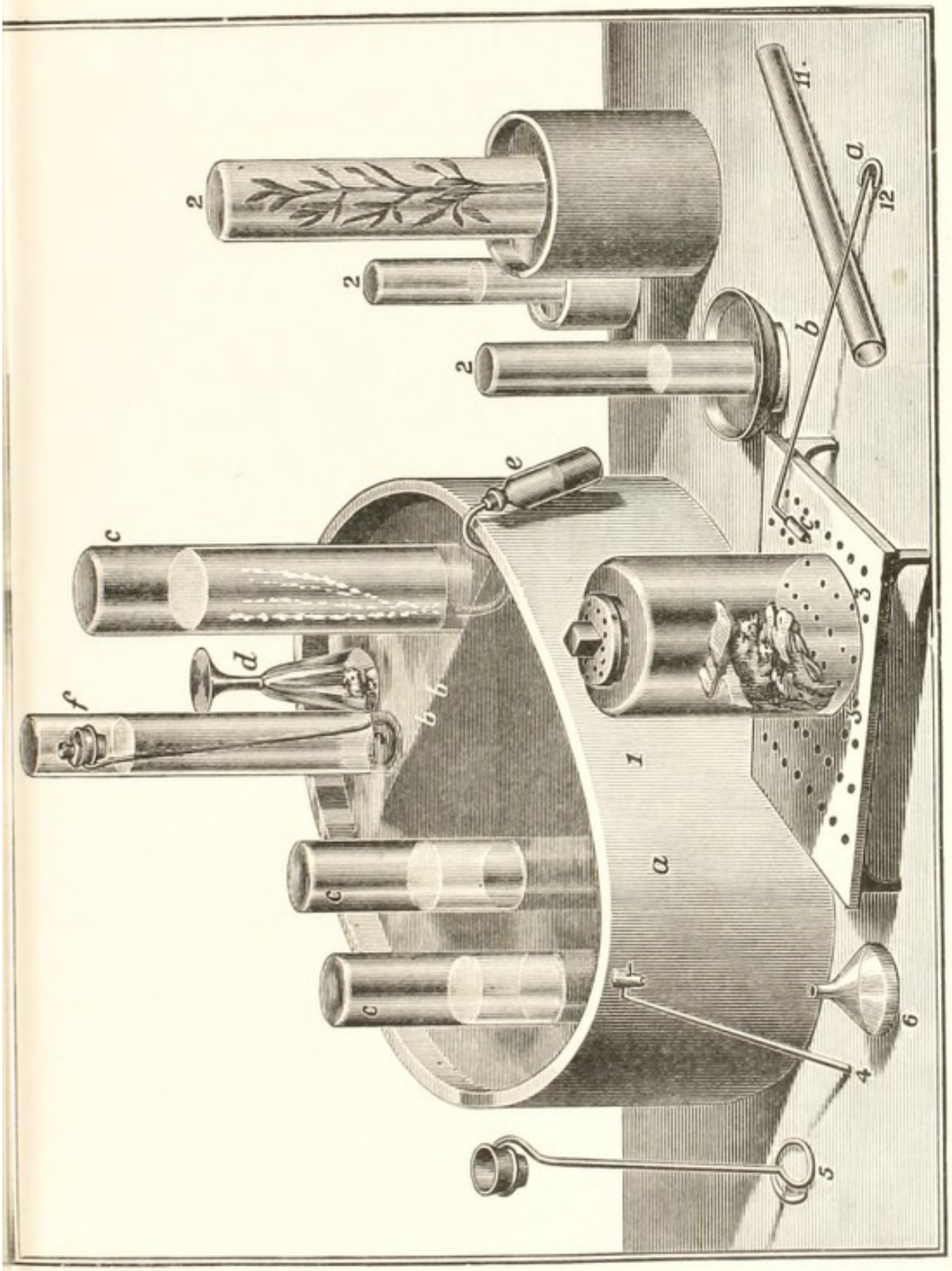


FIG. 20.—PRIESTLEY'S APPARATUS (First Plate).

filled with water and supported near the surface of the trough.

The *gun-barrel*, 7 (second plate : compare Hales, Fig. 19*b*), with a tobacco-pipe stem, or glass tube luted to the open end, was used to expel gases from solid substances. To reduce the volume of air, the gun-barrel was filled up with dry sand. In the figure, the gas is being collected over *mercury* ; Cavendish had transferred to a basin of mercury, a bottle full of fixed air which was too soluble to be stored long over water, but this is the first use of mercury for collecting gases ; a carefully-shaped MERCURY TROUGH was introduced by Lavoisier (Fig. 33). An apparatus for collecting over mercury gases expelled from liquids by heat, or set free by the action of acids, is shown at 8, where *a* is a basin of mercury, *b* a tube filled with it, *c* the tube from which the gas is expelled and *d* a glass trap to condense out moisture ; the apparatus used for generating and collecting gases not freely soluble in water is shown at *e* in the first plate.

The *bladder* 9, provided with funnel and delivery tube, was used to receive gas from a jar standing in water and then to transfer it free from water to a vessel standing in mercury. A bladder is also shown in the apparatus, 10, used for impregnating liquid with gas, *e.g.*, water with fixed air ; the gas generated in *c* was collected in the bladder and then squeezed out through the *flexible leathern tube*, *d*, into the flask *a*.

The *candle*, 12*a* (first plate), mounted on the end of a wire *b*, was used to test the air in the narrow tube 11 ; the candle, *c*, was used in the wider cylinders, from which it could be withdrawn through the water as soon as it was extinguished.

The *syphon*, 13 (second plate), was used to suck air out from a cylinder as at *f* (compare Hales, Fig. 19*a*).

The *receiver*, 14, exhausted by an air-pump, was used

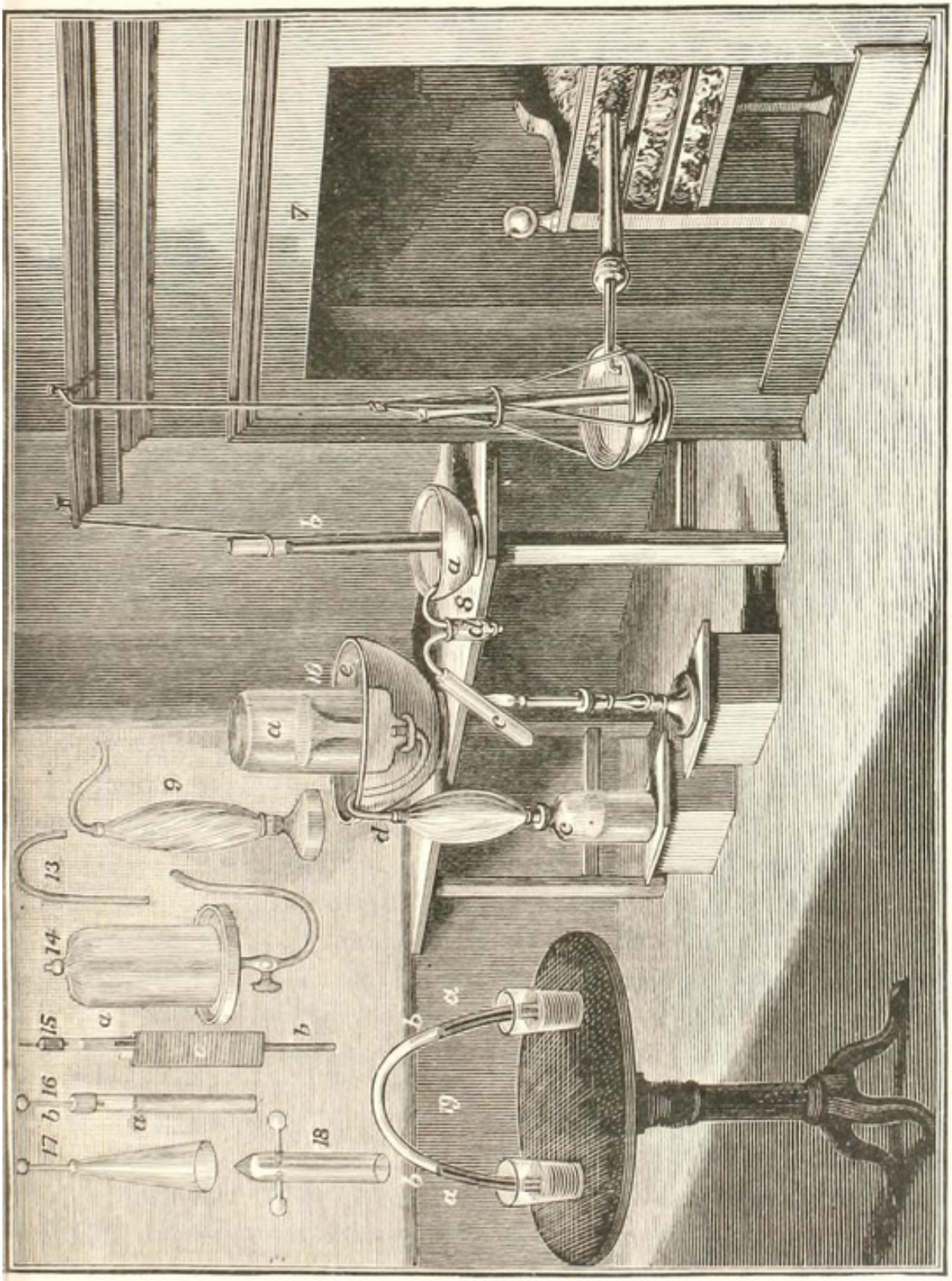


FIG. 20—PRIESTLEY'S APPARATUS (Second Plate).

when a dry powder had to be surrounded by gas drawn from a vessel standing in water.

The *eudiometer*,[1] 15, was used for mixing minute quantities of nitrous air and common air; two bubbles were introduced into the narrow tube *a* with the help of the iron-wire plunger *b*, then measured, mixed, and measured again.

Apparatus for *sparking* small quantities of gas is shown in the second plate at 16, 17, 18, 19, anticipating in part the apparatus used by Volta (Fig. 27) and by Cavendish (Fig. 39).

Summary and Supplement

A. Fixed air and inflammable air

Van Helmont (*b.* 1577; *d.* 1644) recognised the existence of two "gases," a poisonous "gas sylvestre" and an inflammable "gas pingue," analogous with the "choke-damp" and "fire damp" of miners.

John Mayow, *Medico-physical Works*, 1674, collected gases prepared artificially by the action of iron on *aqua fortis* and on dilute oil of vitriol contained in an inverted flask; he showed that they possessed the same elastic properties as common air, but was not sure that they were essentially different from it.

Stephen Hales, *Vegetable Statics*, 1727, by heating different substances, prepared many gases which he collected over water in a separate "receiver"; he also mixed different gases and studied the changes of volume produced in them by the action of different agents; but he did not recognise these gases as distinct substances, and supposed that all had the same density.

Joseph Black, *Experiments upon Magnesia Alba*, 1755, proved that chalk and the alkalis contain a gas which he called **fixed air** (carbonic anhydride or carbon dioxide, CO_2), but he did not at that time collect or handle it.

Henry Cavendish, *On Factitious Air*, 1766, measured the density of fixed air from a variety of sources, and of **inflammable air** (hydrogen) prepared by the action of acids on different metals, thus :—

[1] This name was first used in 1776 (*Experiments on Air*), 1777, III. 379 and 380).

Zinc on Vitriolic Acid, $Zn + H_2SO_4 \rightarrow ZnSO_4 + H_2$;
Zinc on Spirit of Salt, $Zn + 2HCl \rightarrow ZnCl_2 + H_2$;
Iron on Vitriolic Acid, $Fe + H_2SO_4 \rightarrow FeSO_4 + H_2$;
Tin on Spirit of Salt, $Sn + 2HCl \rightarrow SnCl_2 + H_2$.

By these measurements he proved the identity of the different samples, and established the method of investigating gases by the exact measurement of their physical properties. He found that water dissolved an equal volume of fixed air, which escaped when the water was boiled or exposed to the air; fixed air could, however, be stored permanently in a bottle inverted over mercury.

Joseph Priestley, *Experiments on Air*, Vol. I. 1774; Vol. II. 1775; Vol. III. 1777, prepared a large number of gases and studied their chemical properties very thoroughly. He examined fixed air and inflammable air, prepared three gases by the action of nitric acid on metals, discovered oxygen, and collected over mercury a series of gases which were too soluble to be collected over water.

B. GASES DERIVED FROM NITRIC ACID

Nitrous air (nitric oxide, NO), was prepared by van Helmont, by Mayow, and by Hales, by the action of nitric acid on metals, but was first recognised as a distinct substance by Priestley (1772), who named it nitrous air.

It dissolves in ten volumes of water, but is freely soluble in solutions of green vitriol (ferrous sulphate), forming a dark brown liquid from which the gas can be recovered by gentle heating. The preparation of the gas from copper and nitric acid is often represented by the equation—

$$3Cu + 8HNO_3 \rightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O,$$

but many other products are formed at the same time.

Diminished nitrous air, or "laughing gas" (nitrous oxide, N_2O), was prepared by Priestley (1772) by the action of iron filings on nitrous air.

$$2Fe + 6NO \rightarrow Fe_2O_3 + 3N_2O.$$

Berthollet (1785) prepared it by heating ammonium nitrate.

$$(NH_4)NO_3 \rightarrow N_2O + 2H_2O.$$

It is readily soluble in water, but is expelled by boiling. A candle burns in it with an enlarged flame, as in oxygen. The pure gas can be breathed with impunity (Davy), and has been used as an anæsthetic in dentistry since 1800.

The formation of soluble brown **nitrous fumes** (nitrogen dioxide, NO_2) on mixing nitrous air with common air had been noticed by Hales. In presence of water the action is more complex, both nitric and nitrous acid being produced (see Chapter X), thus :

Without water $2NO + O_2 = 2NO_2$
(Nitrogen dioxide.)

With water $4NO + 3O_2 + 2H_2O = 4HNO_3$
(Nitric acid.)

$4NO + O_2 + 2H_2O = 4HNO_2$
(Nitrous acid.)

When common air is mixed over water with an excess of nitrous air (nitric oxide) all the oxygen is absorbed, together with as much of the nitrous air as has combined with it ; Priestley used the contraction produced by mixing equal volumes of the two gases in a *eudiometer* as a measure of the "goodness" of air.

The brown nitrous fumes were prepared in an impure state by Priestley by the action of bismuth on nitric acid—

$$\underset{\text{(Nitric acid.)}}{Bi + 6HNO_3} \rightarrow \underset{\text{(Bismuth nitrate.)}}{Bi(NO_3)_3} + \underset{\text{(Nitrogen dioxide.)}}{3NO_2} + 3H_2O.$$

But this gas is better prepared by heating lead nitrate—

$$\underset{\text{(Lead nitrate.)}}{2Pb(NO_3)_2} \rightarrow \underset{\text{(Litharge.)}}{2PbO} + \underset{\text{(Nitrogen dioxide.)}}{4NO_2} + O_2.$$

It can be purified by condensing it to a liquid. Priestley noticed that the gas darkened in colour when heated, but became light when cooled again. The loss of colour is due to the formation of a more complex compound (dinitrogen tetroxide)—

$$\underset{\text{(Brown.)}}{2NO_2} \rightleftharpoons \underset{\text{(Colourless.)}}{N_2O_4},$$

which can be frozen out as a colourless ice (Chapter XX, p. 525), but begins to decompose as soon as it is melted. The mixture of these two oxides is called "nitrogen peroxide."

C. ACID AIR AND ALKALINE AIR

Acid air (hydrogen chloride, HCl). Glauber prepared "spirit of salt" by the action of oil of vitriol on salt,

$$2NaCl + H_2SO_4 \rightarrow Na_2SO_4 + 2HCl,$$

but he was only able to collect the gas by absorbing it in water. Priestley (1774) collected it over mercury as a "permanently elastic fluid." He found it to be extremely soluble in water, which dissolved 576 times its volume of the gas.

Alkaline air (ammonia, NH_3). The pungent gas present in "spirit of hartshorn" was expelled by warming, and collected over mercury by Priestley (1774), who called it "alkaline air"; the name "ammonia" was given to it by Bergman in 1782. Priestley also prepared it from slaked lime and sal-ammoniac,

$$\begin{array}{ccccccc} Ca(OH)_2 & + & 2NH_4Cl & \rightarrow & CaCl_2 & + H_2O + & 2NH_3, \\ \text{Slaked} & + & \text{sal} & \rightarrow & \text{muriate} & + \text{water} + & \text{ammonia} \\ \text{lime} & & \text{ammoniac} & & \text{of lime} & & \end{array}$$

and obtained a very strong spirit by dissolving it in water, which absorbed 336 volumes of the gas. It differed from acid air in being lighter instead of heavier than common air. A mixture of alkaline air and acid air produced sal-ammoniac,

$$\underset{\text{(Ammonia.)}}{NH_3} + \underset{\text{(Hydrogen chloride.)}}{HCl} \rightarrow \underset{\text{(Ammonium chloride.)}}{NH_4Cl} \text{ (sal-ammoniac).}$$

A mixture of alkaline air and fixed air produced sal-volatile,

$$\underset{\text{(Ammonia.)}}{2NH_3} + \underset{\text{(Carbon dioxide.)}}{CO_2} \rightarrow \underset{\text{(Ammonium carbamate.)}}{(NH_3)_2CO_2} \text{ (sal-volatile.)}$$

CHAPTER VI

THE COMPOSITION OF FIXED AIR, CARBON, CARBONIC ACID, AND THE CARBONATES

A. The Composition of Fixed Air.

Fixed air a product of combustion.—Van Helmont derived the name of his poisonous "gas sylvestre" from its presence in the fumes of a fire of wood-charcoal (Latin *sylva*, a wood or forest). But as the only test which he applied was that of a lighted candle, no importance attaches to the fact that he gave the same name to the gases liberated in fermentation, and by the action of acids upon chalk.

The recognition by **Black**, in 1755, of fixed air as a constituent of chalk provided for the first time a test by which a gas differing from common air could be detected and identified with certainty. By its power of reconverting lime into chalk, he proved the presence of fixed air in substances such as magnesia, sal-volatile, and the mild alkalis, as well as in natural waters and in common air. **Cavendish**, in 1766, added to these tests the method of measuring the physical constants (density and solubility) of the gas, and proved that these were the same for fixed air prepared from alkaline substances and by the fermentation of sugar. These physical tests could not be applied to the crude gas

obtained by burning charcoal in air; but Cavendish showed that "a quantity of common air was reduced from 180 to 160 ounce measures, by passing through a red-hot iron tube filled with the dust of charcoal" and "observed, that there had been a generation of fixed air in this process, but that it was absorbed by soap leys" (quoted by Priestley, *Experiments on Air*, I. 129).

Fixed air is formed during the burning of charcoal (Priestley, 1772) and the reduction of metallic calces (Lavoisier, 1774).—**Priestley,** in 1772, by means of a burning mirror, or lens, heated fragments of charcoal in air confined over water. He found that the volume of the air was diminished by one-fifth, that the residue extinguished flame, was noxious to animals, and suffered no further diminution of volume when exposed to the action of iron filings and sulphur, or when mixed with nitrous air; the air had therefore been deprived of all its "goodness" (the discovery of oxygen was not made until two years later) whilst the production of fixed air was shown by the cloudiness which was produced when the gas was confined over lime-water. When mercury was used instead of water, the volume of the air was not diminished by the burning charcoal until lime-water was added, when one-fifth of the air was absorbed ("Of Air infected with the Fumes of Burning Charcoal," *Experiments on Air*, 1774, I. 129–132).

About the same time, **Lavoisier** (*Physical and Chemical Essays*, 1774, Chapter V; *Works* I, 598–613) found that a large volume of "air" was produced when minium or red lead was reduced by heating with charcoal in an iron retort (Fig. 21.) A very large quantity of gas was set free, 560 cubic inches being liberated in the production of about $\frac{3}{4}$ cubic inch of lead, although the charcoal heated alone gave only eight cubic inches of gas in the course of two days. The gas dissolved in lime-water, and extinguished a lighted candle; a rat died almost instantly in it. The

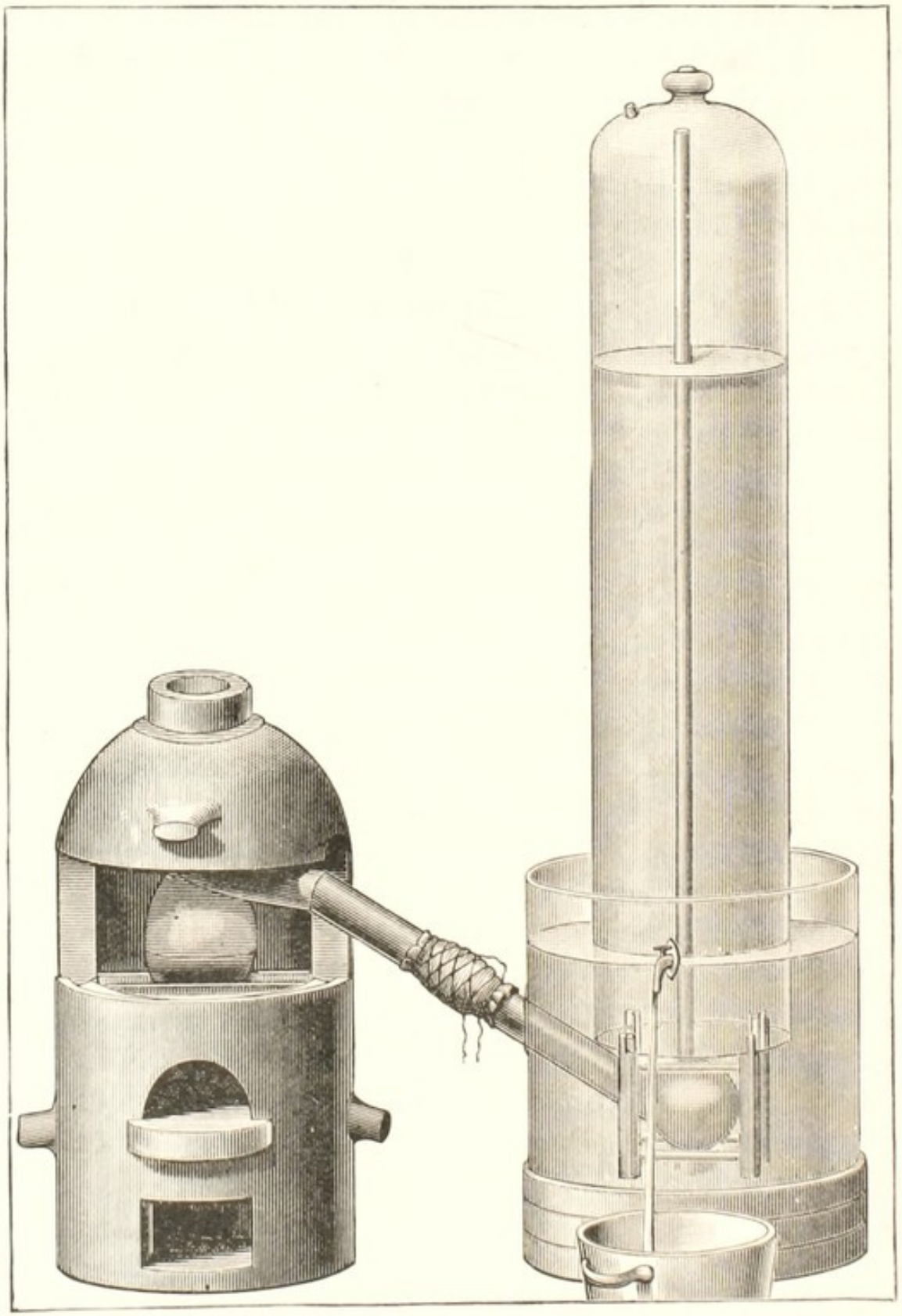


FIG. 21—LAVOISIER'S APPARATUS FOR COLLECTING THE GAS PRODUCED BY HEATING RED-LEAD AND CHARCOAL IN AN IRON RETORT.

The air could be drawn out from the bell-jar through the small aperture shown at the top of the jar, or it could be removed by means of an air-pump which has not been reproduced in the figure.

production of fixed air during the reduction of the calx was thus clearly proved; but it was not until Priestley had discovered oxygen, as described in Chapter III, that Lavoisier was able to give a satisfactory explanation of what had occurred in this reduction.

Lavoisier (1774) proves that fixed air is an oxide of carbon.—The crucial experiments by which fixed air was proved to be an oxide of carbon were made by Lavoisier in November, 1774, after Priestley had demonstrated to him the method of making oxygen from the red calx of mercury.

By heating an ounce of this calx with forty-eight grains of charcoal in a tiny glass retort he was able to collect, in a bell jar over water, 64 cubic inches of gas. This gas dissolved in water, communicating to it the properties of the natural acidulated waters, destroyed animals brought into it, at once extinguished candles and other burning substances, precipitated lime-water, and combined readily with the alkalis, removing their causticity and enabling them to crystallise. "All these properties are exactly those of the kind of air known as fixed air."

Lavoisier found that the red precipitate heated alone gave 78 cubic inches of a gas which did not dissolve in water, did not precipitate lime-water, did not unite with alkalis or diminish their caustic qualities, but which could be used again for the calcination of metals. "In conclusion, it had none of the properties of fixed air; far from being fatal, like it, to animals, it seemed, on the contrary, more proper for the purposes of respiration; candles and burning bodies not only were not extinguished by it, but burned with an enlarged flame in a very remarkable manner; the light they gave was much greater and clearer than in common air; charcoal burned in it with a brilliancy almost like that of phosphorus, and all combustible substances were consumed in it with surprising rapidity. All these circumstances convinced me that this air, far from

being fixed air, was even more respirable, more combustible, and consequently more pure even than the air in which we live."

The calx heated alone gave oxygen and mercury; when heated with charcoal it gave fixed air and mercury. Fixed air was therefore evidently a compound of charcoal with oxygen. Lavoisier argued that—

"Since carbon disappeared entirely in the revivification of mercury from its calx, and since there result from this operation only mercury and fixed air, one is forced to conclude that the principle which has hitherto been known as fixed air is the result of the combination of eminently respirable air with charcoal" ("On the Nature of the Principle which combines with metals during their Calcination and increases their Weight," *Works*, II. 122–128).

The charcoal (French *charbon*) used in experiments such as these always left behind when burnt a larger or smaller proportion of ash. Lavoisier and his colleagues, therefore, introduced in 1787 "the modified name of CARBON,[1] which indicates the pure and essential principle of charcoal," thus "distinguishing it from charcoal according to the vulgar acceptation" and isolating it "from the small quantity of foreign matter which it generally contains and which constitutes the ash" (*Method of Chemical Nomenclature*, tr. 1788, p. 32).

In their system of nomenclature, fixed air became an OXIDE OF CARBON: its production during the burning of charcoal was represented by the equation:

$$carbon + oxygen = \underset{\text{(oxide of carbon)}}{fixed\ air}$$

whilst the reduction of a calx was shown by the equation:

$$\underset{\text{(oxide of metal)}}{carbon + calx} = \underset{\text{(oxide of carbon)}}{fixed\ air} + metal.$$

[1] French *carbone*.

Diamond and graphite.—Newton had suspected (*Opticks*, 1704, II. 75) that the diamond, with its high refractive power, might be a combustible substance. This idea was confirmed by several notable experiments in which the combustion was effected both by powerful burning-glasses and by means of furnaces. But as the experiments were always made in the open, no idea could be formed of the nature of the products; indeed, it was generally believed that the diamonds had merely been vaporised without burning at all.

To Lavoisier belongs the credit of having shown, in 1772, in conjunction with Macquer and Cadet, that if air be completely excluded, the diamond remains unaltered at the highest temperature of the furnace; the burning of the diamond is therefore a true combustion. In order to determine the nature of the products of combustion, Lavoisier employed a very large burning glass (compare Fig. 22) to heat diamonds supported in air or oxygen contained in glass jars inverted over water or over mercury. No water, smoke, or soot was produced; when mercury was used the volume of gas was not altered, but in contact with water the volume was somewhat diminished; in both cases the gas in which the diamond had been burnt turned lime-water milky ("Destruction of the Diamond by Fire," 1772, *Works*, II. 38–88). Charcoal behaved in just the same way as the diamond. There was, therefore, no doubt that each of these substances gave rise to fixed air as the sole product of combustion. A few years later, in 1797, Tennant (an English chemist who had already shown that carbon could be recovered from fixed air by the action of phosphorus vapour on red hot chalk), burned diamonds by means of melted saltpetre, and showed that they gave rise to precisely the same quantity of fixed air as when charcoal was used. This observation was confirmed by the combustions carried out many years later by Dumas and Stas (Chapter VIII, p. 150);

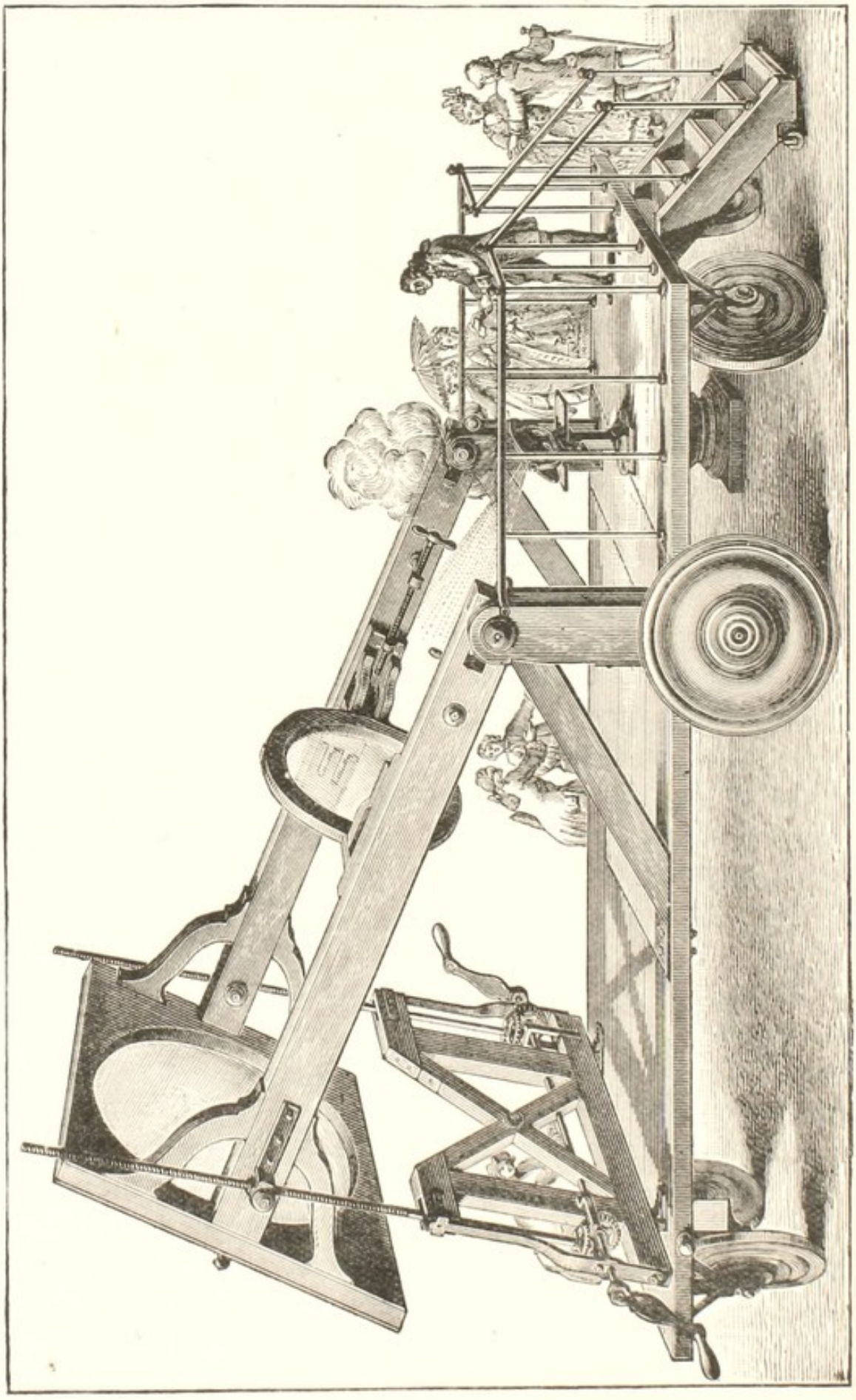


FIG. 22—LAVOISIER'S LARGE BURNING GLASS.

it showed clearly that the diamond, like charcoal, must be regarded as a variety of carbon.

The mineral GRAPHITE, also known as PLUMBAGO or BLACK LEAD, was shown by Scheele, in 1779, to give rise to fixed air when fused with nitre. Other workers showed that (if allowance were made for the ash which it always contains) it gave the same proportion of gas as charcoal and diamond, and must therefore be regarded as a third variety of carbon.

Such varieties of an element as charcoal, diamond, and graphite were described by Berzelius, in 1840 (*Jahresbericht*, **20**, Chem. p. 13), as ALLOTROPES.

B. Carbonic Acid and the Carbonates.

Bergman (1774) regards fixed air as an acid.—It is uncertain to what extent Black recognised that fixed air had the properties of a weak acid. He was aware that it was attracted by the caustic alkalis and by lime, and that it blunted and diminished their caustic and alkaline properties. But the small quantity of liquid which could be condensed when distilling chalk or magnesia differed so completely from the mineral acids produced by distilling green vitriol or nitre, that it is not surprising that Black hesitated to describe fixed air as an acid.

The clear recognition of its acid properties was due to the Swedish chemist **Torbern Bergman** (1735–1784), who in 1774 published a full description of its properties in a paper "On the Aerial Acid" (Bergman's *Essays*, translated by E. Cullen, 1784, pp. 1–90).

In support of this view he mentions:

(1) Its solubility in water, as measured by Cavendish (Chapter V).

(2) The acid taste which it imparts to natural and artificial aerated waters, as noticed by Brownrigg and by

Priestley. In a paragraph headed "Fixed Air has an Acid Taste," Bergman writes:

"As this air is in form of an elastic vapour, it can hardly be tasted by itself, at least distinctly; but if it be united with water, which is in itself void of flavour, being accumulated and rendered less volatile by this union, it readily affects the tongue with a weak but agreeable acidity. This is the real spirit of the cold mineral waters, which undoubtedly occasioned them to be called acidulous; and by means of which, together with a due proportion of suitable salts, we may perfectly imitate the Seltzer, Spa, and Pyrmont waters. Such artificial waters I have now been using for eight years with signal advantage" (*Essays*, p. 12).

(3) Its power of imparting to litmus a transient red coloration:

"Syrup of violets, and such other blue vegetable juices as I have hitherto tried are not reddened by fixed air, the tincture of tournsole [litmus] is of all known tinctures most easily acted on by acids, therefore the slightest vestiges, which cannot by any other means be discovered, are by this tincture easily detected" (*Essays*, p. 16).

Thus if water "be tinged with tournsole to a perfect blue, when fixed air sufficient to fill about the 1/50 of the vessel has passed through it, it will be manifestly red . . . In like manner one part of water, saturated with fixed air, makes 50 parts of the above tincture distinctly red. This change of colour, however occasioned by the fixed air, soon disappears in an open vessel, particularly if it be exposed to heat, or the rays of the sun; a circumstance which indicates the volatile nature of the acid that produces the change (*Essays*, pp. 14–15).

(4) Its power of combining with mild alkalis to form neutral crystalline compounds, as discovered by Black and confirmed by Cavendish (pp. 69 and 108).

(5) Its power of dissolving chalk and magnesia, discovered by Cavendish (p. 103).

(6) Its power of dissolving iron (giving rise to artificial

chalybeate waters, as discovered by the English apothecary Lane in 1769), and of dissolving zinc.

(7) Its power of precipitating substances dissolved in alkalis, *e.g.* sulphur dissolved in lime-water.

On account of the acid properties of its solutions the French chemists in 1787 gave to the gas the name CARBONIC ACID.

"As fixed air has been perceived to be produced by the direct combination of *charcoal* with *vital air*, by the assistance of combustion, the name of this gaseous acid can no longer be arbitrary, but necessarily must be derived from its radical, which is the pure carbonic matter; therefore it is *carbonic acid* and its compositions with different bases are *carbonates*" (*Chemical Nomenclature*, tr. 1788, p. 32).

But as Bergman recognised, this acidity belongs to the solution rather than to the gas. For this reason the name "carbonic acid" is now restricted to the solution of the gas in water, whilst the gas itself[1] is called CARBONIC ANHYDRIDE. The recognition of carbonic acid as an acid necessitated a change in the classification of the mild alkalis, which were now regarded as salts under the name of CARBONATES. In later years the term 'alkali' became associated almost exclusively with the caustic alkalis, instead of the mild effervescent salts to which the name had been applied for a thousand years previously.

Cavendish (1767) discovers that chalk and magnesia are rendered soluble by fixed air.—To Cavendish belongs the credit of discovering that chalk is rendered soluble in water by the presence of fixed air. This discovery was made in the course of his "Experiments on Rathbone-Place Water" (*Phil. Trans.*, 1767, **57**, 92). He found that 494 ounces of a water, which on boiling liberated one-seventh of its volume of fixed air,[2] deposited 271 grains of a calcareous

[1] Following Laurent (1854); see Chapter XII.

[2] 411 ounces of water liberated 66 ounce-measures of fixed air and $8\frac{3}{4}$ ounce-measures of common air.

earth consisting almost entirely of chalk. That chalk was actually held in solution by fixed air was proved by mixing lime-water with an excess of water saturated with the gas, when a clear solution was produced, whereas the use of less fixed air caused the lime to be precipitated in the form of chalk. Cavendish writes :

"Calcareous earths, in their natural state, *i.e.* saturated with fixed air, are totally insoluble in water ; but the same earths, entirely deprived of their fixed air, *i.e.* converted into lime, are in some measure soluble in it ; for lime-water is nothing more than a solution of a small quantity of lime in water. It is very remarkable, therefore, that calcareous earths should also be rendered soluble in water, by furnishing them with more than their natural proportion of fixed air, *i.e.* that they should be rendered soluble, both by depriving them of their fixed air, and by furnishing them with more than their natural quantity of it. Yet strange as this may appear, the following experiments, I think, show plainly it is the real case."

"A bottle full of rain water was inverted into a vessel of rain water, and some fixed air forced up into the bottle, at different times, till the water had absorbed as much fixed air as it could readily do ; 11 ounces of this water were mixed with $6\frac{1}{2}$ of lime water. The mixture became turbid on first mixing, but quickly recovered its transparency, on shaking, and has remained so for upwards of a year."

"Lest it should be supposed, that the reason why the earth was not precipitated in the foregoing experiment, was, that it was not furnished with a sufficient quantity of fixed air, the following mixture was made, which contains the same proportion of earth as the former, but a less proportion of fixed air : $4\frac{3}{4}$ ounces of the above-mentioned water, containing fixed air, were diluted with $6\frac{1}{4}$ of rain water, and then mixed with $6\frac{1}{2}$ ounces of lime-water. A precipitate was immediately made on mixing, which could not be re-dissolved on shaking" (*Phil. Trans.*, 1767, **57**, 101 and 104–105).

This observation was confirmed by Lavoisier, and also by Bergman, who noticed that if

"a small portion of lime-water be dropped into water impregnated with fixed air, slight clouds are immediately formed, occasioned by the saturation of the lime by the fixed air; these clouds, however, disappear upon gently shaking the vessel, the lime being dissolved by the superabundant fixed air" (*Essays*, p. 34).

Bergman also recorded the fact that crystals of calcareous spar (Fig. 23) were dissolved by water containing fixed air, and that minute crystals of similar shape were sometimes deposited

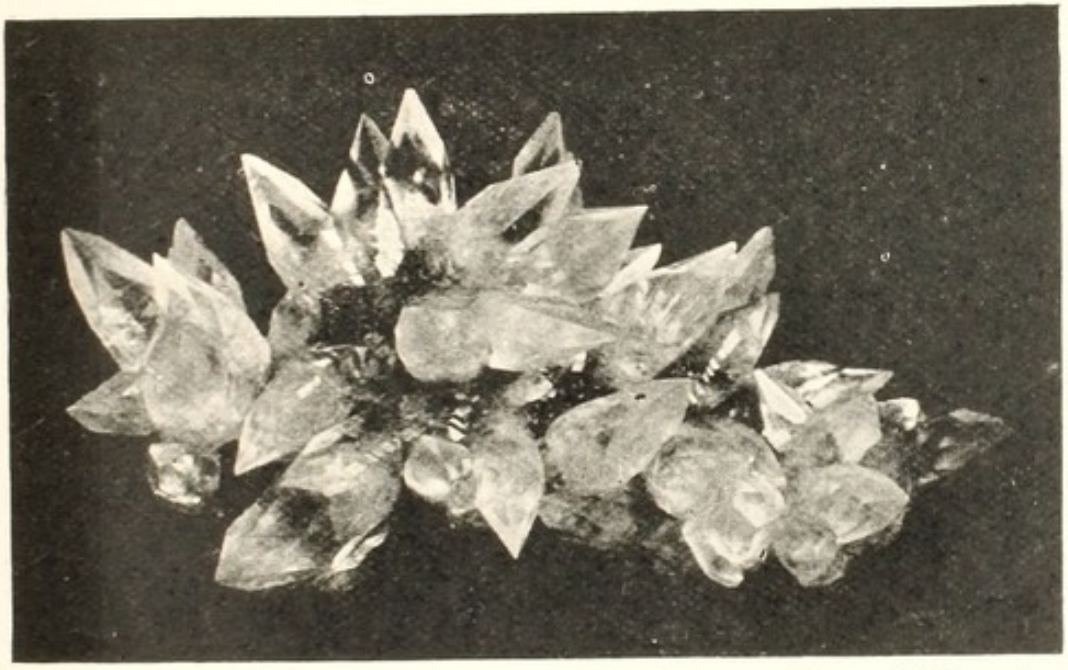


FIG. 23—CRYSTALS OF CALC-SPAR. British Museum (Natural History).

when chalk was reprecipitated by the escape of the fixed air which held it in solution. These observations were important as affording a clue to the way in which crystalline calc-spar may have been produced; they also afforded a satisfactory explanation of the formation of stalactites (Fig. 24) and stalagmites by the escape of fixed air from the dripping water of caverns in limestone districts.

The hardness of water due to salts of lime and magnesia.—The mineral matter held in solution by fixed air makes a water "hard," *i.e.* the water gives a curd with soap instead of a lather. As this hardness is removed

when the water is boiled it is called TEMPORARY HARDNESS. Cavendish showed that the whole of the chalk in such a water could be "precipitated . . . by the addition of a proper quantity of lime-water" (*loc. cit.* p. 107). This method of removing the fixed air and so precipitating the chalk from a hard water is used on a large scale in order to "soften" the water-supply in chalky districts such as that of the Caterham Valley.

Magnesia, of which Cavendish detected a small quantity mixed with the chalk from Rathbone Place water,[1] also owes its solubility to fixed air. It dissolves to a larger extent than chalk, and the solution is used in medicine as a gentle alkali under the name of "fluid magnesia." Like chalk, the magnesia produces a temporary hardness, which can be removed by boiling, or by the addition of lime; but the precipitation of the magnesia, and the softening of the water, takes place much more slowly than in the case of chalk.

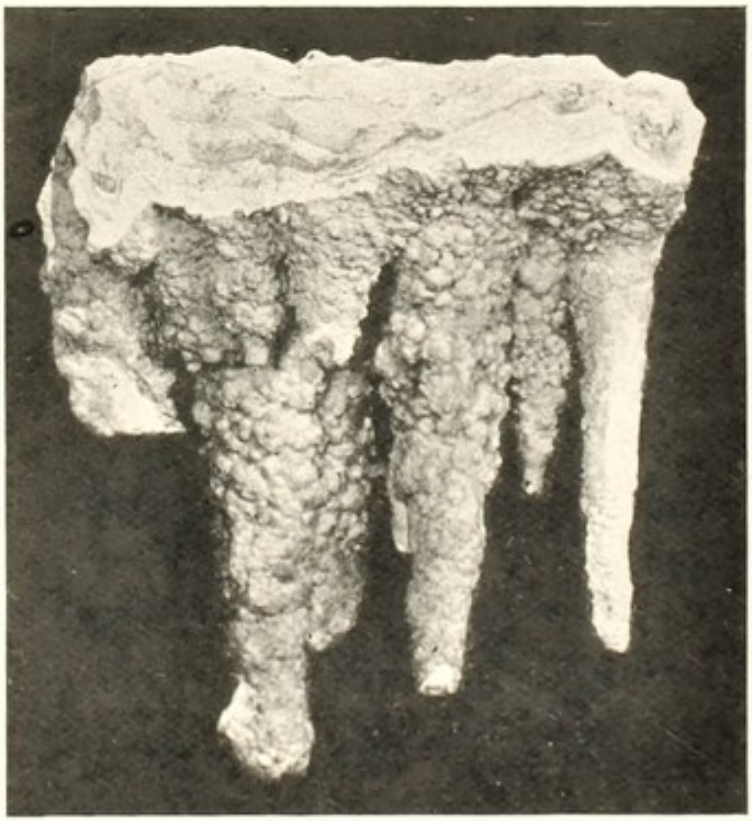


FIG. 24—STALACTITE, *i.e.*, CHALK DEPOSITED BY THE ESCAPE OF FIXED AIR FROM DRIPPING WATER. British Museum (Natural History).

Gypsum or selenite (of which Cavendish collected 39

[1] By acting on the earthy precipitate with oil of vitriol the chalk was converted into sparingly-soluble selenite or gypsum, and the magnesia into Epsom salts, of which 18 grains were extracted.

grains by evaporating 494 ounces of the water to a bulk of three ounces) shares with all the soluble salts of lime the property of rendering water hard. As the gypsum is not precipitated when the water is boiled, the hardness which it produces is called PERMANENT HARDNESS. This permanent hardness can be removed by adding to the water a mild alkali such as soda or potash, which precipitates the lime in the form of chalk and so renders the water soft. This is the method generally used for softening permanently hard waters.

Soluble salts of magnesia (of which Cavendish precipitated 36 grains by the addition of fixed alkali) also contribute to the permanent hardness of water. Sea water, which contains a little gypsum, and a relatively large proportion of Epsom Salts, is so hard that it is practically impossible to make it lather, even by using a very large amount of soap. The precipitation of soap by the mineral matter present in hard waters was discussed by Bergman ("Of the Analysis of Waters," *Essays*, pp. 90–192), who made use of a solution of soap in alcohol as a means of detecting such substances in water, thus,

"Soap is not soluble in every kind of water; this is occasioned either by a disengaged acid, or by a large proportion of . . . salt with an earthy or metallic base . . .: such waters are generally called hard waters, and are unfit for washing cloths, as also for boiling pulse, and the harder kinds of flesh."

"If there be present in a can of water but 8 grains of alum, [muriate of] magnesia or [muriate of] lime, a single drop of this water occasions a turbidness in a solution of soap in alcohol, diluted with an equal bulk of distilled water" (*Essays*, p. 139).

Lane (1769) discovers that fixed air will dissolve iron.—Fixed air also possesses the power of dissolving iron, giving rise to chalybeate waters. In these waters the iron

is held in solution by fixed air in much the same way as the chalk and magnesia in the water investigated by Cavendish. This property of fixed air was discovered by T. Lane, an English apothecary, who described his experiments in the *Philosophical Transactions* for 1769, as follows:

"A wide-mouthed bottle, containing half a pint of distilled water and sixty grains of steel filings, was suspended forty-eight hours over some distiller's molasses, in brisk fermentation; so as to receive the fixed air escaping from the fermenting liquor; the surface of which was ten inches below the mouth of the bottle. Immediately after its removal, the clear water was decanted from the filings and ochrous sediment."

"This liquor had a brisk and ferruginous taste, with a flavour of the molasses. An infusion of galls, or green tea, soon changed part of it to a colour like ink. The remainder, being exposed to the open air, presently became turbid, threw up a party coloured pellicle, and deposited a yellowish sediment."

"The water now retained but little power of tinging with galls; and in a few days lost this property entirely" ("On the Solubility of Iron in Simple water, by the intervention of Fixed Air," *Phil. Trans.*, 1769, **59**, 218).

These simple experiments, carried out 140 years ago, disclose the two essential features of the modern theory of the rusting of iron, namely, (1) that iron is dissolved by carbonic acid to a colourless solution, and (2) that this solution deposits a yellow rust on exposure to the air.

Black (1755) discovers a second series of salts derived from fixed air.—Whilst there is some uncertainty as to whether Black recognised fixed air as an acid, there is no doubt as to his discovery of the existence of a salt containing a larger proportion of fixed air than ordinary potash.

"That the fixed alkali, in its ordinary state, is seldom entirely saturated with air, seems to be confirmed by the following experiment. I exposed a small quantity of a pure

vegetable fixed alkali to the air, in a broad and shallow vessel, for the space of two months; after which I found a number of solid crystals, which resembled a neutral salt so much as to retain their form pretty well in the air, and to produce a considerable degree of cold when dissolved in water. Their taste was much milder than that of ordinary salt of tartar; and yet they seemed to be composed only of the alkali, and of a larger quantity of air than is usually contained in that salt, and which had been attracted from the atmosphere: for they still joined very readily with any acid, but with a more violent effervescence than ordinary; and they could not be mixed with the smallest portion of vinegar. . . . without emitting a sensible quantity of air" (A.C.R. XVII. 42).

The same salt was prepared by Cavendish and by Bergman by the direct action of fixed air on a solution of the alkali. Cavendish, who examined it in 1766, found that in comparison with ordinary potash it contained twice as much fixed air relatively to its power of neutralising acids. Bergman also examined this salt, and made a rough analysis, which showed that it contained both water and fixed air in combination with the mild alkali (*Essays*, p. 18).

Such salts, which contain a double portion of fixed air, were described by Bergman as "aerated vegetable alkali," "aerated magnesia," and so forth, but are now known as BICARBONATES. It is remarkable (as Bergman noticed) that whilst the excess of fixed air converts the mild alkalis into *less* soluble neutral salts, the solubility of chalk and magnesia in water depends on their conversion into *more* soluble bicarbonates. Similar soluble bicarbonates are probably formed when iron and zinc are dissolved by carbonic acid, since the carbonates of these metals are insoluble in water.

SUMMARY AND SUPPLEMENT.

Priestley (1772) showed that fixed air is produced when charcoal is burnt in air confined over water, or over mercury;

in the latter case no change is produced in the volume of the air

$$C + O_2 \rightarrow CO_2 \text{ (fixed air).}$$
$$\text{Carbon} + \text{oxygen} \rightarrow \text{carbonic anhydride.}$$

Lavoisier (1774) showed that fixed air is produced during the reduction of a calx by charcoal, *e.g.*

$$2PbO + C \rightarrow 2Pb + CO_2$$
$$\text{Litharge} + \text{carbon} \rightarrow \text{lead} + \text{carbonic anhydride.}$$

By heating oxide of mercury (*a*) with charcoal and (*b*) alone, he proved that fixed air is the oxide of a pure charcoal, which he called (1787) *carbon.*

$$2HgO + C \rightarrow 2Hg + CO_2$$
$$2HgO \text{ (alone)} \rightarrow 2Hg + O_2$$

Since diamond and graphite give when burnt the same weight of fixed air as pure charcoal, they are also composed of carbon, which thus exists in three *allotropic* forms (Berzelius, 1841).

Bergman (1774) recognised fixed air as an "aerial acid." **Lavoisier** and his colleagues, in 1787, called it *carbonic acid*; it is now called *carbonic anhydride.* The salts (such as chalk and the mild alkalis) which contain fixed air in combination with a base were called *carbonates*, thus:

Fixed air became carbonic acid
(now carbonic anhydride, CO_2).
Potash became carbonate of potash
(now potassium carbonate, K_2CO_3).
Soda became carbonate of soda
(now sodium carbonate, Na_2CO_3).
Chalk became carbonate of lime
(now calcium carbonate, $CaCO_3$).
Magnesia became carbonate of magnesia
(now magnesium carbonate, $MgCO_3$).

Black (1755), also Cavendish (1766) and Bergman (1774), prepared a less soluble salt by combining potash with fixed air: this salt, the *bicarbonate* of potash, is decomposed by heat into (mild) potash, water, and fixed air (Bergman).

$$2KHCO_3 \rightarrow K_2CO_3 + H_2O + CO_2.$$
Bicarbonate of potash (potassium bicarbonate) → carbonate of potash (potassium carbonate) + water + fixed air

Cavendish (1766), "On Rathbone Place Water," discovered that chalk and magnesia are rendered soluble by the presence of fixed air. This action is due to the production of soluble bicarbonates, thus :

$CaCO_3 + H_2O + CO_2 \rightarrow CaH_2(CO_3)_2$ (calcium bicarbonate).

$MgCO_3 + H_2O + CO_2 \rightarrow MgH_2(CO_3)_2$ (magnesium bicarbonate).

The solution of magnesium bicarbonate is sold as "fluid magnesia." The chalk and magnesia dissolved in this way give rise to *temporary hardness* ; they are thrown down when the fixed air is expelled by boiling or removed by the addition of lime. *Permanent hardness* is caused by soluble salts of lime and magnesia, such as the chloride and sulphate ; it may be removed by adding a mild alkali, *e.g.*

$$CaSO_4 + Na_2CO_3 \rightarrow CaCO_3 + Na_2SO_4$$
$$MgCl_2 + Na_2CO_3 \rightarrow MgCO_3 + 2NaCl.$$

Lane (1769) discovered that iron is dissolved by water containing fixed air, producing chalybeate waters.

$$\underset{\text{(Carbonic acid)}}{H_2CO_3} + Fe \rightarrow \underset{\text{(Ferrous carbonate)}}{FeCO_3} + H_2$$
$$FeCO_3 + H_2CO_3 \rightarrow \underset{\text{(Ferrous bicarbonate)}}{FeH_2(CO_3)_2}$$

By the action of air on the solutions a yellow rust is deposited ; at the same time the carbonic acid is set free to act again on a further quantity of iron.

$$\underset{\text{(Ferrous bicarbonate)}}{2FeH_2(CO_3)_2} + H_2O + \tfrac{1}{2}O_2 = \underset{\text{(Ferric hydroxide)}}{2Fe(OH)_3} + 4CO_2$$

CHAPTER VII

THE BURNING OF INFLAMMABLE AIR, AND THE COMPOSITION OF WATER

Priestley (1781) notices the formation of water as a product of combustion.—In ancient times the theory was held that all matter was derived from four "elements,"—earth, air, fire, and water. The discovery of the composite nature of earths (such as the metallic oxides) and of air has been described in Chapter III; in the same chapter an account has been given of the experiments which proved that fire is not a material substance, and cannot of itself add to, or subtract from, the weight of things. The composite nature of water was not suspected[1] until a later period, although it was supposed to give birth to many material substances, and even to vegetable and animal tissues.[2]

[1] "There are, I believe, very few maxims in philosophy that have laid firmer hold upon the mind, than that air, meaning atmospherical air (free from various foreign matters, which were always supposed to be dissolved, and intermixed with it), is a *simple elementary substance*, indestructible and unalterable, at least, as much so as water is supposed to be" (Priestley, *Experiments on Air*, II. 30—31).

[2] Van Helmont (1577—1644) planted a willow tree weighing five pounds in 200 pounds of dry earth, and watering it with rain or distilled water, found that after five years it weighed 169 lbs., although the earth had only lost two ounces. He knew nothing of the air as a source of the combustible part of a plant, and concluded that 164 pounds of wood, bark, roots, etc., had been produced from the water alone.

The observation which led to the discovery of the compound nature of water was made by Priestley, in 1781, in the course of "a mere random experiment, made to entertain a few philosophical friends" (*Experiments and Observations*, 1781, V. Appendix, p. 398). This consisted in exploding a mixture of common air and inflammable air by means of an electric spark in a closed glass vessel. After the explosion the sides of the vessel were seen to become covered with dew. Further experiments made by Mr. Warltire (*ibid.*, pp. 395–397) with a copper vessel appeared to indicate a slight loss of weight, owing, it was thought, to the heat which had escaped. This experiment attracted the attention of Cavendish, who repeated it in 1781, and published an account of his work in the *Philosophical Transactions* of the Royal Society for 1784, under the title "Experiments on Air" (A.C.R. III).

Cavendish (1781) prepares water by burning inflammable air with common air.—Using a large explosion vessel capable of holding 24,000 grains of water, Priestley's experiment "was repeated several times with different proportions of common and inflammable air." The best conditions were reached when 423 measures of inflammable air were exploded with 1000 measures of common air, whereby the volume of the air was reduced to 811 measures, and practically all the oxygen was removed. But, whatever the proportions in which the gases were mixed, Cavendish "could never perceive a loss of weight of more than one-fifth of a grain, and commonly none at all." Although the supposed loss of weight could not be confirmed, Cavendish found himself in agreement with Priestley when he noticed that:

"In all the experiments, the inside of the glass globe became dewy . . .; but not the least sooty matter could be perceived" (A. C. R. III. 13).

"The better to examine the nature of this dew, 500,000 grain measures of inflammable air were burnt with about $2\frac{1}{2}$

times that quantity of common air, and the burnt air made to pass through a glass cylinder eight feet long and three-quarters of an inch in diameter, in order to deposit the dew. The two airs were conveyed slowly into this cylinder by separate copper pipes, passing through a glass plate which stopped up the end of the cylinder; and as neither inflammable nor common air can burn by themselves, there was no danger of the flame spreading into the magazines from which they were conveyed. Each of these magazines consisted of a large tin vessel, inverted into another vessel just big enough to receive it. The inner vessel communicated with the copper pipe, and the air was forced out of it by pouring water into the outer vessel; and in order that the quantity of common air expelled should be $2\frac{1}{2}$ times that of the inflammable, the water was let into the outer vessels by two holes in the bottom of the same tin pan, the hole which conveyed the water into that vessel in which the common air was confined being $2\frac{1}{2}$ times as big as the other."

"In trying the experiment, the magazines being first filled with their respective airs, the glass cylinder was taken off, and water let, by the two holes, into the outer vessels, till the airs began to issue from the ends of the copper pipes; they were then set on fire by a candle, and the cylinder put on again in its place. By this means upwards of 135 grains of water were condensed in the cylinder, which had no taste nor smell, and which left no sensible sediment when evaporated to dryness; neither did it yield any pungent smell during the evaporation; in short, it seemed pure water."

"By the experiments with the globe it appeared, that when inflammable and common air are exploded in a proper proportion, almost all the inflammable air, and near one-fifth of the common air, lose their elasticity, and are condensed into dew. And by this experiment it appears, that this dew is plain water, and consequently that almost all the inflammable air, and about one-fifth of the common air, are turned into pure water" (A. C. R. III. 14—15).

Cavendish prepares water by exploding inflammable air with oxygen.—Having thus shown that only one-fifth of the air was condensed by the explosion of ordinary air

with inflammable air, Cavendish repeated his experiments with oxygen in place of air.[1]

"In order to examine the nature of the matter condensed on firing a mixture of dephlogisticated and inflammable air, I took a glass globe, holding 8800 grain measures, furnished with a brass cock and an apparatus for firing air by electricity. This globe was well exhausted by an air-pump, and then filled with a mixture of inflammable and dephlogisticated air, by shutting the cock, fastening a bent glass tube to its mouth, and letting up the end of it into a glass jar inverted into water, and containing a mixture of 19500 grain measures of dephlogisticated air, and 37000 of inflammable; so that, upon opening the cock, some of this mixed air rushed through the bent tube, and filled the globe.[2] The cock was then shut, and the included air fired by electricity, by which means almost all of it lost its elasticity. The cock was then again opened, so as to let in more of the same air, to supply the place of that destroyed by the explosion, which was again fired, and the operation continued till almost the whole of the mixture was let into the globe and exploded. By this means, though the globe held not more than the sixth part of the mixture, almost the whole of it was exploded therein, without any fresh exhaustion of the globe" (A. C. R. III. 15—16).

The gas remaining in the globe was found to be 2,950 grain measures, of which about 1,000 consisted of unburnt oxygen. The residue, which was usually not more than one-fiftieth of the original mixture, Cavendish attributed to impurities in the gases used, and concluded that if these "could be obtained perfectly pure the whole would be condensed."

The liquid condensed in the globe weighed thirty grains.

[1] Cavendish does not give any illustration of his apparatus; it was evidently very similar to that of Monge (Fig. 26), but differed in that the gases were not drawn from separate reservoirs but from an inverted jar containing an explosive mixture of the two gases.

[2] "In order to prevent any water from getting into this tube, while dipped under water to let it up into the glass jar, a bit of wax was stuck upon the end of it, which was rubbed off when raised above the surface of the water."

Cavendish noticed that it "was sensibly acid to the taste," an observation which formed the starting-point of his experiments on the composition of nitric acid, described in Chapter X. The formation of acid was, however, only incidental, since when no excess of oxygen was used the liquid condensed after the explosion was pure water.

Lavoisier (1777—1782) studies the burning of inflammable air.—The products resulting from the burning of inflammable air were being investigated in France about the same time that Cavendish was carrying out his experiments in England.

Macquer, in 1776, "having presented a fragment of white porcelain to the flame of inflammable air burning quietly at the mouth of a bottle, observed that the flame was not accompanied by any smoke; he found the fragment merely moistened with droplets of a colourless liquid . . . which he recognised . . . as pure water" (Lavoisier's *Works*, II. 335).

Lavoisier, who had obtained acid products on burning sulphur, phosphorus, and carbon, carried out in 1777 the experiment of burning inflammable air in a flask containing lime-water. He found that no fixed air was produced by burning the gas prepared from oil of vitriol and iron. Four years later, in 1781—1782, he repeated the experiment with oxygen in place of air.

"We took a bottle of six pints, which we filled with inflammable air; we lighted it quickly, and poured into it two ounces of lime-water; we closed the bottle at once with a wooden stopper, traversed by a pointed copper tube, connected by a flexible pipe with a reservoir filled with vital air. Contact between the inflammable air and the atmospheric air having been interrupted by the stopper, the surface of the inflammable air ceased to burn, but there formed at the end of the copper tube, in the interior of the bottle, a beautiful point of brilliant flame, and we saw with great pleasure the vital air burning in the inflammable air,

in the same manner and with the same circumstances as inflammable air burns in vital air" ("Decomposition and Recomposition of Water," *Works*, II. 334–359; p. 336).

The experiment was repeated twice, with distilled water and with a diluted alkali in place of the lime-water; the water, after the combustion, was as pure as before; it gave no signs of acidity, and the alkaline liquor was precisely in the same condition as before the experiment.

In June, 1783, the experiment was carried out on a larger scale, inflammable air and vital air from two large reservoirs being burnt together in a bell jar, inverted over mercury. Half an ounce of water was collected.

"This water, submitted to all the tests that one could imagine, appeared as pure as distilled water: it did not redden tincture of tournesol; it did not turn syrup of violets green; it did not precipitate lime-water; finally, by all the known tests, one could not discover the least sign of any impurity" (*ibid.* p. 338).

Lavoisier was able to interpret his observations very clearly and simply by means of his theory that burning meant combination with oxygen and not loss of phlogiston. In order to express his view that water was simply a compound of inflammable air with oxygen, in the formation of which "phlogiston played no part whatever," Lavoisier and his colleagues suggested in 1787 the name HYDROGEN, or "water-producer," for the inflammable gas. They say:

"It is the only substance which produces water by its combustion with oxygen gas . . ., and we have therefore called it *hydrogen*, from ὕδωρ, *water*, and γείνομαι, *I beget*; experiments having proved that water is nothing but oxygenated hydrogen, or the immediate production of the combustion of oxygen gas with hydrogen gas, deprived of the light and caloric which disengage during the combustion" (*Chemical Nomenclature*, tr. 1788, p. 24).

Lavoisier (1784) decomposes water by means of iron.—Having shown that water must be regarded as a compound of inflammable air with oxygen, Lavoisier argued that it should be possible to obtain inflammable air by the removal of oxygen from water. This he succeeded in doing by passing steam through an iron gun-barrel (Fig. 25) heated in a charcoal furnace (Meusnier and Lavoisier, "Decomposition of Water," 1784; *Works*, II. 360—373).

Lavoisier writes:

"If, when the gun-barrel is red and incandescent, water is allowed to flow drop by drop in very small quantities, it is decomposed completely, and none of it escapes from the lower opening of the gun; the oxygen of the water combines with the iron and calcines it; at the same time the inflammable constituent of the water, set free, passes into the gaseous state, with a specific weight about 2/25 of that of common air. At the beginning of the experiment, the production of inflammable air is very rapid; it soon becomes slower, and reaches a uniform condition, which lasts several hours; finally, at the end of eight to ten hours, more or less, according to the thickness of the barrel, the passage of inflammable air becomes slower, and the water ends by escaping entirely from the gun, as it entered it, without decomposing. If this operation has been pushed to the end, all the substance of the iron which composed the gun-barrel is converted into a black, brilliant substance, crystallised in facets like specular iron ore . . .: this substance occupies a much greater volume than the iron from which it was produced; the gun-barrel is consequently increased in thickness, and its internal diameter considerably diminished."

"The phenomena are very different if a metal is used for which oxygen has less affinity than for inflammable air: if, for example, one substitutes, in the preceding experiment, a copper barrel for one of iron, the water is reduced to vapour by passing through the incandescent part of the tube, but it condenses by cooling in the worm; the process is then only an ample distillation without loss, and there is neither

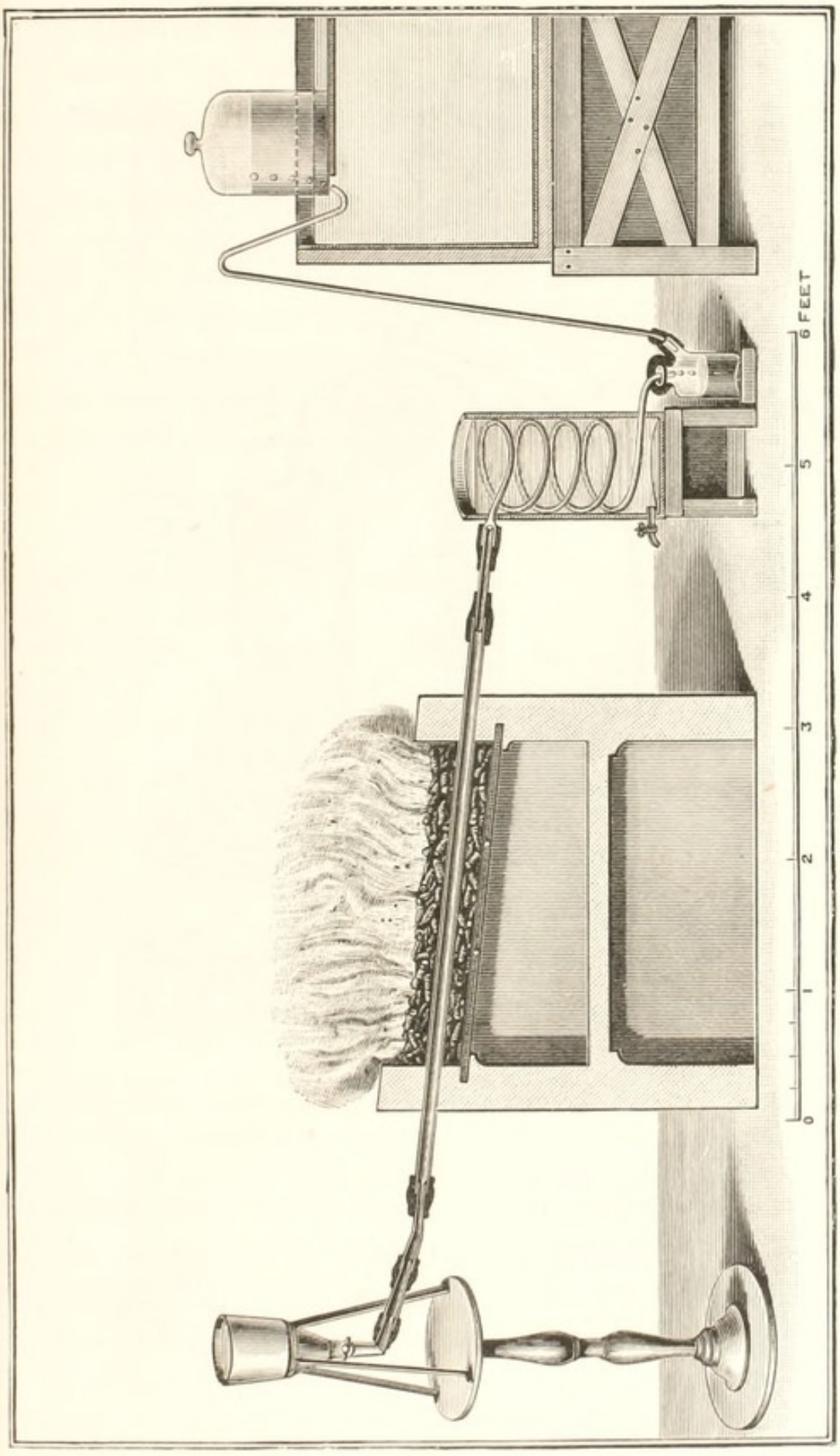


FIG. 25.—LAVOISIER'S APPARATUS FOR DECOMPOSING STEAM IN A RED-HOT GUN-BARREL.

calcination of the copper, nor production of inflammable air" (*Works*, II. 352—353).

Early quantitative experiments on the composition of water.—Almost simultaneously with the work of Cavendish and Lavoisier, the formation of pure water as the sole product of burning hydrogen and oxygen was noticed by

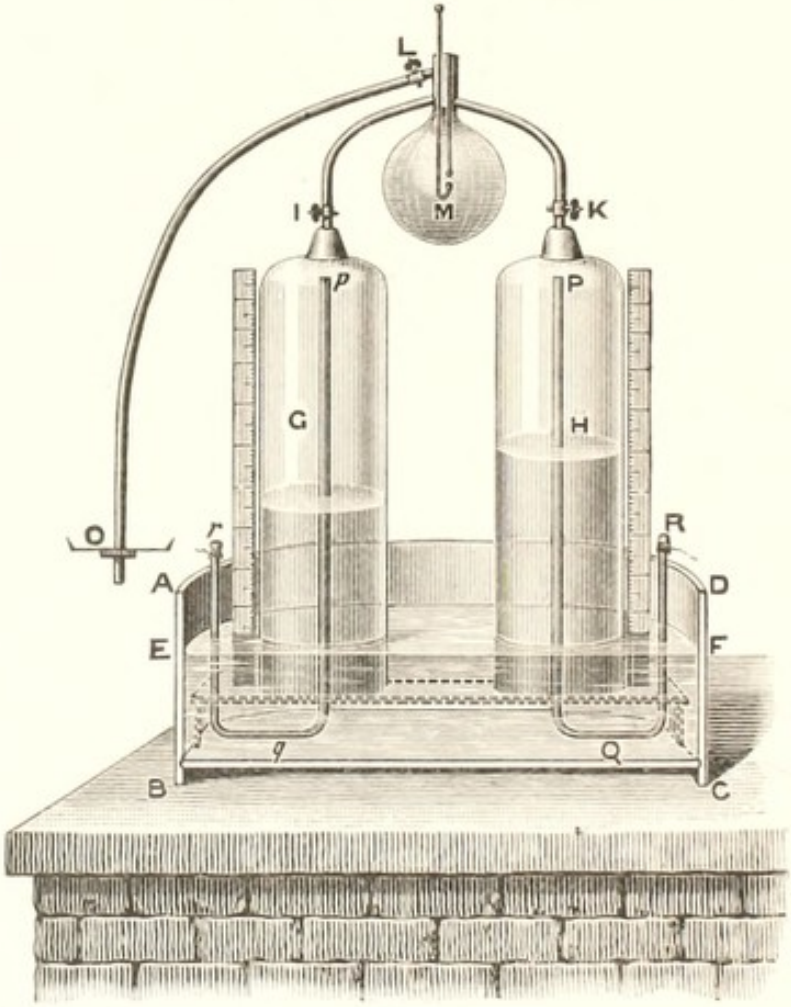


FIG. 26—MONGE'S APPARATUS FOR EXPLODING HYDROGEN AND OXYGEN IN AN EXHAUSTED GLOBE.

The gases were admitted through syphon-tubes, *pr*, *PR*, into the graduated measuring-cylinders, *GH*; they passed through the taps, *IK*, to the globe, *M*, which was exhausted through a tap, *L*, leading to an air-pump at *O*.

Monge, who carried out a series of careful quantitative experiments in the year 1781 (*Mem. Acad. Sci*, Paris, 1783, 78—88). Using the apparatus shown in Fig. 26, he exploded measured volumes of hydrogen and oxygen in an exhausted glass globe, and thus collected a large

quantity of the liquid product. The method of procedure was to admit $\frac{1}{12}$ volume of oxygen, fill up with hydrogen, and explode; by admitting fresh quantities of oxygen to the excess of hydrogen six further explosions could be made. A fresh supply of hydrogen was then admitted and the process repeated until 137 explosions had taken place; the globe was then found to be filled with a residue of non-explosive gas, which was drawn out by means of a pump, collected and measured. At the end of three series of experiments, in which 372 explosions were made, the quantities of gas used were:

Hydrogen	$145\frac{91}{144}$ pints.
Oxygen	$74\frac{9}{16}$,,

The weight of gas, calculated from the measured densities, was:

Hydrogen	442·03 grains.
Oxygen	1786·53 ,,
	2228·56 ,,
Or corrected for changes of pressure	2187·56 ,,

The products were:

Liquid	1917·10 grains.
Unburnt gas (7 pints)	171·91 ,,
	2089·01 ,,
Deficiency	98·55 grains.

"This liquid, perfectly transparent, reddened imperceptibly paper tinted blue by tournesol, much less than that obtained in a previous experiment, less even than saliva. This acidity can not be attributed to fixed air, because the liquid did not precipitate lime-water, and because distilled water, equally acidulated by fixed air, at once rendered lime-water milky; it scarcely whitened a solution of silver in nitric acid, and a little more sensibly that of mercury in the same acid. In addition to its slight acidity, it has also the empyreumatic taste that water always acquires in distilla-

tion; this product must then be regarded as pure water charged with the small quantity of vitriolic acid which inflammable air carries when prepared by the dissolution of iron."

"It follows from this experiment, that when inflammable air and dephlogisticated air, both pure, are exploded, there is no other product but pure water, heat, and light" (*loc. cit.*, pp. 86 and 87).

Monge's experiments agreed with those of Cavendish and with the later experiments of Humboldt and Gay Lussac (*Journ. de Physique*, 1805, **60**, 129—168), in showing that the volume of hydrogen used in the explosion is about twice as great as that of the oxygen. But, owing to the use of moist gas, the density of the hydrogen and its proportion by weight were greatly over-estimated. It is, however, noteworthy that the method used by Monge in 1781 was essentially the same as that employed 115 years later in the classical experiments of Scott and of Morley, who determined the composition of water with very great accuracy by measuring the densities of the two gases and the ratio of their combining volumes.

Volta's eudiometer.—The fact that oxygen and hydrogen (unlike nitrous air and oxygen, Chapter X, p. 201) combine together in a definite ratio, was used by the Italian physicist **Alexandro Volta** (1745—1827) (*Annali di Chimica*, 1790, I. 171—232; 1791, II. 261—286; 1791, III. 36—45) to estimate these gases. In order to explode the gases together, Volta introduced a metal cap, *b*, carrying an insulated wire, *c*, into the upper part of the graduated tube which constituted Priestley's "eudiometer." The instrument thus modified was known as VOLTA'S EUDIOMETER (Fig. 27). In order to estimate oxygen, for instance in atmospheric air, an excess of hydrogen was added and the mixture exploded; as two volumes of hydrogen combined with one of oxygen to form water, one-third of the decrease of volume was due to oxygen, the volume of which could thus be estimated very

accurately. This method of analysis had two advantages (1) the hydrogen need not be pure, and (2) the volume of hydrogen added need not be adjusted accurately.

In the hands of Gay-Lussac, Berthollet, Cruikshank, and others, Volta's eudiometer became an important instrument, not only for the estimation of oxygen and hydrogen, but for the examination and analysis of other combustible gases.

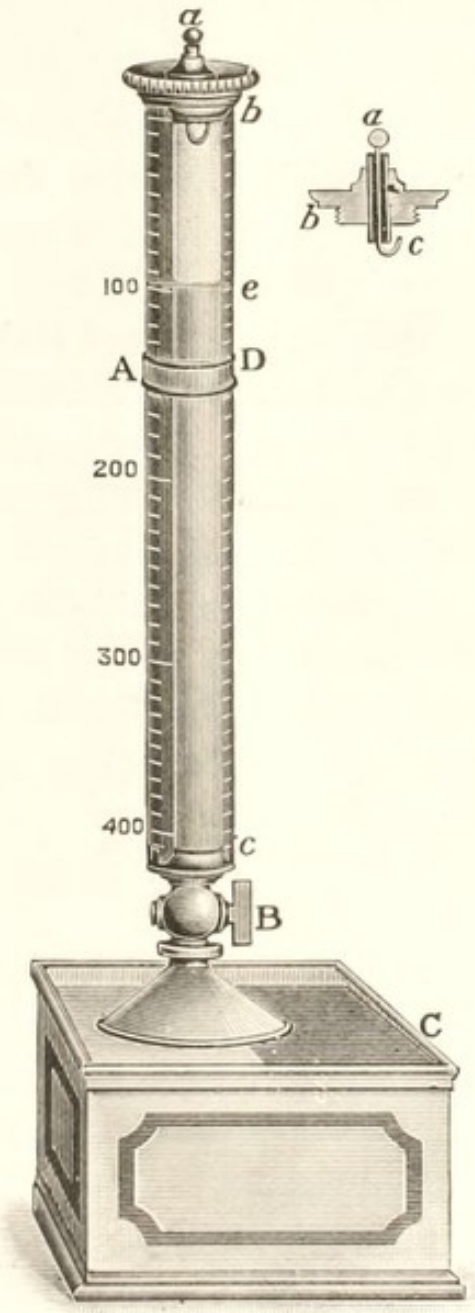


FIG. 27—VOLTA'S EUDIOMETER.

The funnel at the base was used to collect the gas over water contained in the trough *C*. The ring *AD* was used to read off the position of the meniscus, *e*, on the graduated scales which enveloped the greater part of the tube. Details of the sparking-device are shown at *abc*.

Water is produced by the action of inflammable air on metallic calces.—The revivification of metallic calces by inflammable air was discovered in 1785 by Priestley (*Experiments and Observations*, 1786, VI. 5).

By means of a burning glass, he heated red lead in a bell-jar inverted over water and filled with the inflammable gas. As soon as the red lead became dry the inflammable air was absorbed [1] and metallic lead was produced; no other product was seen and Priestley concluded that:

red lead + *inflammable air* (phlogiston) = *lead*,

the inflammable air being regarded by him as pure phlogiston.

[1] 101 volumes of the gas were reduced to 2, which still consisted of inflammable air (*loc. cit.* p. 7).

Lavoisier called attention to the fact that the calx was diminished in weight by its combination with inflammable air, and concluded that some other product, namely water, must be formed in addition to lead, thus :

red lead + hydrogen = lead + water.

Water was also produced in small quantities when red lead was revivified by means of charcoal, showing that the charcoal contained hydrogen as well as carbon (Lavoisier's *Works*, II. 344—348).

Oxidation and reduction.—The oxides of copper and iron can be reduced like red lead by heating them in a current of hydrogen, but the refractory oxide of zinc is not acted on by the gas. The case of iron is of interest because red-hot iron is oxidised by heating in a current of steam (p. 118) but the oxide is reduced when a current of hydrogen is passed over it. The action is therefore reversible, proceeding in one direction or the other, as shown by the two arrows, according as hydrogen or steam is present in excess.

$$iron + steam \rightleftarrows iron\ oxide + hydrogen.$$

It should be noticed that the term OXIDATION is often used to describe the removal of hydrogen as well as the addition of oxygen, whilst the converse process of REDUCTION may result either in the removal of oxygen or the addition of hydrogen.

Dumas's experiments on the composition of water, (1842).—The reduction of copper oxide by hydrogen was used by Berzelius and Dulong in 1820 (*Ann. de Chimie*, **15**, 386–395) to determine the composition of water. Instead of weighing the two gases of which it is composed, they weighed the water and calculated the weight of the oxygen from the loss in weight of the copper oxide ; the difference between these weights gave the weight of the hydrogen.

They found the ratio:

$$\textit{oxygen} : \textit{hydrogen} = 88{\cdot}9 : 11{\cdot}1$$
$$= \mathbf{8{\cdot}01 : 1}$$

This experiment was repeated on a very large scale by the French chemist **Jean Baptiste Dumas** (1800–1884) in 1842 ("Researches on the Composition of Water," *Ann. de Chimie*, 1843, **8**, 189–207). In Dumas' experiments (Fig. 28), the hydrogen, prepared by the action of zinc on dilute oil of vitriol, was purified and dried by passing through seven **U**-tubes, each a metre in height; the purifying agents were (1) lead nitrate solution to remove sulphuretted hydrogen, (2) silver sulphate solution to remove arseniuretted hydrogen, (3) potash (three tubes) to remove acid vapours. The drying agent was (4) sulphuric acid cooled in ice, or phosphoric anhydride (two tubes). The purifying agents were distributed over broken glass or pumice in order to secure proper contact with the gas. After the purification no odour could be detected even when a hundred litres of the gas were allowed to escape into the air.

The copper oxide was contained in a large bulb of hard glass provided with a beak a metre long to condense the water formed on reduction. The bulb was weighed, after removing the air by means of a pump. Before heating, the air in the apparatus was displaced by hydrogen, but a correction was needed for the fact that the sulphuric acid used in making the gas contained a little oxygen, which contributed something to the weight of water produced.[1] During the reduction, which occupied 10 to 12 hours, the bulb was heated by a large spirit lamp. After allowing the copper to cool, the hydrogen in the apparatus was displaced by air; the bulb was again exhausted by means of a pump and the loss of weight was determined by a second weighing of the bulb.

[1] In later experiments this was got rid of by passing the gas over hot copper before drying it.

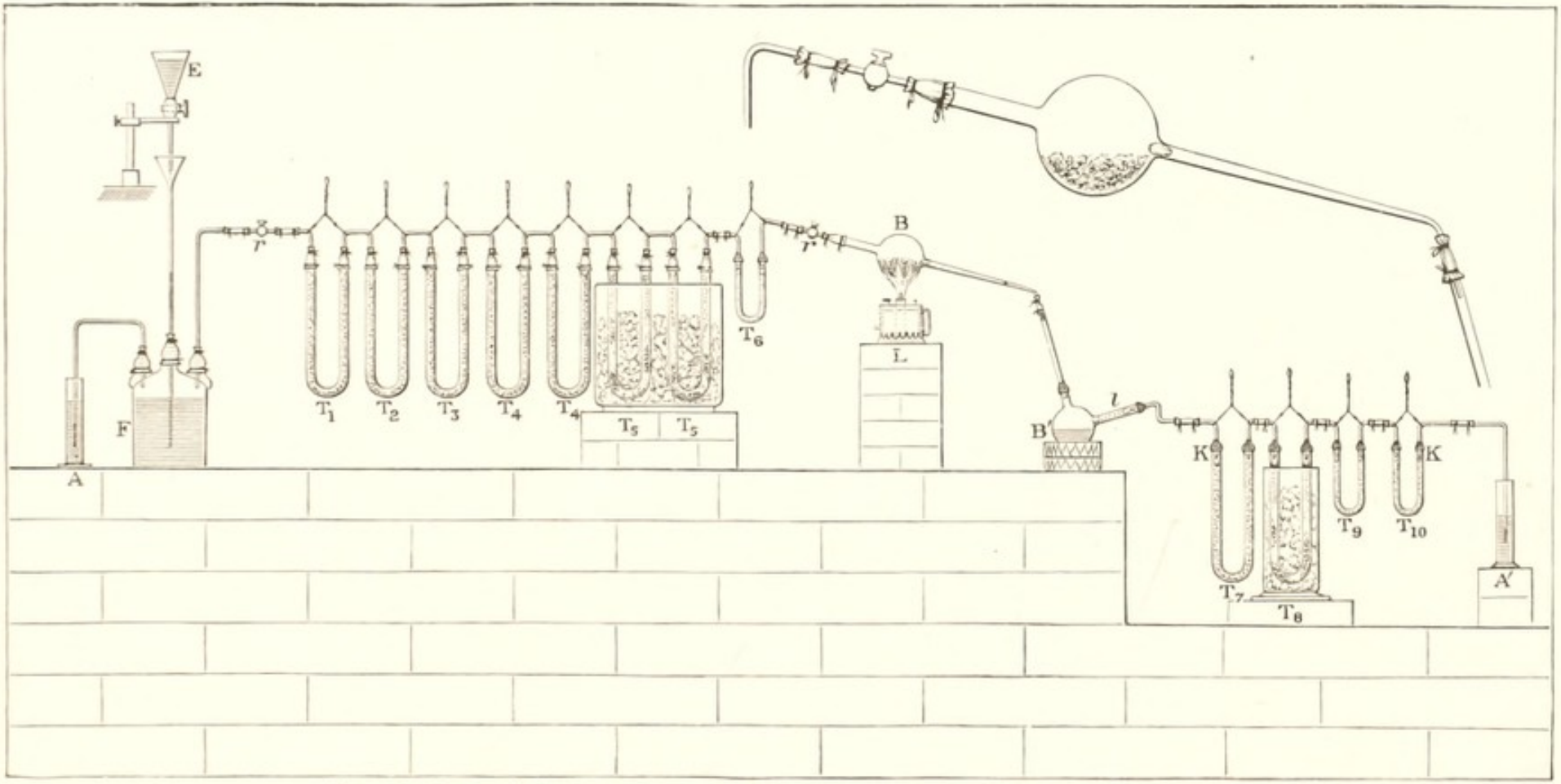


FIG. 28—DUMAS' APPARATUS FOR DETERMINING THE COMPOSITION OF WATER.

The inset shows the copper oxide bulb on a larger scale. The details of the apparatus are as follows:—F, Flask for generating hydrogen; E, Tap-funnel containing sulphuric acid; **A**, Safety-valve of mercury; T_1, Tube containing glass moistened with lead nitrate; T_2, Tube containing glass moistened with silver sulphate; T_3, Tube containing (*a*) alkaline pumice, (*b*) solid potash: T_4T_4, Ignited potash, broken; T_5T_5, Tubes containing pumice coated with phosphoric anhydride and cooled with a freezing mixture; T_6, Guard tube containing pumice and phosphoric anhydride; B, Bulb containing copper oxide, with tap *r* above, and pointed beak below to carry off water; L, Spirit lamp; B', Receiver for water, with fragments of calcium chloride at *l*; T_7, Ignited potash; T_8, Phosphoric anhydride in a freezing mixture; T_9, Guard tube containing phosphoric anhydride; T_{10}, Phosphoric oxide (not weighed) to exclude moisture; A', Valve containing sulphuric acid, for escape of hydrogen.

The water was collected in a smaller bulb, followed by a series of drying tubes, similar to those used to dry the hydrogen. The water could not be weighed in a vacuum, but the observed weight was corrected for the buoyancy of the air which it displaced. In all, more than a kilogram of water was collected.

In a typical experiment, using phosphoric anhydride as the drying agent, the figures were:

Exhausted bulb and copper oxide	673·280	grams.
,, ,, copper	613·492	,,
Oxygen =	59·788	,,
Bulb and drying tubes	931·487	,,
,, ,, ,, with water	998·700	,,
	67·213	,,
Air correction	0·069	,,
Water =	67·282	,,
Hydrogen combined with 1 part of oxygen =	0·12533	,,
Ditto, corrected for air in the sulphuric acid =	0·12508	,,

From nineteen experiments Dumas concluded that the ratio of hydrogen to oxygen lay between 0·1250 and 0·1256. This gives the ratio of oxygen to hydrogen as 8·00 to 7·96, or taking a mean value,

oxygen : hydrogen = **7·98 : 1.**

Scott's determination of the composition of water.— The figures obtained from the laborious experiments of Dumas remained unchallenged for almost half a century. In 1893, however, Alexander Scott (*Phil. Trans.*, 1893, **184**, 543–568) obtained an independent value for the composition of water by reverting to the method of finding the composition by weight from the densities and combining volumes of the gases. The densities had been determined with very great care by Lord Rayleigh. Scott measured the combining volumes by exploding the moist gases after carefully

comparing their volumes at atmospheric temperature and pressure.

The hydrogen was prepared by the action of metallic sodium on steam, with or without absorption by palladium (see footnote, p. 130). The oxygen was prepared by heating silver oxide. Both gases were of the highest degree of purity, the residue of impurity left after explosion being usually less than one part in 100,000. The ratio of the combining volumes was found to be **2·00245** at 14° to 18° C. Lord Rayleigh's determination of the densities of the gases had given the ratio 15·882 : 1, the combining weights of the two gases were therefore in the ratio,

$$\textit{oxygen} : \textit{hydrogen} = \mathbf{7{\cdot}931 : 1}.$$

Morley's experiments on the composition of water.— The redetermination of the composition of water by E. W. Morley in the year 1895 (*Smithsonian Contributions to Knowledge, tr. Zeit. physikal. Chem.*, 1895, **20**, 68, 242, 417) was carried out with extraordinary care and accuracy, and has already become one of the classics of scientific literature.

In these experiments the use of copper oxide was again discarded; the hydrogen and oxygen were weighed directly, as in the earliest experiments, but with all the added resources which had accrued from the experimental work of the intervening century.

The density of oxygen (prepared by heating potassium chlorate or by electrolysing dilute sulphuric acid) was determined by weighing it directly in globes of 20 litres capacity, suspended in pairs[1] in a large desiccator-cupboard from the pans of a balance (Fig. 29). In a typical experiment the data were :

[1] The method of weighing a glass globe against a counterpoise of similar form was introduced by Regnault : it serves to eliminate most of the errors caused by variations of barometric pressure and of the amount of moisture in the atmosphere.

Volume... ..	21568·4 c.c.	Weight ...	28·4308 grams.
Temperature ...	17·48° C.	Corrected ...	17·40° C.
Barometer ..	745·91 mm.	Corrected ...	746·29 mm.
Weight of 1 litre of oxygen at sea level in 45° latitude, at 0° C. and 760 mm. pressure ...			1·42883 grams.

The mean of three complete series of experiments, in which different methods were used for measuring temperature and pressure, gave the value **1·42900 ± 0·000034**.

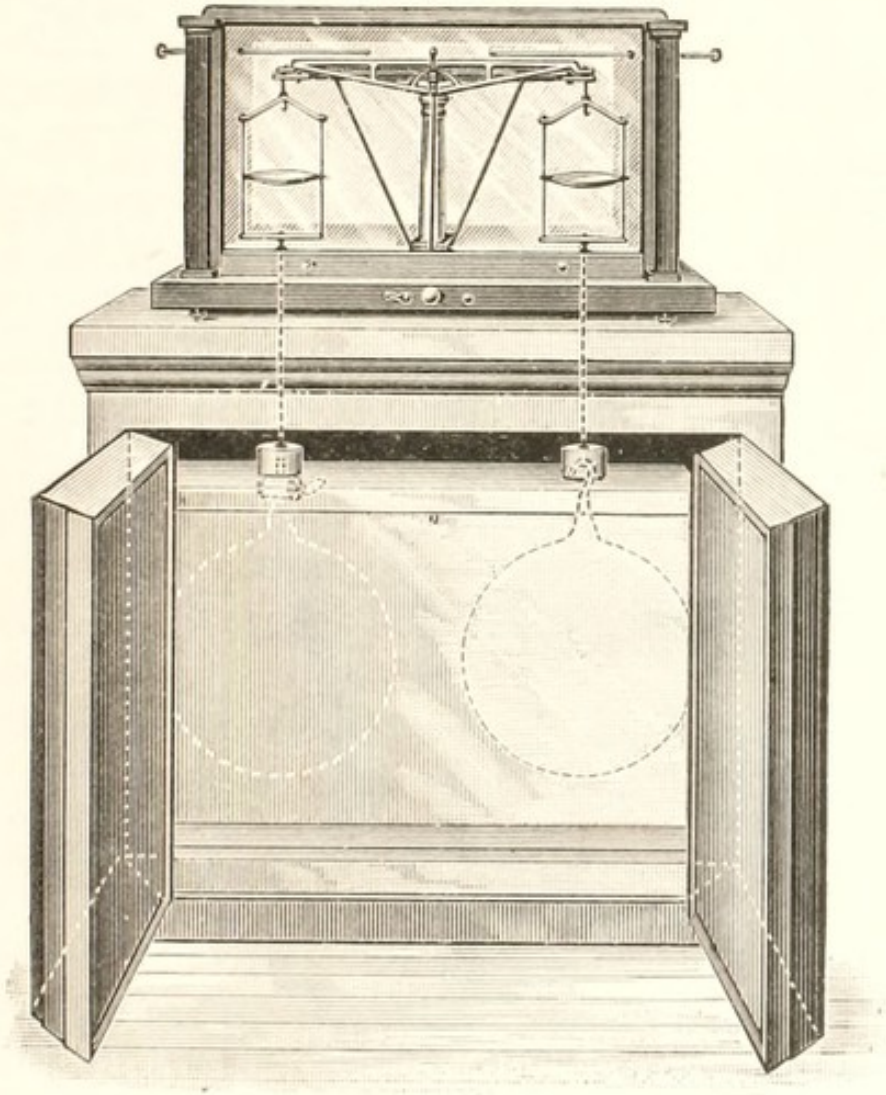


FIG. 29—MORLEY'S APPARATUS FOR MEASURING THE DENSITY OF OXYGEN.

The density of hydrogen was determined in a different way, both on account of the difficulty of weighing 1·8 grams of gas in a globe 600 times heavier, and also because of the risk that this small weight might be increased appreciably

by the presence of mercury vapour. In the final series of experiments, therefore, the gas was weighed in a tube filled with metallic palladium (Fig. 30);[1] on heating the tube the gas was expelled into three large globes immersed in ice; the pressure produced in these globes by a known weight of gas was measured. In a typical experiment the data were:

Volume of three globes...	43·2574	litres.
,, ,, air space in manometer	0·0536	,,
,, ,, leads...	0·0365	,,
Temperature, 0° C. Total volume ... =	43·3475	,,
Pressure (corr.), 725·30 mm. Weight =	3·7158	grams.
Density of hydrogen... ...	0·089864	gram per litre.

Twenty-five experiments made in this way gave an average value

0·089873 ± 0·0000027.

In order to find the weights of the gases which combined together to form water, it was necessary next to determine

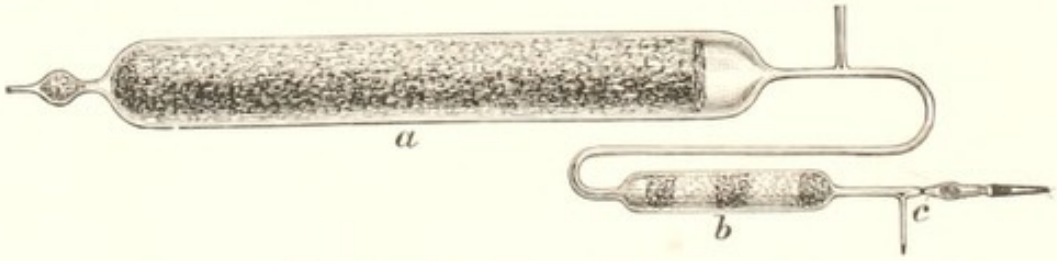


FIG. 30—MORLEY'S PALLADIUM-TUBE FOR WEIGHING HYDROGEN.

a Is a bulb containing 600 grams of palladium; *b* contains phosphoric anhydride to dry the gas; *c* is a seal of fusible metal.

the ratio of their combining volumes. For this purpose Morley prepared a mixture of the two gases by passing an electric current through dilute potash cooled in ice. The apparatus was provided with drying tubes and a tap, and was arranged so that it could be weighed before and after

[1] Morley used 600 grams of palladium; he found that this quantity absorbed 3·8 grams of hydrogen and liberated 3·7 grams, occupying over 40 litres. This method of purifying and weighing hydrogen was introduced by Chirikoff in 1882; it forms one of the most important of the advances that have been made in the methods of determining the composition of water since the work of Dumas.

delivering the gas. The density of the gas was determined in the same way as in the case of hydrogen, by finding the pressure produced in the three large globes by a known weight of the gas. In a typical experiment 23·0269 grams of the gas produced a pressure of 753·97 mm. in a volume of 43·3628 litres; density 0·535513; mean of 10 experiments 0·535510 ± 0·000010. From this density the proportion of hydrogen to oxygen was calculated, after making various corrections, to be 2·00357. By exploding the gas in a eudiometer it was found that there was a slight excess of hydrogen, amounting to 0·000293 of the total volume or 0·00088 of the volume of the oxygen. The combining volumes were therefore in the proportion

hydrogen : oxygen = **2·00269 : 1.**

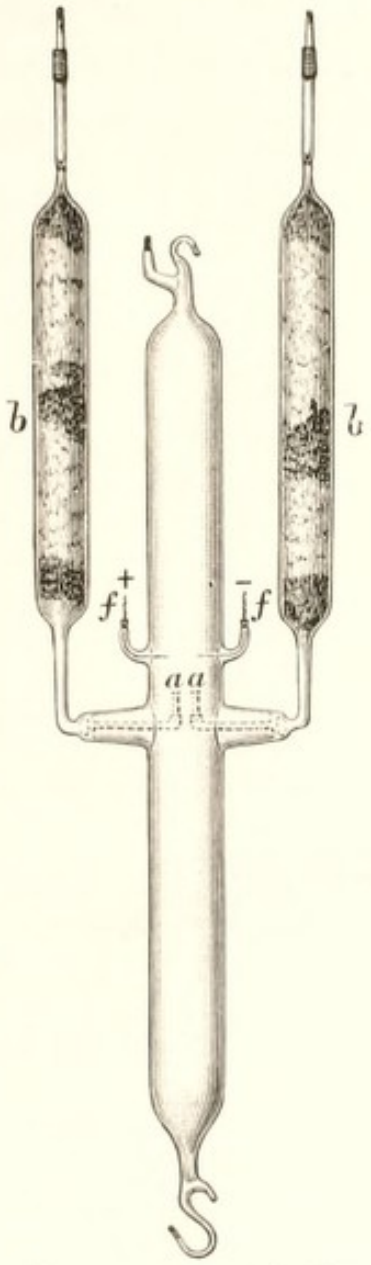


FIG. 31—MORLEY'S COMBUSTION-TUBE.

The gases were admitted by jets *aa* after passing through drying tubes *bb*; they were ignited by sparking at *ff*.

A second method of determining the composition of water was by weighing the water produced by the combination of known weights of hydrogen and oxygen. The hydrogen (21 litres) was drawn from a palladium bulb *a* (Fig. 30) provided with a drying tube of phosphoric anhydride *b*, and a tiny plug of fusible metal *c* in place of a tap. The oxygen (42 litres) was drawn from two large globes which were weighed in the same way as in the density experiments.

The combustion was carried out in a cylindrical glass tube (Fig. 31) surrounded with cold water (Fig. 32) and

provided with two jets *a a* and a pair of wires *f f* for a spark to ignite the gas. The tube was exhausted before and after the combustion; the water produced was frozen before exhausting, and drying tubes *b b* were provided on either side in order that none of the water might be lost. The gas remaining

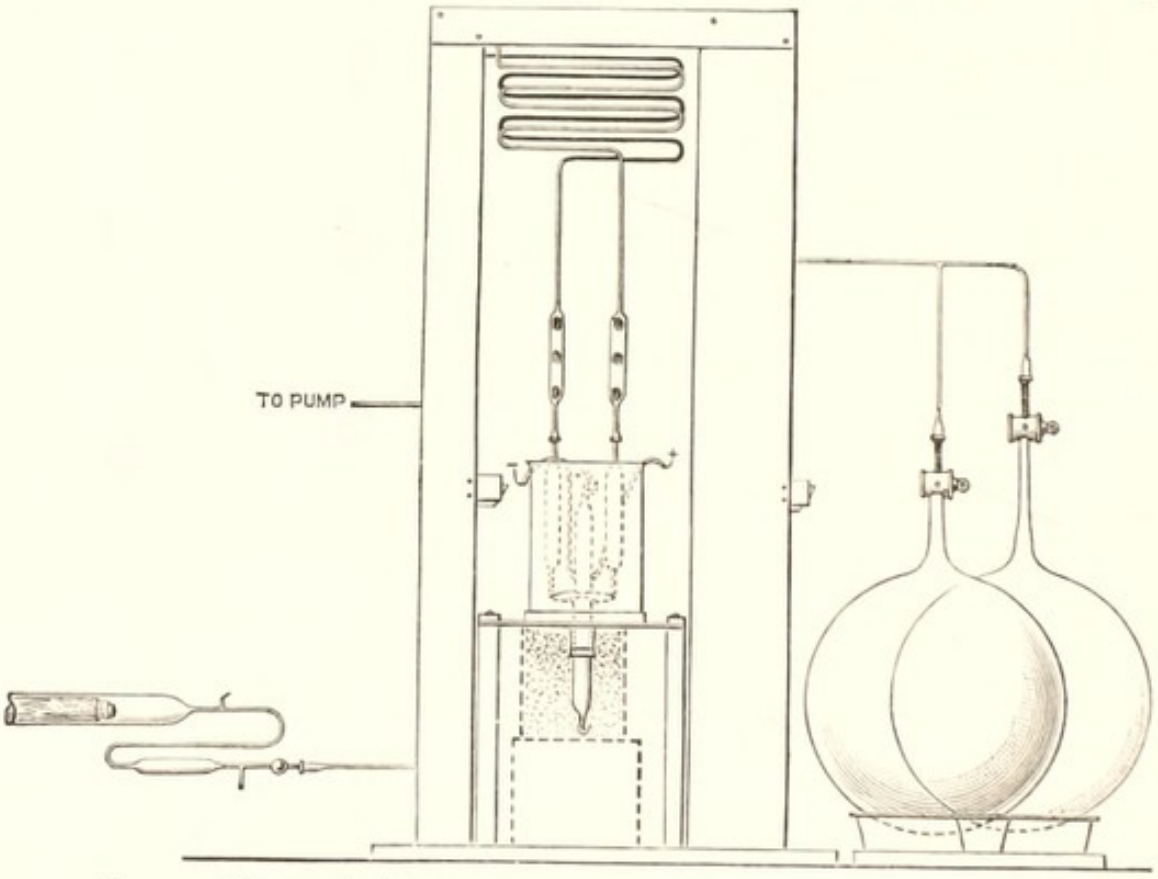


FIG. 32—MORLEY'S APPARATUS FOR THE COMBUSTION OF HYDROGEN AND OXYGEN.

The leads for the hydrogen (on the left) and for the oxygen (on the right), with the regulating taps are hidden behind the wooden frame. They are joined to the combustion-tube by long, flexible, glass leads, terminating in drying tubes. The upper part of the combustion-chamber is surrounded by water, the lower part by a freezing-mixture.

in the chamber at the end of the experiment was collected and analysed. In a typical experiment the weights were:

Hydrogen	3·8223 − 0·0012 =	3·8211	grams.
Oxygen	30·3775 − 0·0346 =	30·3429	,,
Total	=	34·1640	,,
Water	=	34·1559	,,
Whence *oxygen to hydrogen*	=	7·941	
water to hydrogen	=	8·939	

The mean of twelve experiments in which 400 grams of water were produced gave the ratios

oxygen to hydrogen = **7·9396**
water to hydrogen = **8·9392**

From the ratio 15·9002 of the densities and 2·00269 of the combining volumes, the two constituents are in the ratio

oxygen : hydrogen = **7·9395 : 1.**

The high order of accuracy reached in these modern measurements on the composition of water is shown by the following comparison of the values for 0° C. and 760 mm. pressure.

Ratio of densities ...	...	Rayleigh	15·882
		,, (reduced to 0°C.)	15·900
		Morley	15·9002
Ratio of volumes ...	...	Scott	2·00245
		,, (reduced to 0°C.)	2·00285
		Morley	2·00269
Ratio of weights ...	...	Rayleigh & Scott ...	7·931
		Morley (*a*)	7·9396
		(from oxygen : hydrogen)	
		Morley (*b*)	7·9392
		(from water : hydrogen)	
		Morley (*c*)	7·9395
		(from combining volumes)	

Summary and Supplement.

A. Water an Oxide.

Cavendish, in 1781 ("Experiments on Air," Part I, published in 1784), showed that pure water, without taste or smell, was produced by exploding or burning a mixture of inflammable air with 2½ times its volume of common air. Water was also formed when that gas was exploded with ½ volume of oxygen, but in this case the product was slightly acid.

Lavoisier, in 1783, prepared half an ounce of pure water by burning oxygen and inflammable air. He also proved the presence of oxygen in water by passing steam through a red-hot iron gun-barrel, when inflammable air and magnetic oxide of iron were produced. These experiments showed that water

was not an element, as had been supposed previously, but a compound of inflammable air with oxygen. Lavoisier and his colleagues in 1787 therefore gave to the inflammable air the name "hydrogen" or water-producer (compare German *wasserstoff*). Lavoisier's "Decomposition and Recomposition of Water" may be represented by the equations :

$$3Fe + 4H_2O \rightarrow Fe_3O_4 + 4H_2$$
$$\text{Iron} + \text{steam} \rightarrow \text{oxide of iron} + \text{hydrogen}$$
$$2H_2 + O_2 \rightarrow 2H_2O$$
$$\text{Hydrogen} + \text{oxygen} \rightarrow \text{water-vapour.}$$

Priestley, in 1785, showed that many metallic oxides could be reduced to metals by heating them in hydrogen ; Lavoisier showed that water is also produced. The action may be represented by equations such as the following :

$$PbO + H_2 \rightarrow Pb + OH_2$$
$$\text{Litharge} + \text{hydrogen} \rightarrow \text{lead} + \text{water-vapour}$$
$$CuO + H_2 \rightarrow Cu + OH_2$$
$$\text{Copper oxide} + \text{hydrogen} \rightarrow \text{copper} + \text{water-vapour.}$$

Iron oxide is also reduced by hydrogen ; this action is therefore reversible :

$$Fe_3O_4 + 4H_2 \rightleftarrows 3Fe + 4OH_2,$$

the action proceeding in one direction or the other according as hydrogen or steam predominates in the gas.

B. The Composition of Water.

Cavendish, in 1781, showed that water was formed by the combination of two volumes of hydrogen with one volume of oxygen. This proportion was confirmed by **Lavoisier, Monge,** and others, who burnt or exploded together large volumes of the two gases, as well as by the careful experiments on the explosion of hydrogen and oxygen which **Gay-Lussac** and **Humboldt** carried out in 1805 with the help of Volta's "eudiometer." Monge used the measured densities of the two gases to calculate the composition of water by weight, but obtained very erroneous results as the hydrogen was not dried.

Berzelius and **Dulong**, in 1820, made the first successful determination of the composition of water by using copper

oxide to oxidise the hydrogen and measuring the weight of water produced and the loss in weight of the copper oxide

$$CuO + H_2 \rightarrow Cu + OH_2.$$

They found the ratio

Oxygen : *hydrogen* = **8·01 : 1.**

This method was used on a large scale by **Dumas** in 1842. He purified the hydrogen
from *sulphuretted hydrogen* by means of lead nitrate solution ;
from *arseniuretted hydrogen* by means of silver sulphate solution ;
from *acid vapours* by means of potash ;
from *water-vapour* by means of oil of vitriol cooled in ice, or by means of phosphoric oxide ;
these purifying agents were contained in seven **U**-tubes, each 1 metre in height. The copper oxide and copper were weighed in a large vacuous bulb provided with a beak one metre in length ; during the reduction the bulb was heated by a large spirit lamp. In 19 experiments Dumas prepared one kilogram of water and found the ratio

Oxygen : *hydrogen* = **7·98 : 1.**

Scott, in 1893, reverted to the method used by Monge. He exploded pure hydrogen and oxygen and found the combining volumes to be in the ratio **2·00245 : 1.** When combined with densities measured by Rayleigh, this gave the compesition

Oxygen : *hydrogen* = **7·931 : 1.**

Morley, in 1895 (1), by weighing the gas in large globes containing 22 litres found the density of oxygen to be
1·42900 grams per litre at 0° C. and 760 mm. pressure.
(2) By measuring the pressure produced in three globes of 43 litres capacity when a known weight of hydrogen was expelled from palladium, he found the density of hydrogen to be
0·089873 gram per litre at 0° C. and 760 mm. pressure.
(3) By exploding a mixture of hydrogen and oxygen he found the combining volumes to be in the ratio **2·00269 : 1** at 0° C. Whence the composition by weight is found to be

Oxygen : *hydrogen* = **7·9395 : 1.**

(4) By burning together in a special combustion-chamber known weights of hydrogen and oxygen (weighed as in the

density measurements), Morley found the composition of water by weight to be

$$Oxygen : hydrogen = 7{\cdot}9396 : 1;$$

whilst the weights of the oxygen and water gave the ratio

$$Oxygen : hydrogen = 7{\cdot}9392 : 1;$$

mean,

$$Oxygen : hydrogen = 7{\cdot}9394 : 1.$$

CHAPTER VIII

THE BURNING OF INFLAMMABLE GASES, LIQUIDS, AND SOLIDS

A. An Inflammable Oxide of Carbon.

Lassone (1776) prepares an inflammable gas by reducing the calx of zinc with charcoal.—The loss of weight, which takes place when a calx such as litharge is reduced to a metal by heating it with charcoal, was proved by Lavoisier to be due to the escape of a very large volume of fixed air (carbonic anhydride). A different, and somewhat perplexing, result was observed when the white calx of zinc was reduced in this way. This experiment, which was carried out by Lassone in 1776, gave rise to an inflammable gas, but one that differed in a very marked way from the inflammable air (or hydrogen) which he obtained by the action of alkalis, as well as of acids, upon the metal.

"From a mixture of a half-ounce [288 grains] of zinc calx and a gros [72 grains] of charcoal powder put into a pistol barrel, I extracted in the fire of a forge 96 cubic inches of a gas, which burns rapidly without detonating; the flame is blue: this kind of air at first permanent mixes afterwards little by little with water, it does not redden nitrous air."

"Two gros [144 grains] of Prussian blue submitted in a pistol barrel to the action of a forge fire, gave more than

34 cubic inches of air which burns without detonating, producing a very beautiful blue flame."

"These two last experiments give an inflammable air of quite a peculiar character; for it does not make the smallest explosion, nor the least noise when inflamed, after mixing with common air or with dephlogisticated air;[1] from which it follows that there appear to exist up to the present two distinct kinds of inflammable gas; one which inflames rapidly with explosion and great noise when mixed with common atmospheric air, and which detonates still more strongly when mixed with dephlogisticated, or pure air; and the second, which although mixed with the two preceding gases, always burns quietly without noise." (*Mem. Acad. Sci., Paris*, 1776, **90**, 686–696; p. 691.)

Priestley (1785) prepares an inflammable gas from smithy scale.—A few years later, in 1785, Priestley noticed the production of a similar inflammable gas during the reduction of SMITHY SCALE, or FINERY CINDER, the bluish-black calx formed when iron is burnt in air.

"Having made the scales of iron, and also the powder of charcoal very hot, previous to the experiment, so that I was satisfied that no air could be extracted from either of them separately by any degree of heat, and having mixed them together while they were hot, I put them into an earthen retort, glazed within and without, which was quite impervious to air. This I placed in a furnace, in which I could give it a very strong heat; and connected with its proper vessels to condense and collect the water which I expected to receive in the course of the process. But, to my great surprise, not one particle of *moisture* came over, but a prodigious quantity of *air*, and the rapidity of its production astonished me; so that I had no doubt but that the weight of the air would have been equal to the loss of weight both in the scales and in the charcoal; and when I examined the air, which I repeatedly did, I found it to contain one-tenth of fixed air, and the inflammable air, which remained when the fixed air

[1] *i.e.*, oxygen.

was separated from it, was of a very remarkable kind, being quite as heavy as common air" (*Experiments and Observations*, 1786, VI. 109).

This observation attracted a great deal of attention. According to Lavoisier's theory the reduction of an oxide with charcoal should give rise to the metal and fixed air; in this experiment hydrogen appeared to be produced instead. The only explanation that the French chemists were able to give of the production of the inflammable gas was that the charcoal, even when strongly heated, retained a certain amount of hydrogen, which it released only when burnt with the help of a suitable oxide.

Cruikshank (1801) recognises an inflammable oxide of carbon.—The real nature of this inflammable gas was discovered in 1801 by W. Cruikshank of Woolwich (*Nicholson's Journal*, April 1801, **5**, 1–9), who proved it to be an oxide of carbon. This was generally regarded as an impossible view, on account of the low density of the gas. The French chemist, **C. L. Berthollet** (1748—1822), for instance, in 1809 (*Mem. Soc. Arcueil*, 1809, II., 68—93, p. 85), pointed out that this oxide would be "the only example that one can quote, in which the gaseous compound would be lighter than the lightest of its component elements" and argued that the gas must contain hydrogen.

Cruikshank examined the gases formed by reducing the black oxide of iron and the white oxide of zinc, and then proceeded to study the reduction of the red oxide of copper, of litharge, and of the black oxide of manganese described by Scheele (p. 210). He found:

(1) "That all metallic oxides capable of enduring a red heat, will, when mixed with charcoal, not only yield carbonic acid, but also a very considerable quantity of an inflammable gas.

(2) "That those oxides which retain their oxygen most obstinately, yield the greatest quantity of inflammable gas;

and on the contrary, that those which part with it readily, afford the greatest proportion of carbonic acid.

(3) "That the carbonic acid gas was chiefly disengaged at the beginning of the process, and the purest and greatest quantity of inflammable gas towards the conclusion of it" (*loc. cit.*, p. 3).

The gas, after washing with lime water to remove the carbonic anhydride, had a density 22/23 of that of air. When exploded with oxygen in a Volta eudiometer it was converted into fixed air. But it required for its combustion less oxygen than was present in the fixed air produced from it. The gas therefore contained carbon already combined with oxygen, the proportion of carbon being greater and the proportion of oxygen less than in fixed air. Cruikshank described the gas as the GASEOUS OXIDE OF CARBON, but it soon became known as CARBONIC OXIDE.

Cruikshank prepares carbonic oxide by reducing carbonates with iron.—Cruikshank showed that many gallons of the gas could be prepared by heating carbonated baryta or common chalk with iron plates. In this experiment fixed air combined with baryta or with lime was reduced to carbonic oxide by the iron, which removed from it a part of the oxygen which it contained. This method of preparation had the advantage of giving a gas which was free from hydrogen; the gas prepared from charcoal always contained hydrogen, thus affording some justification for Berthollet's view that the gas was a hydrogen-compound.

Désormes and Clément (1801) investigate the inflammable oxide of carbon.—The composition of this gas was also investigated in France, by Désormes and Clément. They found, in 1801, that the inflammable gas prepared by heating zinc oxide with charcoal gave no deposit of dew when burnt under a cold bell-jar, and that no drops of water were formed when it was exploded with oxygen over oil. They measured the volume of oxygen used and

the volume of carbonic anhydride produced in the explosion, and concluded that, whilst carbonic anhydride contained 28% of carbon, the inflammable oxide contained 53% of carbon and 47% of oxygen ("On the Reduction of the White Oxide of Zinc by Carbon, and on the Gaseous Oxide of Carbon which is produced." *Ann. de Chimie*, 1801, **39**, 26–64.)

Désormes and Clément prepare carbonic oxide by the reduction of carbonates.—Having established the nature of the gaseous oxide, Désormes and Clément proved that the same gas is formed during the reduction with charcoal of refractory carbonates, such as that of baryta. This carbonate resembles chalk in that it effervesces when acids are added to it; but it differs from chalk in that it is not readily decomposed by heat. Whereas carbonated magnesia can be decomposed in glass vessels, and chalk in an earthenware retort (Ch. IV., p. 49), carbonated baryta must be decomposed by heating *with charcoal*: the fixed air is then reduced and escapes in the form of carbonic oxide. It should be noted that Cruikshank prepared carbonic oxide from the same carbonate by the action of iron (p. 140).

Désormes and Clément describe their experiments as follows:

"The preceding experiments show that the gas generated by the reduction of oxide of zinc, was only oxygen and carbon which, meeting at a high temperature, combined in different proportions from those of carbonic acid. It seemed possible to form this combination by uniting carbon and carbonic acid.

"One recalled the experiment of Pelletier who, by the addition of charcoal to carbonate of baryta, succeeded in driving out the carbonic acid from it by simple heat, and one believed that in this experiment the carbonic acid combining with the carbon, had formed a gas similar to that obtained in the reduction of oxide of zinc, and was separated easily from the baryta on account of its greater elasticity.

"The experiments were made and the results agreed perfectly with our view.

"To 16 grams of carbonate of baryta made directly, 5 grams of charcoal were added and the mixture was heated in an apparatus similar to that used for the reduction of the oxide of zinc.

"After three hours' heating, a hole was formed in the retort, and the heating was stopped: there had been collected three litres of a gas of which the first portions contained 1/6 of carbonic acid and 5/6 of an inflammable gas similar in every respect to carbonic oxide. The last portions contained hardly any carbonic acid.

"In the residue were found 1·64 gram of pure baryta." (*loc. cit.*, p. 45.)

Désormes and Clément prepare carbonic oxide by reducing carbonic anhydride with charcoal.—Désormes and Clément made many attempts to prepare carbonic oxide by the direct combination of carbon with air or oxygen. They found that carbonic anhydride was invariably formed as the first product of combustion, but that this gas could be reduced to carbonic oxide by passing it through red-hot iron tubes packed with charcoal (*loc. cit.*, p. 46). The gas was passed to and fro until no further increase of volume was caused by the reduction. At the present time large quantities of inflammable gas are manufactured in this way, by passing air through hot coal or coke; the oxygen first forms carbonic anhydride, which is then converted into carbonic oxide by the excess of hot fuel; the product, known as PRODUCER GAS, consists mainly of carbonic oxide and carbonic anhydride, diluted with large volumes of nitrogen.

Désormes and Clément decompose water by means of charcoal.—It was well known that large quantities of inflammable gas could be produced by heating moistened charcoal. The nature of this process was elucidated by Désormes and Clément, who showed that the charcoal

reduces the water, liberating hydrogen from it, and is itself converted into carbonic oxide (*loc. cit.*, p. 52). This gas is now prepared by blowing steam into fuel that has been made hot by an air-blast, and is known as WATER GAS; it consists mainly of hydrogen, carbonic oxide, and carbonic anhydride. As the steam cools the fuel, water-gas can only be prepared alternately with producer gas; a mixture prepared by blowing in steam and air together is known as SEMI-WATER GAS.

B. Quantitative Experiments on the Composition of the Oxides of Carbon.

Composition by volume.—It was noticed by Priestley and by Lavoisier that charcoal burnt in air or oxygen does not cause any change of volume, until the fixed air produced is absorbed by water, by lime-water, or by an alkali. Oxygen thus suffers no change of volume when it combines with carbon to form carbonic anhydride; at the same time carbonic anhydride is shown to contain its own volume of oxygen, thus:

carbon + oxygen $\longrightarrow$ carbonic anhydride
1 *vol.* 1 *vol.*

The composition of carbonic oxide is less easily determined, because it is necessary to use a pure gas for the analysis. Désormes and Clément found that 100 parts of the gas exploded with about 40 parts of oxygen, and gave about 80 parts of carbonic anhydride. Cruikshank obtained similar numbers for gas prepared by means of charcoal; but gas prepared by means of iron gave 19/20 of its volume of carbonic anhydride when exploded with oxygen. Berthollet (quoted by Gay-Lussac, A.C.R. IV. 15) found that 100 parts of the gas combined with 50 parts of oxygen to give 100 parts of carbonic anhydride. From Berthollet's values it follows that carbonic oxide takes up

one half its volume of oxygen in forming carbonic anhydride, but does not suffer any change of volume in the process, thus :

$$\underset{1\ vol.}{\text{carbonic oxide}} + \underset{\frac{1}{2}\ vol.}{\text{oxygen}} \longrightarrow \underset{1\ vol.}{\text{carbonic anhydride}}$$

Carbonic anhydride, on the other hand, parts with half its oxygen and doubles in volume when it combines with carbon to form carbonic oxide, thus :

$$\underset{1\ vol.}{\text{carbonic anhydride}} + \text{carbon} \longrightarrow \underset{2\ vols.}{\text{carbonic oxide.}}$$

Dalton decomposes carbonic anhydride by sparking.— An independent proof of these relationships was obtained by **John Dalton** of Manchester (1766–1844), who found that carbonic anhydride (18 vols.) was decomposed by the electric spark into carbonic oxide (16 vols.) and oxygen (9 vols.). The combustion of carbonic oxide is therefore a reversible process, as shown by the equation :

$$\underset{1\ vol.}{\text{Carbonic oxide}} + \underset{\frac{1}{2}\ vol.}{\text{oxygen}} \rightleftharpoons \underset{1\ vol.}{\text{carbonic anhydride}}$$

Dalton writes :

"Carbonic acid is decomposed by electricity into carbonic oxide and oxygen. I assisted Dr. Henry in an experiment in which 52 measures of carbonic acid were made 59 measures by 750 shocks ; the gas after being washed became 25 measures, whence these had arisen from the decomposition of 18 measures of acid[1] ; these 25 measures consisted of 16 carbonic oxide and 9 oxygen ; for, a portion being subjected to nitrous gas, manifested 1/3 of its bulk to be oxygen ; and the rest was fired by an electric

[1] 59 – 25 = 34 measures of carbonic acid gas remained after sparking, out of the 52 measures originally taken.

spark, and appeared to be almost wholly converted into carbonic acid. (*New System of Chemical Philosophy*, 1810, II. 382.)

Berzelius and Dulong (1820) calculate the composition by weight of carbonic anhydride.—The earliest estimations of the proportion by weight of carbon and of oxygen in carbonic anhydride, were (like the early numbers for the composition of water) dependent on a knowledge of the densities of the gases concerned in the combustion.

As the volume of carbonic anhydride produced was equal to the volume of oxygen used, the composition of the anhydride could be deduced directly from a knowledge of the densities of these two gases. This method was employed by Berzelius and Dulong, working in Berthollet's laboratory at Arcueil (*Ann. de Chimie*, 1820, **15**, 393), in deducing the value which was accepted as authoritative from 1820 to 1840. Taking the density of oxygen as 1·1026 times that of air, and that of carbonic anhydride as 1·524, it followed from the equality of the volumes of the two gases that 1·524 parts by weight of carbonic anhydride were made up of 1·1026 parts of oxygen and 1·524 − 1·1026 = 0·4214 part of carbon. The percentage composition of the anhydride was therefore :

Oxygen = **72·35%**
Carbon = **27·65%**

Lavoisier's combustion of charcoal.—Berzelius's numbers were in close agreement with those which had been given nearly 40 years earlier by Lavoisier ("Decomposition and Recomposition of Water," 1783; *Works*, II. 345) as a result of a careful quantitative investigation of the reduction of red lead by charcoal. In this experiment the weight of oxygen was deduced from the loss in weight of the oxide; the weight of fixed air or carbonic anhydride was calculated from its volume and density. Lavoisier found that :

	Grains.			Grains.
Red lead	3,456	gave:	Lead	3,108
Charcoal	432		Unburnt charcoal ...	342
			Fixed air	379¼
Total	3,888			3,829¼
			Loss	58¾
				3,888

The loss was due to the production of water, the composition of which was reckoned to be:

	Grains.
Oxygen	51·05
Inflammable air	7·70
	58·75

By subtracting the weight of hydrogen in the charcoal and the weight of oxygen used in burning it, these numbers give:

	Grains.
Weight of carbon burnt ... ... 432 - 342 - 7·7	= 82·30
Weight of oxygen used to burn carbon 3,456 - 3,108 - 51·05	= 296·95
Fixed air (carbonic anhydride)	= 379·25

The composition of carbonic anhydride is, therefore:

Oxygen = 72·125%, say **72·1%**
Carbon = 27·875%, „ **27·9%**

The burning of spirit of wine, of olive oil, and of a candle.—Having established the composition of carbonic anhydride, Lavoisier made use of his numbers to determine the proportions of carbon and hydrogen contained in various liquid and solid fuels. ("Combination of Oxygen with Spirit of Wine," 1784; *Works*, II. 586–600.)

The following numbers were obtained by burning a small spirit-lamp over mercury in a bell-jar filled with air[1] (Fig. 33) and supplied with oxygen from a second bell-jar inverted over water.

[1] An explosion was always produced when the attempt was made to burn the lamp in pure oxygen.

	Grains.
Spirit of Wine burnt ...	93·50
Oxygen used	110·32
Total	203·82

	Grains.
Fixed air produced, 137·09 cubic inches, weighing	95·28
Water produced (by difference)	108·54 [1]
	203·82

The fixed air contained :

	Grains.
Oxygen	68·60
Carbon	26·68
	95·28

The water contained :

	Grains.
Oxygen	92·26
Hydrogen	16·28
	108·54

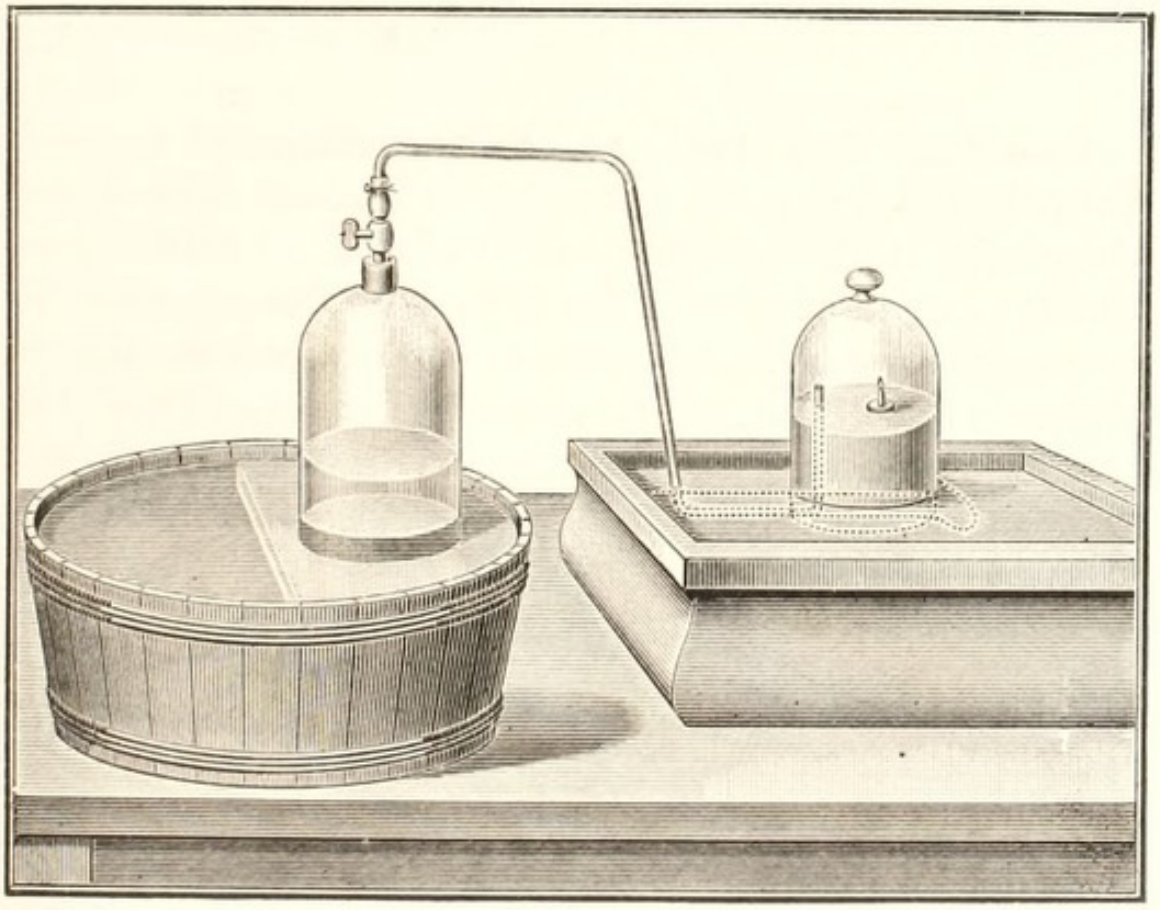


FIG. 33.—LAVOISIER'S APPARATUS FOR THE COMBUSTION OF SPIRIT OF WINE.

The oxygen in these compounds amounted to 160·86 grains, whereas only 110·32 grains had been supplied, the spirit of wine must therefore have contained :

[1] This number agreed closely with the observation that 18 ounces of water could be condensed from the products of combustion of 16 ounces of spirit.

Oxygen	50·54 grains	=54·1%[1]
Carbon	26·68 ,,	=28·5%
Hydrogen	16·28 ,,	=17·4%

or, as Lavoisier preferred to express it:

Carbon	26·68 grains	=28·5%
Hydrogen	7·36 ,,	= 7·9%
Water	59·46 ,,	=63·6%

Similar combustions of olive oil and of candle-wax gave

	Oil.	Wax.
Carbon	79%	82·3%
Hydrogen	21%	17·7%

Both substances contain oxygen, out the quantity was not sufficient to be detected by Lavoisier's method of analysis.

Dumas and Stas (1841) on the composition of carbonic anhydride.—About the year 1840 it became evident that the numbers for the composition of carbonic anhydride, given twenty years previously by Berzelius and Dulong, must be erroneous, since careful analyses of compounds rich in carbon often gave totals exceeding 100%. Thus two typical HYDROCARBONS (*i.e.* compounds of hydrogen and carbon) extracted from coal-tar gave the following figures (Stas's *Works*, I. 270 and 275):

	Naphthalene.	Benzene
Hydrogen	6·24%	7·70%
Carbon...	95·40%	93·53%
	101·64	101·23

In these substances the proportion of hydrogen was so small that no large error could be produced by uncertainty as to the weight of water produced, or the weight of hydrogen which it contained. The excess above 100 per cent. could only be due to over-estimating the proportion of carbon in the carbonic anhydride formed on combustion. To test

[1] The numbers now accepted for pure alcohol are: Oxygen 34·8%, Carbon 52·2%, Hydrogen 13·0%; Lavoisier's spirit of wine evidently contained about half its weight of water.

this, Dumas and Stas carried out in 1841 an elaborate investigation of the weight of carbonic anhydride produced by the combustion of different forms of carbon (*Ann. de Chimie*, 1841, **1**, 5—111; Stas's *Works*, I. 235—287).

For their combustion they used (1) Natural graphite, freed from mineral matter by igniting with potash, extracting with acids, and finally heating to a white heat in a current of chlorine gas (Chap. XI) during twelve to fifteen hours. (2) Artificial graphite separated from cast iron and purified in the same way. (3) Diamonds, of which 10 to 12 grams were burnt; these were used mainly because the purified graphite had become so porous that it was difficult to weigh it free from condensed air and moisture.[1]

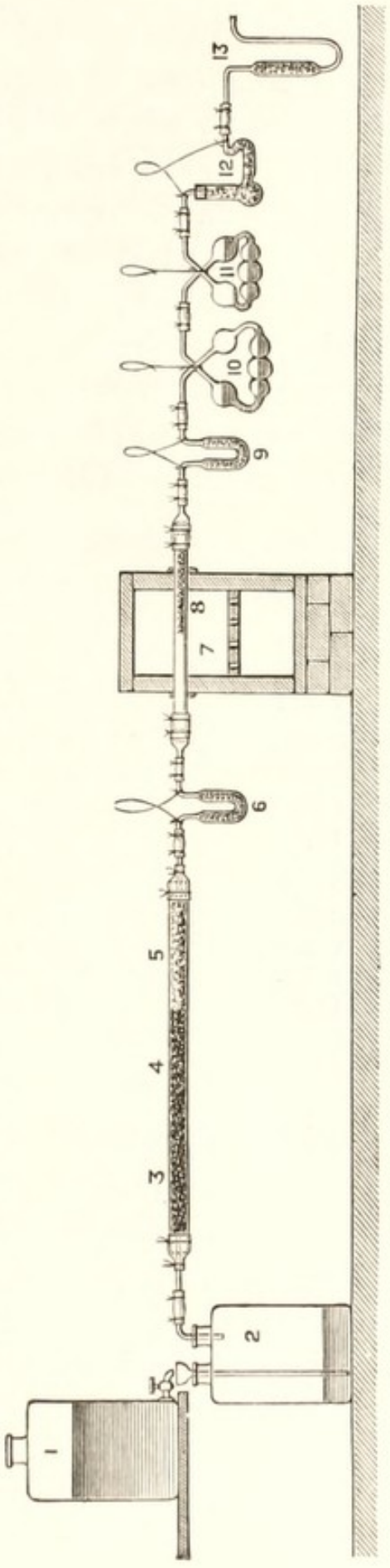


FIG. 34.—DUMAS AND STAS'S APPARATUS FOR THE COMBUSTION OF GRAPHITE AND OF DIAMONDS.

1, Alkaline water; 2, Oxygen; 3, Alkaline pumice; 4, Fragments of potash; 5, Sulphuric acid; 6, Acid pumice; 7, Platinum boat 8, Oxidised copper turnings; 9, Acid pumice; 10 and 11, Liebig apparatus; 12, Alkaline pumice and powdered potash; 13, Aspirator protected by potash.

[1] The property, which charcoal possesses in a remarkable degree, of condensing gases in its pores, was discovered by Fontana in 1777 and has been used largely in recent work.

The combustion was carried out in a current of oxygen, which was freed from carbonic anhydride by means of potash and dried by means of sulphuric acid. The carbon, contained in a platinum boat, was burnt in a porcelain tube heated strongly in a furnace (Fig. 34). The carbonic anhydride was absorbed by potash and weighed directly, with the help of absorption-apparatus devised by Liebig. A small tube containing sulphuric acid was provided to collect any water that might be produced, but in none of the experiments was any gain in weight observed. The numbers obtained were as follows (*Works*, I. p. 252):

	Carbon.	Carbonic Anhydride.	Percentage of Carbon.
	1·000	3·671	27·24
Natural	0·998	3·660	27·27
Graphite	0·994	3·645	27·27
	1·216	4·461	27·26
	1·471	5·395	27·27
	0·992	3·642	27·24
Artificial	0·998	3·662	27·26
Graphite	1·660	6·085	27·28
	1·465	5·365	27·31
	0·708	2·598	27·25
	0·864	3·1675	27·27
Diamond	1·219	4·465	27·30
	1·232	4·517	27·26
	1·375	5·041	27·28
		Mean	27·27

The composition of carbonic anhydride was therefore:

Oxygen = **72·73%**
Carbon = **27·27%**

The reduction in the percentage of carbon from 27·67 to 27·27 provided the correction that was needed in the analysis of the hydrocarbons, which now gave:

Naphthalene	H	6·24	C	94·02	Total	100·26
	H	6·30	C	93·80	,,	100·10
	H	6·29	C	93·86	,,	100·15
	H	6·31	C	93·84	,,	100·15
Benzene	H	7·7	C	92·2	,,	99·9

Stas's analysis of carbonic oxide (1849).—Eight years later, in 1849, Stas (*Works*, I. 287–308), carried out a masterly analysis of carbonic oxide, in which 128·367 grams of oxygen were used in eight experiments to burn 224·683 grams of the gas to 353·050 grams of carbonic anhydride. The experimental methods were very similar to those used by Dumas to determine the composition of water. Thus, instead of using free oxygen to burn the gas, the oxygen was supplied by copper oxide which was reduced to copper by heating it in a current of carbonic oxide. The gas was not weighed directly : its weight was calculated from the difference between the weight of oxygen used and the weight of carbonic anhydride produced. The carbonic anhydride was absorbed and weighed in combination with potash.

The chief difficulty of the experiment was to provide a supply of carbonic oxide free from carbonic anhydride, oxygen, water, hydrogen and other inflammable gases. The gas was prepared by heating oxalic acid with oil of vitriol : the product, a mixture of carbonic oxide and carbonic anhydride, was passed through potash into a reservoir holding eighty to ninety litres (Fig. 35). From this reservoir the gas was displaced, not by water, but by an alkaline solution capable of absorbing both oxygen and carbonic anhydride.[1] The chief means of removing oxygen, consisted, however, in passing the carbonic oxide through a heated tube containing copper, in which the free oxygen would have every opportunity of being converted into carbonic anhydride. Both before and after passing through this tube the gas was freed from carbonic anhydride and from water by contact with potash and sulphuric acid. The gas prepared in this way contained a little nitrogen but was practically free from all other impurities.

[1] A 5% solution of stannous oxide in potash, made with boiled water, was used.

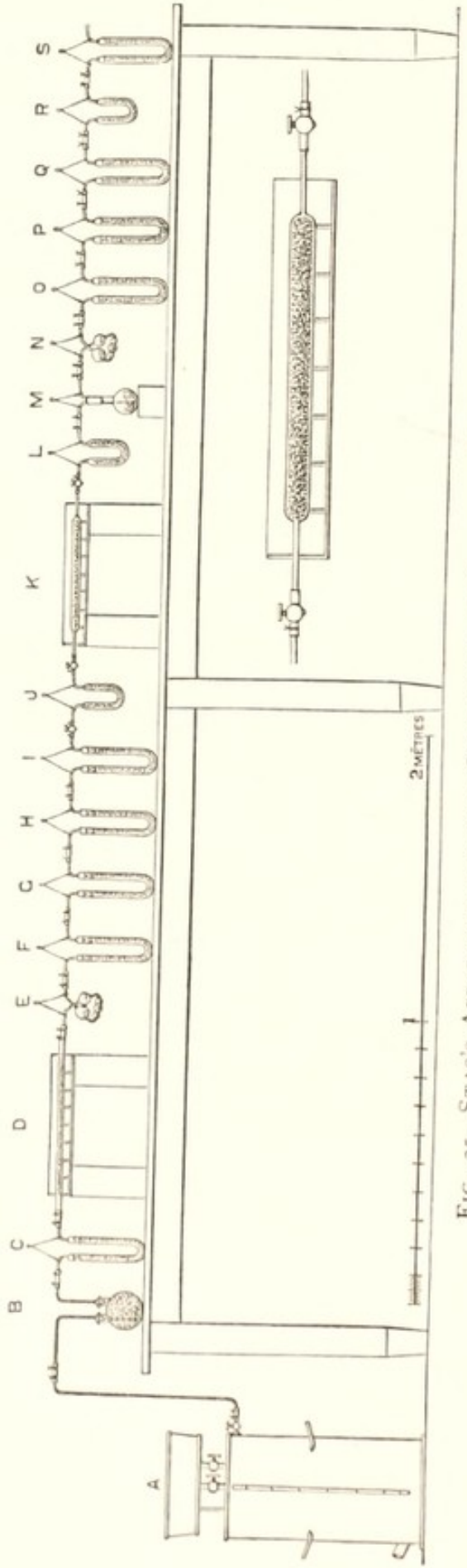


FIG. 35—STAS'S APPARATUS FOR THE COMBUSTION OF CARBONIC OXIDE.

A, Gasometer (80–90 litres) containing carbonic oxide over an alkaline solution of stannous chloride; B, Potash on pumice; C, Sulphuric acid on pumice; D, Glass tube containing hot copper turnings; E, Aqueous potash; F, G, Potash on pumice; H, Powdered potash; I, Sulphuric acid on pumice; J, Guard-tube (with taps) containing sulphuric acid on pumice (weighed); K, Glass tube (50 cm. long, 2½ cm. diameter) containing copper oxide (weighed); L, Drying tube (weighed); M, Aqueous potash in bulb (weighed); N, Liebig potash-bulbs (weighed); O, Potash on pumice (weighed); P, (*a*) Potash on pumice (*b*) Fused potash in powder on pumice to exclude moisture from air. Q, Sulphuric acid on pumice (weighed); R, Guard-tube containing sulphuric acid on pumice (weighed); S, Sulphuric acid

The glass tube K is shown on a larger scale as an inset.

In these experiments, as in those of Dumas and of Dumas and Stas, the purifying agents were distributed over pumice stone, or broken glass, or were used in a granular form in order to secure ample contact with the gas. The air in the pumice stone was removed by repeatedly exhausting the apparatus and filling it again with pure carbonic oxide.

The copper oxide, prepared by calcination, was contained in a glass tube drawn out at each end. Taps were provided so that the tube could be exhausted before weighing. During the reduction the tube was heated quite gently over charcoal. In a series of blank experiments the tube was found to vary in weight by only a milligram on a total of 540 grams when heated, provided that some hours were allowed to elapse before re-weighing.

The gas escaping from the copper oxide tube was passed through sulphuric acid to absorb any water that might be formed; the quantity collected was usually about ten milligrams. It then passed into a bulb containing potash, where most of the carbonic anhydride was absorbed. A set of Liebig bulbs filled with potash and three U-tubes, the last filled with solid potash,[1] were used to absorb the remainder of the gas. The weight of carbonic anhydride was corrected for the buoyancy of the air displaced by the increased bulk of the potash after absorbing the gas.

The composition of carbonic oxide was shown by these experiments to be:

Oxygen	57·16%
Carbon	42·84%

C. Marsh Gas and Olefiant Gas.

The burning of inflammable gases.—The existence of inflammable gases other than those prepared by the action of metals on the acids had been known from very early

[1] The solid potash served to prevent the loss of moisture from the absorbing apparatus.

times and was clearly recognised in van Helmont's work on "gas pingue." But no definite chemical investigation of these gases was made until the composition of water was determined in 1781. It was then proved clearly by the work of Cavendish, of Lavoisier, and of Monge that the gas from metals and acids gave rise to water as *the only product of combustion*, and in particular that no fixed air was produced. Every other inflammable gas that was examined differed from hydrogen in giving rise to larger or smaller quantities of fixed air. Water was also produced in nearly every case, but Cruikshank in 1801, and Désormes and Clément in the same year, succeeded in preparing carbonic oxide so far free from hydrogen that no water was produced when it was burned.

Apart from hydrogen and carbonic oxide, every inflammable gas gave both water and fixed air, and was therefore composed of carbon and hydrogen, with or without oxygen. Gases of this kind were prepared by heating wood, charcoal, and oil, by passing spirit of wine through a red hot tube, and so forth. They were examined by Cruikshank, by Berthollet, and by a number of other workers, who determined their relative densities, and their behaviour when exploded with oxygen in Volta's eudiometer, as regards (1) the volume of oxygen used, (2) the contraction after explosion, and (3) the volume of carbonic anhydride produced. But as all the gases examined were mixtures, no concordant results could be obtained.

Olefiant gas or heavy carburetted hydrogen.—The first gaseous compound of carbon and hydrogen to be prepared and examined in a pure state was OLEFIANT GAS. This gas was investigated in 1794 by a group of Dutch chemists ("Researches on the different kinds of gas which are obtained by mixing concentrated sulphuric acid with alcohol," by J. R. Deiman, A. Paets van Troostwyck, N. Bondt and A. Lauwerenburgh, *Jour. de Physique*, 1794,

45, 178–191). They proved that it was a HYDROCARBON, *i.e.*, a compound of carbon and hydrogen only. They distinguished it as "oily carburetted hydrogen," now OLEFIANT GAS, from the property which it possessed of combining with chlorine gas (Chapter XI) to form an oil known as DUTCH LIQUID. The gas is now called ETHYLENE, and the liquid ETHYLENE CHLORIDE.

The gas was also investigated by **Dalton**, who describes it as follows:

"Olefiant gas may be produced by mixing 2 measures of sulphuric acid with 1 measure of alcohol; this mixture in a gas bottle must be heated to about 300° [Fahrenheit] by a lamp, when the liquid exhibits the appearance of ebullition, and the gas comes over: it should be passed through water, to absorb any sulphurous acid which may be generated."

"This gas is unfit for respiration, and extinguishes flame, but it is highly combustible. . . . Olefiant gas burns with a dense, white flame. It explodes with uncommon violence when mixed with oxygen and electrified. . . .: unless a great excess of oxygen be used, the charcoal is partly thrown down, and it makes the gas turbid after explosion; the result in this case affords less carbonic acid than is due" (*New System*, 1810, II. 438 and 440).

Composition of olefiant gas.—Dalton investigated the volumetric relationships of the gas. He showed that it combined with its own volume of chlorine (*loc. cit.*, p. 439). When exploded with an excess of oxygen, some carbon remained unburnt, but a large contraction occurred, the proportional volumes being (*loc. cit.*, p. 440):

olefiant gas + oxygen → carbonic anhydride + water;
100 *vols.* 270 to 300 *vols* 185 or 190 *vols.*

or roughly

1 *vol.* <3 *vols.* <2 *vols.*

When mixed with only its own volume of oxygen and exploded, an expansion was produced instead of a contrac-

tion (*loc. cit.*, p. 442), the carbon being burnt to carbonic oxide, and the hydrogen liberated, thus :

olefiant gas	+	oxygen	⟶	carbonic oxide	+	hydrogen
1 *vol.*		1 *vol.*		< 2 *vols.*		< 2 *vols.*

When sparked alone the gas was decomposed into carbon and twice its volume of hydrogen, thus :

olefiant gas	⟶	carbon	+	hydrogen
1 *vol.*				2 *vols.*

Olefiant gas was thus shown to contain twice its volume of hydrogen, and enough carbon to give twice its volume of carbonic oxide, or of carbonic anhydride.

Marsh gas or light carburetted hydrogen.—The formation of an inflammable gas during the decay of vegetable and animal matter was known from classical times, and was noted by van Helmont, who described all such gases as "gas pingue."

The first accurate work on the subject was that of **Volta** who showed in 1776 (*Letters on the Inflammable Air of Marshes*), that whilst the gas from metals and acids required for its combustion twice its volume of air, the MARSH GAS collected from putrid marshes required from ten to twelve volumes. The gas was also examined about the same time by Priestley in England and by Franklin in America. It was investigated very carefully in 1804, by **Dalton,** who gave to it the name CARBURETTED HYDROGEN. Dalton describes its preparation and properties as follows :

"It was in the summer of 1804, that I collected at various times, and in various places, the inflammable gas from ponds ; this gas I found always contained some traces of carbonic acid and a portion of azote ; but when cleared of these, it was of a uniform constitution. After due examination, I was convinced that just one half of the oxygen expended in its combustion, in Volta's eudiometer, was applied to the

hydrogen, and the other half to the charcoal. This leading fact afforded a clue to its constitution."

"The properties of carburetted hydrogen are:

"It is unfit for respiration and for the support of combustion.

"Its specific gravity when pure, from my experience, is very near 0·6.

"Water absorbs $\frac{1}{27}$ of its bulk of this gas." (*New System*, 1810, II. 445–446.)

Olefiant gas, by contrast, had a specific gravity 0·9 relatively to air, and was absorbed by water to the extent of $\frac{1}{8}$ of its bulk.

Composition of marsh gas.—Dalton showed that of the two volumes of oxygen required for the complete combustion of marsh gas, one was required to burn the carbon, giving rise to an equal volume of carbonic anhydride, whilst the other was used for the combustion of the hydrogen. Marsh gas, therefore, contained, like olefiant gas, twice its volume of hydrogen; but the carbon was only sufficient to produce an equal volume (instead of two volumes) of carbonic anhydride or of carbonic oxide. This view of the composition of the gas was confirmed by sparking it, when the carbon was deposited and two volumes of hydrogen were set free. Dalton writes:

"If 100 measures of carburetted hydrogen be put to upwards of 200 of oxygen, and fired over mercury, the result will be a diminution of near 200 measures, and the residuary 100 measures will be found to be carbonic acid."

"When a portion of carburetted hydrogen gas is electrified for some time, it increases in volume, in the end almost exactly doubling itself; at the same time a quantity of charcoal is deposited. The whole of the gas is then found to be pure hydrogen" (*ibid.* p. 447).

When exploded with an equal volume of oxygen the carbon was burnt to carbonic oxide and half the hydrogen was

burnt to water, leaving a gaseous residue consisting of hydrogen and carbonic oxide in equal proportions.

The contrast between marsh gas and olefiant gas is shown by the equations:

$$\begin{cases} \underset{1\ vol.}{\text{marsh gas (sparked)}} \longrightarrow \text{carbon} + \underset{2\ vols.}{\text{hydrogen}} \\ \underset{1\ vol.}{\text{olefiant gas (sparked)}} \longrightarrow \text{carbon} + \underset{2\ vols.}{\text{hydrogen}} \end{cases}$$

$$\begin{cases} \underset{1\ vol.}{\text{marsh gas}} + \underset{2\ vols.}{\text{oxygen}} \longrightarrow \underset{1\ vol.}{\text{carbonic anhydride}} + \text{water} \\ \underset{1\ vol.}{\text{olefiant gas}} + \underset{3\ vols.}{\text{oxygen}} \longrightarrow \underset{2\ vols.}{\text{carbonic anhydride}} + \text{water} \end{cases}$$

Coal gas.—The inflammable COAL GAS obtained by distilling coal consists largely of marsh gas. Dalton, in describing the properties of marsh gas, writes:

"This gas is obtained nearly pure also by distilling pit-coal with a moderate red heat. It is now largely used as a substitute for lamps and candles, under the name of *coal gas*. According to Dr. Henry's analysis, coal gas does not usually contain more than 4 or 5 per cent. of carbonic acid, sulphuretted hydrogen, and olefiant gas. The rest is principally carburetted hydrogen, but mixed with some atoms of carbonic oxide and hydrogen. The last portion of gas driven off from pit-coal, seems to be entirely carbonic oxide and hydrogen. The distillation of wood and of moist charcoal, and many other vegetable substances, produces carburetted hydrogen, but highly charged with carbonic acid, carbonic oxide and hydrogen; the two last gases always appear exclusively at the end of the process" (*ibid.* pp. 445–446).

SUMMARY AND SUPPLEMENT.

A. CARBONIC OXIDE.

Lassone, in 1776, prepared an inflammable oxide of carbon by heating Prussian blue, and by heating zinc oxide with charcoal,

$$ZnO + C \longrightarrow Zn + CO.$$

It differed from hydrogen in that it burned with a beautiful blue flame, and could not be detonated when mixed with air or oxygen. The same gas was prepared by **Priestley** in 1783 by heating smithy scale with charcoal

$$Fe_3O_4 + 4C \rightarrow 3Fe + 4CO.$$

Cruikshank, in 1801, prepared the gas, free from hydrogen, by heating carbonated baryta (barium carbonate), or chalk (calcium carbonate), with iron plates,

$$4BaCO_3 + 3Fe \rightarrow 4BaO + 4CO + Fe_3O_4,$$
$$4CaCO_3 + 3Fe \rightarrow 4CaO + 4CO + Fe_3O_4.$$

He showed that when exploded with oxygen in Volta's eudiometer it combined with half its volume of oxygen and gave an equal volume of carbonic anhydride; he therefore regarded it as a lower oxide of carbon and called it "gaseous oxide of carbon," now carbonic oxide,

$2CO$	+	O_2	→	$2CO_2$
Carbonic oxide		Oxygen		Carbonic anhydride.
1 *vol.*		$\frac{1}{2}$ *vol.*		1 *vol.*

Désormes and Clément, in 1801, proved by similar experiments that Lassone's inflammable gas was an oxide of carbon which gave an equal volume of carbonic anhydride but no water when burnt. They prepared it by the action of charcoal on carbonated baryta,

$$BaCO_3 + C \rightarrow BaO + 2CO,$$

a refractory carbonate which could not be decomposed by heat alone. They could not prepare it by direct combustion of charcoal in air or oxygen, but found that fixed air could be reduced to carbonic oxide by red-hot charcoal,

$$CO_2 + C \rightarrow 2CO.$$

They also prepared a mixture of carbonic oxide and hydrogen by the action of red-hot charcoal on steam,

$$H_2O + C \rightarrow H_2 + CO.$$

B. Composition of the Two Oxides of Carbon.

Priestley (1772), and **Lavoisier** (1772), showed that carbon burns in air or oxygen without altering the volume of the gas,

$$C + O_2 \rightarrow CO_2$$
$$1\ vol.\quad 1\ vol.$$

This fact was used by **Berzelius and Dulong** (1820) to determine the composition of carbonic anhydride by comparing its density with that of oxygen. The percentage of carbon (27·65%) agreed with an early determination by Lavoisier (27·9%), but was reduced to **27·27%** by the classical experiments of **Dumas and Stas** (1841), the details of which should be noted carefully. **Cruikshank** (1801), **Désormes and Clément**, and **Berthollet** measured the changes of volumes produced by exploding carbonic oxide with oxygen; they found that $\frac{1}{2}$ vol. of oxygen was used and gave 1 vol. of carbonic anhydride.

$$CO + \tfrac{1}{2}O_2 \rightarrow CO_2$$
$$1\ vol.\quad \tfrac{1}{2}\ vol.\quad 1\ vol.$$

Since carbonic anhydride contains an equal volume of oxygen carbonic oxide contains half this volume; the volume of gas is therefore doubled when carbonic anhydride is reduced by carbon to carbonic oxide,

$$CO_2 + C \rightarrow 2CO$$
$$1\ vol.\qquad 2\ vols.$$

Stas, in 1849, determined the gravimetric composition of carbonic oxide by passing the gas over weighed copper oxide and weighing the carbonic anhydride produced,

$$CO + CuO \rightarrow Cu + CO_2$$

The precautions taken to prepare a pure gas should be noted. The proportion of carbon was found to be **57·16%**.

C. Marsh Gas and Olefiant Gas.

Marsh gas (methane, CH_4) was discovered by **Volta** in 1776.

Olefiant gas (ethylene, C_2H_4) was prepared during the alchemistic period by the action of oil of vitriol on alcohol,

$$C_2H_6O - H_2O \rightarrow C_2H_4$$
alcohol – water → ethylene

It was shown to be a **hydrocarbon** by a group of Dutch chemists who called it "oily carburetted hydrogen" (olefiant gas), from the property which it possesses of combining with chlorine to form an oily liquid,

$$C_2H_4 + Cl_2 \rightarrow C_2H_4Cl_2$$
ethylene + chlorine → ethylene chloride

The volumetric relationships of these two gases were studied by Dalton. They are as follows :

By *sparking*, carbon deposited, hydrogen (2 vols.) set free.

$$CH_4 \rightarrow C + 2H_2$$
1 *vol.* 2 *vols.*

$$C_2H_4 \rightarrow 2C + 2H_2$$
1 *vol.* 2 *vols.*

By explosion with excess of oxygen

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$
marsh gas + oxygen → carbonic anhydride + water
1 *vol.* 2 *vols.* 1 *vol.* *Contraction* 2 *vols.*

$$C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O$$
ethylene + oxygen → carbonic anhydride + water
1 *vol.* 3 *vols.* 2 *vols.* *Contraction* 2 *vols.*

When exploded with less oxygen

$$CH_4 + O_2 \rightarrow CO + H_2 + H_2O$$
marsh gas + oxygen → carbonic oxide + hydrogen + water
1 *vol.* 1 *vol.* 1 *vol.* 1 *vol.*

$$C_2H_4 + O_2 \rightarrow 2CO + 2H_2$$
olefiant gas + oxygen → carbonic oxide + hydrog
1 *vol.* 1 *vol.* 2 *vols.* 2 *vols.*
Expansion 2 *vols.*

CHAPTER IX

SULPHUR AND PHOSPHORUS

A. Sulphur, Sulphuric Acid, and the Sulphates.

Native sulphur.—The inflammable mineral known as sulphur, or brimstone (Fig. 36), has been a familiar substance from very early times. Its occurrence in the neighbourhood of volcanoes, and the pungent smell which is produced when it is burnt, caused it to be regarded during many centuries as a symbol of the powers of evil. In alchemistic times it acquired a new significance as one of three principles, *mercury*, *sulphur*, and *salt*, which took the place of the four elements, *earth*, *air*, *fire*, and *water*, of the classical writers. As representing the principle of inflammability, sulphur was supposed to be present in all combustible substances, just as mercury was supposed to be present in all metals; much of the early work of Robert Boyle was devoted to proving the falseness of this assumption.

Sulphur from pyrites.—Sulphur is present in combination with iron in the mineral pyrites or marcasite (Figs. 6, 7, 8, pp. 8—9), and can be separated from it in part by the action of heat. This method was used in the middle ages for the artificial preparation of sulphur; thus Mayow states that "Vitriols are produced from the stone . . . called Marchasite, and from it on the application of fire the flowers of common sulphur are elicited in considerable abundance" (A.C.R. XVII. 28). The presence

of sulphur in the mineral is also shown by the pungent odour of burning sulphur which is produced when pyrites is burnt in a current of air ; at the same time the brilliant metallic nodules of the mineral are converted into a red rust-like ash or calx.

Sulphur present in oil of vitriol.—The presence of sulphur in oil of vitriol was also recognised at an early date. Basil Valentine described a method of preparing the

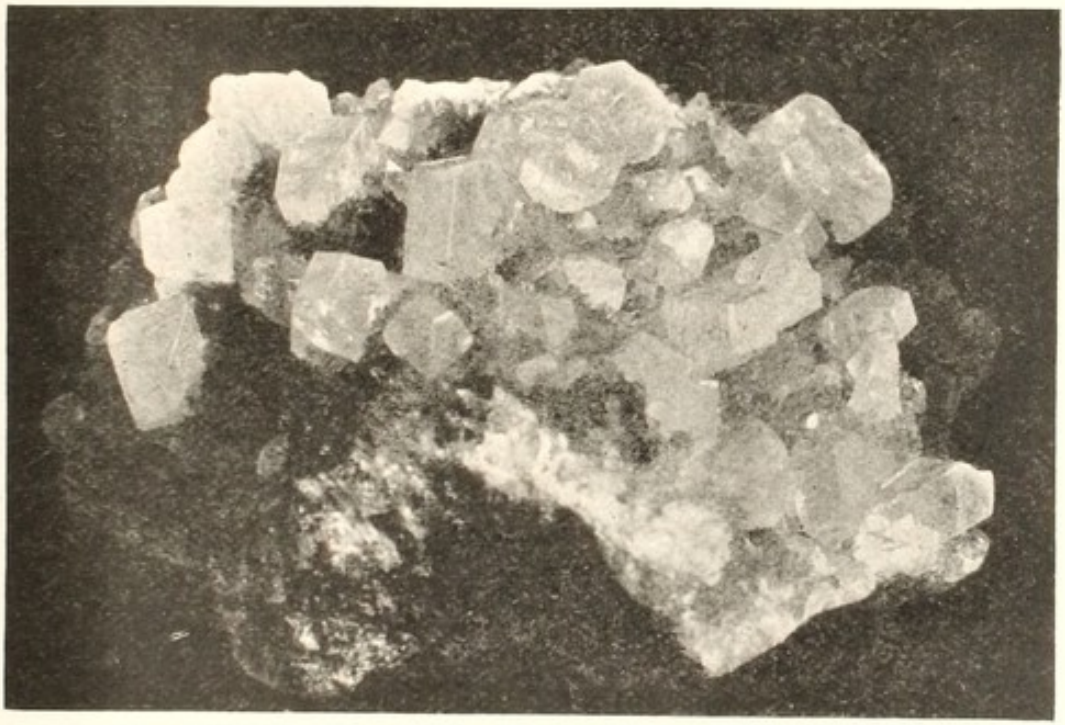


FIG. 36—RHOMBIC CRYSTALS OF SULPHUR. British Museum (Natural History).

acid from sulphur with the aid of saltpetre. Conversely, Glauber was able to prepare "flowers of sulphur" from the acid by heating its salts with coal, extracting with water, and acidifying the solution. On account of this relationship the French chemists in 1787 gave to oil of vitriol the name SULPHURIC ACID, whilst its salts were described as SULPHATES.

Stahl (1702) prepares a volatile acid from burning sulphur.—The product formed by burning sulphur in air is a pungent gas, which dissolves readily in water to a feebly

acid solution and combines with alkalis to form salts. Stahl (1702) describes the process of collecting the acid fumes with the help of linen or tow drenched in alkali; he states that the acid vapour is set free again by the action of oil of vitriol, and that it is the weakest of the mineral acids, though stronger than vinegar. In many respects the "sulphurous acid" from burning sulphur resembles the "carbonic acid" from burning charcoal; but it differs in its obvious acidity, in the greater solubility of the gas in water, and in its power of bleaching coloured substances, such as red rose leaves.

Stahl showed that the salts of the "volatile" sulphurous acid, prepared from burning sulphur, could be converted into salts of the "fixed" oil of vitriol by exposing them to the air. A similar experiment is described by Cavendish (A.C.R. III. 9–11), who collected the fumes of burning sulphur in milk of lime, obtaining a soluble salt which was converted by exposure to the air into selenite or gypsum, the ordinary sulphate of lime. In order to distinguish it from sulphuric acid, the French chemists described Stahl's volatile acid as SULPHUROUS ACID, and its salts as SULPHITES. The name sulphurous acid is, however, now restricted to aqueous solutions of the gas, the pungent gas itself being distinguished as SULPHUROUS ANHYDRIDE.

Priestley (1774) prepares a soluble gas from oil of vitriol.—On account of its great solubility, the gas produced by burning sulphur in air cannot be collected over water. It was therefore not isolated until Priestley had developed Cavendish's method of using mercury to confine those gases which were too soluble to be stored over water.

Priestley prepared the gas in 1774 by heating oil of vitriol with olive oil, and called it VITRIOLIC ACID AIR. He also attempted, but without success, to separate it from oil of vitriol by heat alone. In the course of this experiment some mercury was drawn back into the hot acid,

thereby disclosing an excellent method of separating the gas.

Priestley describes his observations as follows:

"When . . . I got glass phials with ground stopples, perforated, and drawn out into tubes, such as are represented [in Fig 37], I found that heating the oil of vitriol in them produced no air whatever."

"But though I got no air from the oil of vitriol by this process, air was produced at the same time in a manner that I little expected, and I paid pretty dearly for the discovery it occasioned. Despairing to get any air from the longer application of my candles, I withdrew them; but before I could disengage the phial from the vessel of quicksilver, a little of it passed through the tube into the hot acid; when, instantly, it was all filled with dense white fumes, a prodigious quantity of air was generated, the tube through which it was transmitted was broken into many pieces (I suppose by the heat that was suddenly produced) and part of the hot acid being spilled upon my hand, burned it terribly, so that the effect of it is visible to this day."

FIG. 37—STOPPERED FLASK USED BY PRIESTLEY IN PREPARING "VITRIOLIC ACID AIR" (Sulphur Dioxide).

"Not discouraged by the disagreeable accident above-mentioned, the next day I put a little quicksilver into the phial with the ground stopple and tube, along with the oil of vitriol; when, long before it was boiling hot, air issued plentifully from it; and being received in a vessel of quicksilver, appeared to be genuine vitriolic air, exactly like that which I had procured before; being readily imbibed by water, and extinguishing a candle in the same manner as the other had done."

"Copper, treated in the same manner, yielded air very freely, with about the same degree of heat that quicksilver had required, and the air continued to be generated with very little application of more heat. The whole produce

was vitriolic acid air, and no part of it inflammable" (*Experiments on Air*, II. 16–20).

On account of its methods of preparation, Priestley concluded that the volatile sulphurous acid was a "phlogisticated," or reduced, oil of vitriol.

Priestley describes the properties of vitriolic acid air.—Priestley found that "vitriolic acid air," prepared by the action of heat on a mixture of mercury and oil of vitriol, resembled closely the "marine acid air" which he had prepared from muriatic acid by the action of heat alone. Both gases were intensely soluble in water,[1] and each condensed to a white salt when mixed with the "alkaline air" ammonia. The solution of "vitriolic acid air" in water was, however, only weakly acid and the gas could be expelled by gentle heat, or merely by exposure to the air; in these respects the properties of the solution were in marked contrast with those of muriatic acid and of oil of vitriol. Priestley calls attention to this contrast as follows:

"Water being admitted to the vitriolic acid air absorbed it about as readily as the marine acid air; and by its union with it must have formed the volatile or sulphureous acid of vitriol" (*ibid.* p. 7).

"Water impregnated with marine acid air is, in all respects, the very same thing with the common spirit of salt, except that this acid may be made considerably stronger in this manner than any spirit of salt made in the common way, and that it has generally less colour. But water impregnated with vitriolic acid air differs most remarkably from oil of vitriol. Its acidity is now become trifling to what it was; and from being the most fixed, and the strongest, it is now become the weakest, and the most volatile of all acids; the smell of it being intolerably pungent, and almost the whole of it evaporating when it is exposed to the open air" (*Experiments on Air*, 1777, III. 272).

[1] "Water absorbs about 20 times its bulk of this gas at a mean temperature, according to my experience" (Dalton, *New System*, II. 389).

The marked difference between vitriolic acid air and oil of vitriol was attributed by Priestley to the fact that the oil of vitriol had "combined with phlogiston." Lavoisier, however, showed that the change was due to removal of oxygen from the oil of vitriol.

Priestley converts "vitriolic acid air" into oil of vitriol.—Having prepared solutions of "vitriolic acid air," Priestley showed that they resembled oil of vitriol in their power of dissolving metallic zinc (*ibid.* p. 274). He also found that the volatile or "phlogisticated" acid could be reconverted into ordinary oil of vitriol by exposure to air, the acid being held in solution during the experiment by combination with alumina.

"The volatile vitriolic acid, though produced from the fixed vitriolic acid, is very considerably different from it, especially as it may be dislodged from its basis by the vitriolic acid, just as other weaker acids are dislodged by those that are thence called the stronger. But that volatile vitriolic acid is capable, however, of being brought back to the state of the common vitriolic acid, and becoming the same thing that it originally was, several experiments shew. At the time of my last publication I had found that it was capable of dissolving iron and zinc, and of producing inflammable air, which is the property of oil of vitriol: but I had a more decisive proof of the same thing when, to water saturated with vitriolic acid air, I had, for another purpose, put some earth of alum till it was saturated. For, after six months, in which this solution had been exposed in an open phial, and one third of it was evaporated, I observed many transparent crystals formed at the bottom of the phial, as well as an incrustation on the sides of the phial above the surface of the liquor. These crystals were all triangular, of a considerable thickness, connected with each other, and when examined appeared to be *alum*, which is known to be the saline substance formed by the same earth, and the proper vitriolic acid" (*Experiments and Observations*, 1779, IV. 122–123).

He also showed that sulphur could be prepared by heating the solution in a sealed tube during a period of several months (*ibid.* 124–129).

Composition of sulphurous anhydride.—It was observed by Priestley in 1772 (*Experiments on Air*, I. 46) and confirmed by Dalton (*New System*, II. 391–392) that when sulphur is burnt in air over mercury "no material change of bulk is effected in the gas by the combustion; and this is also remarked in the analogous combustion of charcoal." The pungent gas, which is now described as SULPHUROUS ANHYDRIDE, thus resembles carbonic anhydride, in that it contains its own volume of oxygen.

From this observation Dalton was able to calculate the composition of the gas by weight. He had found its density relatively to air to be 2·3, that of oxygen being 1·1. The gas was therefore twice as heavy as oxygen and contained approximately equal weights of the two constituents.

The fact that sulphur gained in weight when burnt was announced to the French Academy by Lavoisier in 1772 (*Works*, II. 103) as the first of his great discoveries in reference to combustion.

Lavoisier's experiments on the composition of sulphuric acid.—Lavoisier recognised that sulphuric acid must be regarded as a compound of sulphurous anhydride with oxygen and with water. He attempted in 1777 (*Works*, II. 194) to determine the proportions of the two gases by acting on the acid with mercury, and collecting the gas liberated (1) during this action and (2) during the decomposition of the sulphate of mercury into sulphurous anhydride, oxygen, and mercury. The experiment was not successful because a part of the sulphate of mercury sublimed without decomposition, but it gave clear qualitative proof that "volatile sulphurous acid is a vitriolic acid partially deprived of oxygen."

Dalton (*New System*, II. 389-390) also attempted to determine the proportions in which the two gases combine, by uniting them over mercury in presence of water or with the help of electric sparks. In the former case the action was incomplete at the end of twelve days; in the latter case he found that "the mercury becomes oxidised, and consequently liable to form a union with either of the acids."

Gay-Lussac's analysis of sulphuric acid (1807).—A successful analysis of sulphuric acid was made by Gay-Lussac in 1807 in the course of an investigation on the "Decomposition of the Sulphates by Heat" (*Mem. Soc. d'Arcueil*, I. 215—251). He found that many of the sulphates could be decomposed; some were decomposed easily, giving as products the oxide of the metal and white fumes of SULPHURIC ANHYDRIDE; others, requiring a higher temperature for decomposition, gave off a gaseous mixture of sulphurous anhydride and oxygen, leaving behind as before a residue of oxide or earth. The quantitative analysis of sulphuric anhydride was effected by decomposing alum, the gases from the decomposition being collected over mercury and analysed by absorption with potash.

Gay-Lussac writes:

"The first sulphate that I heated was sulphate of copper. It first liberated water; but as soon as the retort was red-hot, white vapours of sulphuric acid[1] were produced, which were accompanied by a nebulous gas, smelling strongly of sulphurous acid, and in which after being washed a match inflamed several times. This gas was then a mixture of sulphurous acid[1] gas and oxygen . . . The two gases were in volume almost in the ratio 2 to 1; but I will return later to the exact determination of this ratio, and the way in which the sulphuric acid decomposes" (pp. 217—218).

"Sulphate of iron undergoes the same decomposition by

[1] In this passage the names "sulphurous acid" and "sulphuric acid" are used to describe the anhydrides.

heat as sulphate of copper. The results are only modified by this circumstance, that since the metal may take up a higher degree of oxidation, there is liberated relatively more sulphurous acid[1] than oxygen" (p. 219).

"I took advantage of this decomposition of the sulphates to determine the quantity of oxygen which must be added to sulphurous acid to convert it into sulphuric acid. For this purpose, I distilled over mercury some burnt alum, the base of which neither produces nor absorbs any gaseous principle. I collected gas at different stages of the distillation; and after taking a carefully measured volume, I washed it with caustic potash and measured the residues. I thus found that 100 parts

Of the 1st	portion	contained	32·33 of oxygen.
,, 2nd	,,	,,	33·23
,, 3rd	,,	,,	32·53
,, 4th	,,	,,	32·64
Mean	.	.	32·68

Since the proportion of the two gases was the same throughout the whole course of the operation, one must conclude that the decomposition of sulphuric acid by heat always takes place in the same way, and that sulphurous acid absorbs almost 0·5 of oxygen in passing to the state of sulphuric acid" (pp. 236—237).

It was thus shown that sulphuric anhydride consists of sulphurous anhydride combined with one half its volume of oxygen. Since sulphurous anhydride contained its own volume of oxygen, the proportion of oxygen in sulphuric anhydride was greater in the ratio 3 : 2.

B. Sulphuretted Hydrogen and the Sulphides.

Liver of sulphur.—Amongst the earliest discoveries of the alchemistic period was the fact that alkalis possessed solvent properties comparable with those of the acids. Thus Geber

[1] In this passage the names "sulphurous acid" and "sulphuric acid" are used to describe the anhydrides.

describes how sulphur may be dissolved in potash made caustic with lime, and states that the clear solution becomes milky on the addition of vinegar, yielding a sediment of finely divided sulphur. Glauber, too, records the fact that flint and rock-crystal, which are insoluble in acids, may be dissolved by means of alkalis and precipitated again by adding an acid.

The solutions of sulphur in alkalis were described as LIVER OF SULPHUR and were used extensively in medicine and in the preparation of pure MILK OF SULPHUR, made by dissolving the sulphur in an alkali and then precipitating it again with acid.

Sulphuretted hydrogen.—When liver of sulphur is acted on by acids, only a portion of the sulphur can be recovered; a considerable part is lost in the form of a "fœtid gas having the odour of bad eggs" (Hoffmann, 1772). This gas possesses the property of blackening silver vessels (Boyle, 1663), is inflammable (Meyer, 1764), dissolves readily in water,[1] and is present in natural sulphur-waters, from which, on exposure to the air, sulphur is deposited. On account of its method of preparation from liver of sulphur it was generally described as HEPATIC GAS. Scheele (on "Stinking sulphureous Air," *Essays on Air and Fire*, pp. 186–193) showed that it could be prepared from sulphur by heating it in hydrogen, and that the sulphur could be recovered from it by the action of oxidising agents (nitric acid and chlorine); he therefore regarded it as produced by the union of sulphur with phlogiston. This view was modified by Lavoisier and his colleagues, who regarded it as a compound of sulphur and hydrogen, and gave to it the name of SULPHURETTED HYDROGEN.

Composition of sulphuretted hydrogen.—When sparked, sulphuretted hydrogen is decomposed, sulphur being de-

[1] "Water absorbs just its bulk of this gas; when, therefore, it is mixed with hydrogen, this last will be left after washing in water, or what is still better, in lime-water" (Dalton, *New System*, II. 452).

posited and hydrogen liberated, without any change of volume. Dalton writes:

"From the experiments of Austin, Henry, etc., it has been established, that sulphuretted hydrogen undergoes no change of volume by electrification, but deposits sulphur. I have repeated these experiments, and have not been able to ascertain whether there was increase or diminution. The residue of gas is pure hydrogen" (*New System*, II. 452).

The gas therefore contains its own bulk of hydrogen. The proportion of sulphur as well as of hydrogen can be deduced from its behaviour when exploded.

"When mixed with oxygen, in the ratio of 100 measures to 50 of oxygen (which is the least effective quantity), it explodes by an electric spark; water is produced, sulphur is deposited, and the gases disappear. If 150 or more measures of oxygen are used, then after the explosion over mercury, about 87 measures of sulphurous acid are found in the tube, and 150 of oxygen disappear, or enter into combination with both the elements of the gas" (*New System*, II. 452).

In the first case the hydrogen present in the gas is found to require (like pure hydrogen) half its volume of oxygen for combustion; in the second case an additional volume of oxygen is required to burn the sulphur, and rather less than an equal volume of sulphurous anhydride is produced. The quantity of sulphur in the gas is therefore about the same as in an equal volume of sulphurous anhydride.

Metallic sulphides.—The fact that sulphur combines with the metals was known from the earliest period of alchemy. The compounds which result are similar in many respects to the oxides; they were described by Lavoisier and his colleagues as SULPHURETS, but this name has now been abandoned in favour of the name SULPHIDES.

Compounds of this type are of frequent occurrence amongst minerals, such as :

Pyrites (Fig. 8)	(Iron or copper and sulphur)
Cinnabar	(Mercury and sulphur)
Galena (Fig. 38)	(Lead and sulphur)
Blende	(Zinc and sulphur)

The presence of sulphur was probably detected first in pyrites, a mineral which is very rich in sulphur, and yields

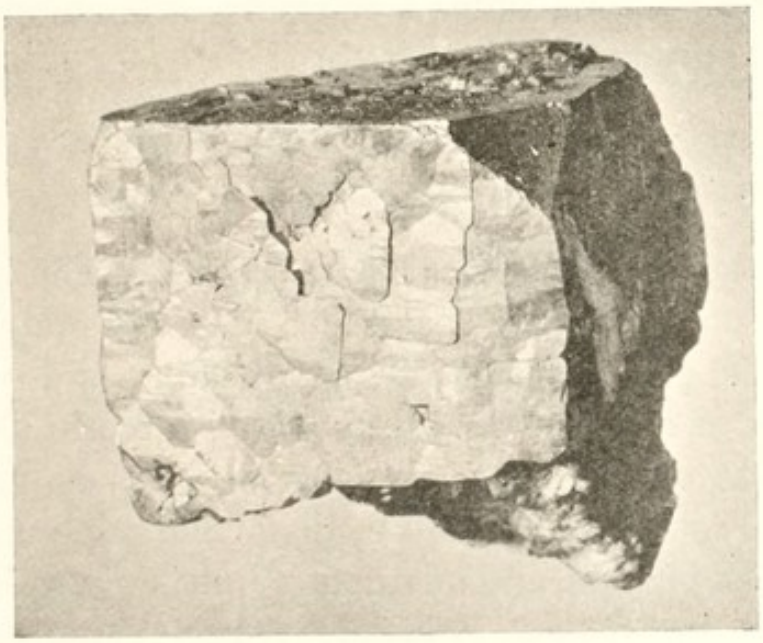


FIG. 38.—LARGE CUBE OF GALENA.
The triangular faces on the top corners are parts of an octahedron.

considerable quantities of this element when distilled ; in other cases its presence was suspected on account of the similarity of the mineral to artificial compounds of the metals with sulphur.

The burning of sulphides.—When a metallic sulphide is heated in air, the metal usually burns to the calx or oxide, whilst the sulphur escapes in the form of sulphurous anhydride. In this way the presence of sulphur may be detected, even when it cannot be separated in the free state.

The burning of sulphide to oxide was used by Berzelius

in 1811–1812 (Ostwald's *Klassiker*, XXXV. 31–34), to determine the proportions of iron and of sulphur in natural iron pyrites, in order to compare it with the artificial sulphide of iron prepared by heating iron with sulphur. He found that:

9·93 grams of iron pyrites[1] gave 6·60 grams of oxide,

whilst, by an indirect method,

2 grams of artificial sulphide gave 1·82 grams of oxide,

the oxide containing 69·34% of iron. The composition of these two substances was therefore:

Pyrites	Iron	46·08	Sulphur	53·92%
Artificial sulphide	,,	63	,,	37%

Conversion of sulphides to sulphates.—The sulphides also oxidise slowly when exposed to air and water, but in this case the product is usually a sulphate, *i.e.*, a compound of the calx or oxide of the metal with sulphuric anhydride. On account of the readiness with which they unite with oxygen, the solutions prepared by dissolving sulphur in potash, soda, lime and baryta, and mixtures of iron filings with sulphur, were used by Hales, Priestley, Scheele and others for absorbing the active part of the air, as well as for "diminishing" nitrous air, *i.e.*, converting nitric into nitrous oxide. It was not, however, until Lavoisier had developed his "oxygen" theory of combustion that these changes were satisfactorily explained. In a paper "On the Vitriolisation of Pyrites," published in 1777 (*Works*, II. 209), Lavoisier showed that the formation of green vitriol only takes place in presence of air and can be stopped by covering the pyrites with oil, or by keeping it under water. On exposing the pyrites in a bell-jar of air over water, he found that the vitriolisation was accompanied by a diminution in

[1] 10 grams of pyrites containing 0·07 gram of silica.

the volume of the air, which ceased after eighteen to twenty days; the air remaining in the bell-jar was found to have been deprived of its oxygen, since it no longer supported combustion, and in all respects resembled the "atmospheric mofette" or azote. Lavoisier concluded that:

"The pyrites is a compound of sulphur and iron; the act of vitriolisation is nothing else than an addition of [oxygen] . . ., an addition which converts the sulphur into vitriolic acid; but, this acid being in contact with the finely-divided iron, attacks and dissolves it as rapidly as it is formed, and iron vitriol is produced" (*Works*, II. 211).

In the case of iron pyrites the action is rendered complex, by the fact that the mineral contains more sulphur than is required to convert the iron into sulphate. But in the case of the other metals, *e.g.* lead, Berzelius found that the proportions of metal and sulphur in the sulphide are exactly the same as in the sulphate: the change from sulphide to sulphate is then a direct combination of the sulphide with oxygen.

The converse change of sulphates into sulphides was accomplished by Glauber, who heated the vitriols with charcoal, and thus converted them into "livers" from which part of the sulphur could be precipitated by the addition of acids.

Sulphuretted hydrogen as an acid.—Sulphuretted hydrogen is most conveniently prepared by the action of acids on artificial sulphide of iron (Scheele, *Air and Fire*, p. 193). Dalton describes an improved method of carrying out this process, as follows:

"The best way I have found to obtain sulphuretted hydrogen in a pure state, is to heat a piece of iron to a white or welding heat in a smith's forge, then suddenly drawing it from the fire, apply a roll of sulphur; the two being rubbed together, unite and run down in a liquid form, which soon fixes and becomes brittle. This compound or

sulphuret of iron, is to be granulated and put into a gas bottle, to which dilute sulphuric acid is to be added, after which the gas comes over plentifully. When the sulphuret of iron is made in a crucible from iron filings and sulphur, it seldom answers well ; it often gives hydrogen mixed with the sulphuretted hydrogen" (*New System*, II. 450–451).

This action is very similar to that whereby muriatic acid is liberated from salt by oil of vitriol, and served to suggest that sulphuretted hydrogen might be regarded as a feeble acid. This view was put forward, in 1796,[1] by Berthollet (*Ann. de Chimie*, 1798, **25**, 233–272), who showed that the salts of silver and lead could be converted into their insoluble sulphides by the addition of sulphuretted hydrogen, just as silver is converted into its insoluble muriate by the addition of muriatic acid, and lead into its insoluble sulphate by the addition of sulphuric acid. These facts were seen to be important when Lavoisier's oxygen-theory of acids became the subject of criticism, for in spite of many endeavours no oxygen could be detected in sulphuretted hydrogen itself, nor in the sulphides derived from it. Berthollet sums up his views as follows :

"Sulphuretted hydrogen dissolved in water, reddens tincture of litmus, litmus-paper and tincture of radish ; it combines with the alkalis, baryta, lime and magnesia ; it forms with these substances compounds which exchange bases when mixed with metallic solutions ; it decomposes soap, displacing the oil from the alkali . . . ."

"Sulphuretted hydrogen possesses then all the properties which characterise the acids. If several other common properties did not demand a separate class of hydrogen-compounds, it would undoubtedly be ranged amongst the acids."

"I will not recall here the observations which I have opposed to the opinion of those who pretend that acidity is

[1] The paper was read before the Paris Academy, 21 Ventose, An. IV.

an attribute which belongs only to oxygen, I will only add that sulphuretted hydrogen contains no oxygen, and that it differs very little, in its acid properties, from carbonic acid, which contains nearly 76 per cent. of oxygen" (*loc. cit.*, 237–238)

Sulphides and polysulphides.—Whilst artificial sulphide of iron is converted by oil of vitriol into sulphuretted hydrogen and sulphate of iron, iron pyrites is found to liberate sulphur as an additional product. Sulphides of this kind, which liberate sulphur when acted on by acids, are distinguished as POLYSULPHIDES. The preparation of "milk of sulphur" from "liver of sulphur" by the action of acids depends in part on the fact that soluble polysulphides are formed when sulphur is dissolved in an alkali.

C. PHOSPHORUS.

The preparation of phosphorus.—The inflammable element PHOSPHORUS was prepared during the 17th and 18th centuries, by a number of chemists, including Brand, Kunkel, and Robert Boyle, by evaporating urine to dryness, mixing it with sand, and heating strongly. It was afterwards prepared from bones.[1] Dalton describes the process as follows :

"Phosphorus . . . . . is usually prepared from the bones of animals, which contain one of its compounds, phosphate of lime, by a laborious and complex process. The bones are calcined in an open fire; when reduced to powder, sulphuric acid diluted with water is added; this acid takes part of the lime, and forms an insoluble compound, but detaches superphosphate of lime, which is soluble in water. This solution is evaporated, and the salt obtained is in a glacial state. The solid is reduced to powder, and mixed with half its weight of charcoal; then the mixture is put into an

[1] A full description of the method is given by Pelletier, *Journal de Physique*, 1785, **27**, 26–32.

earthenware retort, and distilled by a strong red heat, when the phosphorus comes over, and is received in the water into which the tube of the retort is immersed" (*New System*, 1810, II. 240–241).

Properties of phosphorus.—Phosphorus is a wax-like solid, which melts about blood-heat, and is so extremely inflammable that it must be preserved under water. When exposed to the air it undergoes a slow combustion, and exhibits the luminosity from which it derives its name. When gently heated it takes fire and burns very vigorously, emitting white fumes.

The burning of phosphorus.—The burning of phosphorus was investigated in 1772 by Lavoisier, who showed that it gained in weight, in just the same way as sulphur and the metals.

His observations are described in a "Memoir on the Combustion of Phosphorus and on the nature of the acid which results from this combustion" (*Mem. Acad. Sci.*, 1777, p. 65; *Works*, II. 139), as follows:

"If phosphorus is ignited, by means of a burning-glass, under a bell-jar immersed in mercury, one observes:

(1) That only a given quantity of phosphorus can be burned in a given quantity of air, and that this quantity is about 1 grain for 16 to 18 cubic inches of air.

(2) That, when this quantity has been burnt, the phosphorus is extinguished, and cannot be relighted, unless brought into contact with a quantity of fresh air, which has not been used for combustion.

(3) That fresh phosphorus, introduced under the same bell-jar, burns no better than the first.

(4) That, during the burning of the phosphorus, there is formed a great abundance of white flowers or flakes, like very fine snow, which attach themselves everywhere to the interior of the bell-jar, and are nothing else than solid phosphoric acid.

(5) That, at the first moment of combustion, the air in the jar expands considerably, on account of the heat of the

combustion; but that the same air then diminishes considerably in volume, until, when the vessels are cold, it only occupies four-fifths or five-sixths of the space which it occupied before the combustion. If the flowers or white flakes, which are found during this operation, are collected and weighed before they have come into contact with fresh air, and without allowing them to absorb moisture, one observes that they are two and a half times as heavy as the phosphorus used to produce them, in other words, that from a grain of phosphorus $2\frac{1}{2}$ grains of solid phosphoric acid have been produced."

"The air which has thus been diminished as much as possible by the combustion of phosphorus, is not denser than atmospheric air; its specific weight is even diminished rather than increased; it is no longer fit for the respiration of animals nor for the combustion, nor inflammation of substances" (*Works*, II. 139–140).

Phosphoric acid and the phosphates.—The white solid prepared by burning phosphorus in air is now called PHOSPHORIC ANHYDRIDE, the name PHOSPHORIC ACID being reserved for the product obtained by the action of water upon it. Lavoisier showed that phosphoric acid could be prepared by the action of warm nitric acid upon phosphorus (*Works*, II. 277), as well as by burning it in air. He also prepared a number of salts of phosphoric acid, and described them as PHOSPHATES.

Phosphorous acid and the phosphites.—A different acid is produced when phosphorus is allowed to smoulder, *e.g.* by putting small pieces of phosphorus on the sloping sides of a glass funnel, and letting the liquid drop into a bottle as it is formed. The acid was examined by Sage (*Mem. Acad. Sci.*, 1777, **91**, 435). He found that the salts prepared by neutralising it with soda or potash, unlike those prepared by Lavoisier from burnt phosphorus, were not deliquescent, *i.e.* did not become liquid by absorbing moisture from the air. Gengembre noticed that the freshly-prepared acid "is still luminous in the dark, and retains a slight odour of

garlic"; if "one heats it in an open vessel, small flames arise from it from time to time" (Gengembre, *Mem. Math. Phys.*, Paris Academy, 1785, X. 652). The new acid, which contains less oxygen than phosphoric acid, was distinguished by the French chemists in 1787 as PHOSPHOROUS ACID and its salts as PHOSPHITES.

Phosphoretted hydrogen.—An inflammable compound of phosphorus with hydrogen was discovered in 1783 by **Gengembre,** whilst attempting to prepare a "liver" of phosphorus by the action of alkalis upon it. The discovery is described as follows:

"I put some fixed caustic vegetable alkali to digest over phosphorus; at the end of some hours, I saw a multitude of minute bubbles, which adhered to the surface of the phosphorus: then I exposed the whole to a heat of 35 to 40 degrees, to accelerate the action of the alkali. Scarcely was the phosphorus melted, when there arose an unbearable odour of decayed fish, and a considerable quantity of a peculiar gas, which took fire explosively of its own accord, as soon as it came in contact with the air" ("Memoir on a new gas obtained by the action of alkalis on Kunkel's Phosphorus." Read at the Academy, May 3, 1783; *Mem. Math. Phys.*, 1785, X. 651–658; p. 652; compare Crell's *Chemische Annalen*, 1789, I. 450–457; p. 451).

The gas liberated by the action of the alkali at lower temperatures did not take fire spontaneously (*loc. cit.* p. 655). The preparation and properties of the gas were described by Dalton as follows:

"Let an ounce or two of hydrate of lime (dry slacked lime) be put into a gas bottle or retort, and then a few small pieces of phosphorus, amounting to 40 or 50 grains. If the materials are sufficient to fill the bottle, no precaution need be used; but if not, the bottle or retort should be previously filled with azotic gas, or some gas not containing oxygen, in order to prevent an explosion. The heat of a lamp is then to be applied, and a gas comes which may be received

over water. This gas is phosphuretted hydrogen ; but sometimes mixed with hydrogen.—Liquid caustic potash may be used instead of hydrate of lime, in order to prevent the generation of hydrogen.

Phosphoretted hydrogen gas has the following properties : (1) When bubbles of it come into the atmosphere, they instantly take fire ; an explosion is produced, and a ring of white smoke ascends, which is phosphoric acid : (2) It is unfit for respiration, and for supporting combustion : (3) Its specific gravity is 0·85, common air being denoted by unity : (4) Water absorbs $\frac{1}{27}$th of its bulk of this gas : (5) If the gas be electrified, the phosphorus is thrown down, and there finally remains the bulk of the gas of pure hydrogen " (*New System*, II. 456–457).

The same gaseous compound is formed when a solution of phosphorous acid is heated.[1] (Gengembre, 1783, *loc. cit.*) Water is evaporated, phosphoretted hydrogen escapes and finally a residue of phosphoric acid remains. In this action the phosphorous acid undergoes a process of simultaneous oxidation and reduction, one portion being oxidised to phosphoric acid by another portion, which loses all its oxygen, and is converted into phosphoretted hydrogen. A similar process occurs when the gas is made from phosphorus by the action of an alkali : in this case a part of the phosphorus is oxidised with the help of oxygen derived from the decomposition of water, whilst another portion combines with the hydrogen of the water to form phosphoretted hydrogen.

Phosphoretted hydrogen not an acid.—Berthollet points out in his memoir on "Sulphuretted hydrogen " that :

"Water in which phosphoretted hydrogen is dissolved, shows no sign of acidity ; and solutions of potash, lime and ammonia, do not appear to absorb more of the gas than pure water."

[1] Kopp attributes this discovery to Pelletier (1790), seven years after Gengembre's paper was read at the Paris Academy, but I have not been able to find any reference to it in Pelletier's papers.

"Phosphoretted hydrogen has then no acid properties; and this is its principal difference from sulphuretted hydrogen. It follows: (1) that the gas is liberated as fast as it is formed, whilst sulphuretted hydrogen is held in combination with the alkali and the water; (2) that the alkaline phosphides are decomposed in contact with water" (*Ann. de Chimie*, 1798, **25**. 267).

SUMMARY AND SUPPLEMENT.

A. AND B. SULPHUR.

Sulphur or brimstone is found in the free state and also in combination with metals in the mineral *sulphides*, such as:

Iron pyrites	FeS_2	(persulphide of iron)
Copper pyrites	$FeCuS_2$	(sulphide of iron and copper)
Cinnabar	HgS	(sulphide of mercury)
Galena	PbS	(sulphide of lead)
Blende	ZnS	(sulphide of zinc).

A part of the sulphur in iron pyrites can be distilled out:

$$3FeS_2 \rightarrow Fe_3S_4 + S_2.$$

The whole of the sulphur in the mineral sulphides can, however, be removed by burning, whereby both metal and sulphur are converted into oxide, *e.g.*:

$$3FeS_2 + 8O_2 \rightarrow Fe_3O_4 + 6SO_2$$
$$2ZnS + 3O_2 \rightarrow 2ZnO + 2SO_2.$$

Sulphur burns in air, without producing any change of volume, to a pungent gas, *sulphurous anhydride* (sulphur dioxide, SO_2):

$$\underset{1\ vol.}{S} + \underset{1\ vol.}{O_2} \rightarrow \underset{}{SO_2}.$$

The gas dissolves freely in water, forming a weak volatile acid, *sulphurous acid*, H_2SO_3, but is expelled by boiling and by exposure to air. The acid can be fixed by means of alkalis or bases, with which it combines to form salts known as *sulphites*, *e.g.*:

Sulphite of soda or sodium sulphite	Na_2SO_3
Sulphite of potash or potassium sulphite	K_2SO_3
Sulphite of lime or calcium sulphite	$CaSO_3$.

The volatile acid and its salts were prepared in 1702 by **Stahl,** who showed that the salts were converted by exposure to air into salts of the fixed oil of vitriol. This action may be represented by the equation :

$$\underset{\text{Potassium sulphite}}{2K_2SO_3} + O_2 \rightarrow \underset{\text{Potassium sulphate}}{2K_2SO_4}.$$

The gas was isolated in 1774 by **Priestley,** who obtained it from oil of vitriol by the reducing action of olive oil or of mercury :

$$\underset{\text{Mercury}}{Hg} + \underset{\text{Sulphuric acid}}{2H_2SO_4} \rightarrow \underset{\text{Mercuric sulphate}}{HgSO_4} + \underset{\text{Sulphurous anhydride}}{SO_2} + \underset{\text{Water}}{2H_2O}$$

The gas is freely soluble in water, but could be collected and preserved over mercury.

Lavoisier (1777) showed that oil of vitriol might be regarded as a compound of sulphurous anhydride with oxygen and water. He attempted to analyse it by heating it with mercury and collecting all the products, including the mercury which was finally recovered from the action :

$$Hg + 2H_2SO_4 \rightarrow HgSO_4 + SO_2 + 2H_2O$$

$$HgSO_4 \rightarrow Hg + O_2 + SO_2.$$

Gay-Lussac, in 1807, carried out a successful analysis by heating the sulphate of alumina in the form of alum, whereby he obtained a mixture of sulphurous anhydride with half its volume of oxygen :

$$\underset{\text{Sulphate of alumina}}{2Al_2(SO_4)_3} \rightarrow \underset{\text{Alumina}}{2Al_2O_3} + \underset{\text{Sulphurous anhydride}}{6SO_2} + \underset{\text{Oxygen}}{3O_2}.$$

As sulphurous anhydride contains its own volume of oxygen, the proportion in sulphuric anhydride must be 50 per cent. greater.

Sulphuretted hydrogen (SH_2) is set free in the form of a fœtid gas by the action of acids on sulphides, such as the artificial sulphide of iron, which is produced by fusing the metal with sulphur :

$$\underset{\text{Sulphide of iron}}{FeS} + \underset{\text{Oil of vitriol}}{H_2SO_4} \rightarrow \underset{\text{Ferrous sulphate}}{FeSO_4} + \underset{\text{Sulphuretted hydrogen}}{H_2S}.$$

The gas is a very weak acid, but is able to precipitate insoluble sulphides from solutions of many metallic salts, thus :

Silver $2AgNO_3 + H_2S \rightarrow Ag_2S + 2HNO_3$
Lead $Pb(NO_3)_2 + H_2S \rightarrow PbS + 2HNO_3$
Copper $CuSO_4 + H_2S \rightarrow CuS + H_2SO_4$.

In other cases, however, the action proceeds in the opposite direction, the sulphide being dissolved by the mineral acid and sulphuretted hydrogen set free, thus :

Iron $FeS + H_2SO_4 \rightarrow FeSO_4 + H_2S$
Zinc $ZnS + H_2SO_4 \rightarrow ZnSO_4 + H_2S$.

Liver of Sulphur is prepared by dissolving sulphur in an alkali or alkaline earth. The primary action is probably the formation of sulphite and sulphide, thus :

$$\underset{\text{Calcium hydroxide}}{3Ca(OH)_2} + 3S \rightarrow \underset{\text{Calcium sulphite}}{CaSO_3} + \underset{\text{Calcium sulphide}}{2CaS} + 3H_2O.$$

By the addition of acid, sulphur dioxide and sulphuretted hydrogen are produced :

$$CaSO_3 + 2CaS + 6HCl \rightarrow 3CaCl_2 + SO_2 + 2H_2S + H_2O ;$$

these then interact in the solution to produce sulphur and water :

$$SO_2 + 2H_2S \rightarrow 3S + 2H_2O.$$

In the formation of liver of sulphur the converse action takes place, sulphur and water being converted into sulphur dioxide and sulphuretted hydrogen ; this reversal of the usual action may be attributed to the affinity of the alkali for the two gases, both of which possess marked acid qualities.

Further quantities of sulphur may be dissolved owing to the production of *thiosulphate* and *polysulphides*, thus :

$$\underset{\text{Calcium sulphite}}{CaSO_3} + S \rightarrow \underset{\text{Calcium thiosulphate}}{CaS_2O_3}$$

$$\underset{\text{Calcium sulphide}}{CaS} + S_x \rightarrow \underset{\text{Calcium polysulphide}}{CaS_{x+1}}.$$

These substances liberate their additional sulphur when acids are added, giving an increased yield of *milk of sulphur*.

C. Phosphorus

Phosphorus, first prepared by distilling urine with sand, burns very readily to a white, snowy oxide, increasing greatly in weight (Lavoisier, 1777):

$$P_4 + 5O_2 \rightarrow P_4O_{10}.$$

The white oxide, *phosphoric anhydride*, P_4O_{10}, dissolves in water to *phosphoric acid*,

$$P_4O_{10} + 6H_2O \rightarrow 4H_3PO_4,$$

from which series of *phosphates* may be prepared, thus:

Sodium phosphates,	NaH_2PO_4,	Na_2HPO_4,	Na_3PO_4
Potassium phosphates,	KH_2PO_4,	K_2HPO_4,	K_3PO_4
Calcium phosphates,	$CaH_4(PO_4)_2$,	$Ca_2H_2(PO_4)_2$,	$Ca_3(PO_4)_2$.

The smouldering of phosphorus gives rise to *phosphorous acid*,

$$P_4 + 3O_2 + 6H_2O \rightarrow 4H_3PO_3,$$

from which *phosphites* may be prepared, *e.g.*:

Sodium phosphite, Na_3PO_3
Potassium phosphite, K_3PO_3.

In attempting to prepare a liver of phosphorus, **Gengembre**, in 1783, obtained an inflammable gaseous *phosphoretted hydrogen* or *phosphine*, PH_3:

$$P_4 + 3KOH + 3H_2O \rightarrow \underset{\text{Potassium hypophosphite}}{3KH_2PO_2} + \underset{\text{Phosphine}}{PH_3}.$$

The same gas is obtained by heating phosphorous acid:

$$\underset{\text{Phosphorous acid}}{4H_3PO_3} \rightarrow \underset{\text{Phosphine}}{H_3P} + \underset{\text{Phosphoric acid}}{3H_3PO_4}.$$

The gas prepared by Gengembre, by the action of *hot* alkali on phosphorus, was spontaneously inflammable on account of the presence of the vapour of a *liquid phosphoretted hydrogen*, P_2H_4.

CHAPTER X

NITRE, NITRIC ACID, AND NITROGEN

A. NITROGEN

Speculations as to the nature of nitrous air and of azote.—In the preceding chapters the nature and properties of some of the common gases have been described. Thus Black's "fixed air" has been shown to be a product of combustion, a compound substance containing carbon and oxygen. Cavendish's "inflammable air," on the other hand, is a simple substance, which unites with oxygen to form water. The nature of Priestley's "nitrous air" still remains, however, to be discussed.

The fact that nitrous air combines with oxygen to form brown nitrous fumes, and with oxygen and water to form nitric acid suggested that the gas might be the "elementary principle" from which nitric acid was derived, just as carbonic, sulphuric, and phosphoric acids were derived from carbon, sulphur, and phosphorus respectively. On the other hand, the fact that nitrous air could be "diminished" by iron filings and sulphur certainly suggested that it contained oxygen; the product, it is true, did not behave like a deoxidised nitrous air, since it supported combustion almost as well as oxygen itself; but it undoubtedly contained oxygen, which could scarcely be derived from any source but the nitrous air.

Assuming then that nitrous air already contained oxygen, what was the nature of the substance with which the oxygen was combined? and what was the fundamental principle of nitric acid and the nitrates? There was much vague evidence to show that this principle might be identified with "azote," the inactive residue left after depriving air of its oxygen. Thus Priestley had recorded the fact that:

"Nitrous air, which had been confined above a year in contact with iron, standing in water, was in all respects like phlogisticated common air: it neither diminished common air, nor was diminished by nitrous air, and extinguished a candle" (*Experiments on Air*, 1775, II. 177).

Cavendish, too, had noticed that charcoal deflagrated with nitre produced an air which "as far as I can perceive . . . differs in no respect from common air phlogisticated" (A.C.R. III. 21). But in neither case was the evidence sufficiently definite to justify the view that nitrous air was an oxide of azote, or nitric acid a compound of azote with oxygen and water.

This inert gas had, indeed, defied almost all attempts to change it or to ascertain its nature. Priestley, after many experiments on diminishing the volume of gases, could not find any substance which would diminish common air to a larger extent than one-fifth, although nearly every other gas that he had handled could by some means or other be condensed almost entirely, *e.g.*:

acid air and alkaline air by water,
fixed air by lime-water or by potash,
nitrous air by oxygen and water,

and so forth. It was, however, one of his random observations, on the diminution of air by sparking (*Experiments and Observations*, 1779, IV. 284–287), that enabled Cavendish to solve the problem of the nature of azote, and of the various nitrous compounds.

Cavendish (1781) finds nitric acid in the water produced by the explosion of hydrogen and oxygen.—By *burning* hydrogen in air, Cavendish, in 1781, obtained 135 grains of "pure water" "which had no taste nor smell"; but when he *exploded* hydrogen with an *excess* of oxygen the 30 grains of water which he obtained "was sensibly acid to the taste, and by saturation with fixed alkali and evaporation, yielded near two grains of nitre; so that it consisted of water united to a small quantity of [nitric] acid" [1](A.C.R. III. 16).

The explosion of hydrogen with an excess of oxygen always led to the production of nitric acid, even when the oxygen was prepared without using a nitrate, *e.g.*, from red lead and oil of vitriol, or from the leaves of plants by exposing them to sunlight in a vessel filled with water. But when the proportion of oxygen was reduced, so that only about 2% of it remained unburnt, "the condensed liquor was then not acid, but seemed pure water." Cavendish also found that "when inflammable air was exploded with common air . . . the condensed liquor was not in the least acid" (A.C.R. III. 18), although a large excess of oxygen was provided. The production of nitric acid was therefore dependent (1) on the presence of an excess of oxygen, and (2) on the high temperature reached in the explosion of hydrogen with oxygen.

As it seemed improbable that the nitric acid could be derived from the oxygen, Cavendish attributed its formation to the oxidation of azote (present as an impurity) during the explosion.

Cavendish (1784) prepares nitric acid by sparking air.—The high temperature which Cavendish thought to be

[1] Priestley, in 1788, discovered nitrate of copper in the moisture produced by exploding inflammable air with common air in a copper vessel; in one experiment 442 grains of the green liquor contained enough nitric acid (free and combined) to yield 23 grains of nitre (*Experiments and Observations on Acidity, Water, and Phlogiston, Phil. Trans.*, 1788, **78**, 147–157, 313–330).

necessary for the combination of azote with oxygen can be obtained without the addition of inflammable air or of any other foreign substance by using electric sparks. Priestley had noticed that these diminished the volume of air and thought that fixed air was produced. Cavendish confirmed the diminution of volume, but found that the production of fixed air was due "to the burning of some inflammable matter in the apparatus," and "that the real cause of the

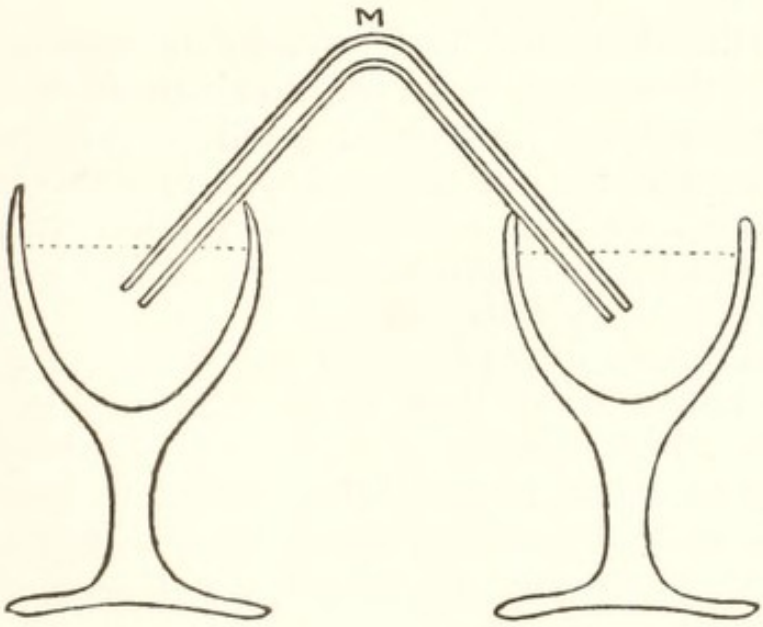


FIG. 39.—CAVENDISH'S APPARATUS FOR SPARKING AIR OVER MERCURY.

diminution" was the conversion of azote into nitric acid. Cavendish writes :

"The apparatus used in making the experiments was as follows. The air through which the spark was intended to be passed was confined in a glass tube *M*, bent to an angle, [as in Fig. 39], which, after being filled with quicksilver, was inverted into two glasses of the same fluid, as in the figure.

By means of a small glass tube suitably bent :

"I was enabled to introduce the exact quantity I pleased of any kind of air into the tube *M* ; and by the same means,

I could let up any quantity of soap-lees, or any other liquor which I wanted to be in contact with the air."

"The bore of the tube *M* used in most of the following experiments was about one-tenth of an inch; and the length of the column of air, occupying the upper part of the tube, was in general from $1\frac{1}{2}$ to $\frac{3}{4}$ of an inch."

"When the electric spark was made to pass through common air, included between short columns of a solution of litmus, the solution acquired a red colour, and the air was diminished, conformably to what was observed by Dr. Priestley."

"When lime-water was used instead of the solution of litmus, and the spark was continued till the air could be no further diminished, not the least cloud could be perceived in the lime-water; but the air was reduced to two-thirds of its original bulk; which is a greater diminution than it could have suffered by mere phlogistication, as that is very little more than one-fifth of the whole."

"When the air is confined by soap-lees, the diminution proceeds rather faster than when it is confined by lime-water; for which reason, as well as on account of their containing so much more alkaline matter in proportion to their bulk, soap-lees seemed better adapted for experiments designed to investigate the nature of this acid, than lime-water" (A.C.R. III. 39–43).

Cavendish found that the diminution of volume on sparking either azote or pure oxygen separately over soap-lees was very small; but when five parts of oxygen "were mixed with three parts of common air,[1] almost the whole of the air was made to disappear" (A.C.R. III. 44). The soap-lees "being evaporated to dryness, yielded $1\frac{4}{10}$ grains of salt, which is pretty exactly equal in weight to the nitre which that quantity of soap-lees would have afforded if saturated with [nitric] acid. This salt was found, by the manner in which paper dipped into a solution of it burned, to be true nitre"

[1] In this experiment $5 + (\frac{1}{5} \times 3) = 5\frac{3}{5}$ volumes of oxygen combined with $\frac{4}{5} \times 3 = 2\frac{2}{5}$ volumes of azote, *i.e.* 7 volumes of oxygen combined with 3 of azote.

(A.C.R. III. 45). It was free from vitriolic and muriatic acids, but gave a precipitate with a solution of silver owing to the fact that a part of the nitre was in the "phlogisticated" (*i.e.* reduced or deoxidised) condition, to which it is brought when heated so as to drive off a part of its oxygen (see below, p. 199).

The composition of air.—It has been seen that air contains about one-fifth of oxygen and a trace (about 1/2500) of fixed air or carbonic anhydride, as well as a variable quantity of moisture. The inert residue, of "azote" is much less easy to analyse. Cavendish writes:

"As far as the experiments hitherto published extend, we scarcely know more of the nature of the phlogisticated part of our atmosphere, than that it is not diminished by lime-water, caustic alkalis, or nitrous air; that it is unfit to support fire, or maintain life in animals; and that its specific gravity is not much less than that of common air" (A.C.R. III. 49).

His experiments had shown that it consisted largely of NITROGEN,[1] *i.e.* of a gas which can be converted into nitre by sparking with oxygen in presence of potash. "Yet it might fairly be doubted whether the whole is of this kind, or whether there are not in reality many different substances confounded together by us under the name of phlogisticated air.[2] I therefore made an experiment to determine, whether the whole of a given portion of the phlogisticated air of the atmosphere could be reduced to [nitric] acid, or whether there was not a part of a different nature from the rest, which would refuse to undergo that change" (A.C.R. III. 49).

For this purpose Cavendish took the usual mixture of air and oxygen and diminished it as much as possible by sparking.

[1] The name was invented by the French chemist and calico-printer Chaptal about 1790 (see the Preliminary Discourse of his *Elements of Chemistry*, tr. 1791, pp. xxxiv. to xxxvi.).

[2] *i.e.* Azote.

He then added some more oxygen to the residue and continued to spark till no further diminution took place. The excess of oxygen was absorbed by means of "liver of sulphur,"

"After which only a small bubble of air remained unabsorbed, which certainly was not more than $\frac{1}{120}$ of the bulk of the phlogisticated air [1] let up into the tube; so that if there is any part of the phlogisticated air [1] of our atmosphere which differs from the rest, and cannot be reduced to [nitric] acid, we may safely conclude, that it is not more than $\frac{1}{120}$ part of the whole" (A.C.R. III. 50).

For 110 years this bubble of gas was thought to be merely a residue of unabsorbed nitrogen; but in 1895 Rayleigh and Ramsay found that the atmosphere actually contained about 0·93% of a gas, ARGON, even more inert than nitrogen; there is therefore no doubt that the bubble which Cavendish noticed was actually a part of the azote "which differs from the rest, and cannot be reduced to nitrous acid." His cautious statement has, indeed, proved to be entirely accurate, in contrast with the hasty assumption of his successors that the azote consisted entirely of nitrogen.

B. Composition of the Gaseous Oxides of Nitrogen.

Oxides of nitrogen.—The experiments of Cavendish showed that nitrogen, the chief constituent of azote, could be converted into ordinary nitre by sparking it with oxygen over potash. This gas was therefore the characteristic constituent of nitric acid. The three gases which Priestley had prepared from nitric acid probably contained the same constituent in combination with oxygen. Experiments were therefore made by different workers to ascertain their composition.

[1] *i.e.* Azote.

Composition of nitrous oxide.—The first successful analysis was carried out by Davy (*circ.* 1800) in the case of the diminished nitrous air or "laughing gas," to which he gave the name NITROUS OXIDE. The gas was analysed by burning charcoal in it: the proportion of oxygen was calculated from the volume of carbonic anhydride produced, whilst the nitrogen left after the combustion was measured directly. The gas, generated from nitrate of ammonia, "was in its highest state of purity, as it left a residuum of $\frac{1}{38}$ only, when absorbed by boiled water."

"Ten cubic inches of it were inserted into a jar graduated to 0·1 cubic inch, containing dry mercury. Through this mercury a piece of charcoal which had been deprived of its hydrogen by long exposure to heat, weighing about a grain, was introduced, while yet warm. No perceptible absorption of the gas took place."

"Thermometer being 46°, the focus of a lens was thrown on the charcoal, which instantly took fire, and burnt vividly for about a minute, the gas being increased in volume. After the vivid combustion had ceased, the focus was again thrown on the charcoal; it continued to burn for near ten minutes, when the process stopped."

"The gas, when the original pressure and temperature were restored, filled a space equal to 12·5 cubic inches" (Davy's *Works*, III. 59–60).

An examination of the residue showed that 5·2 *cubic inches of the gas had been decomposed, giving rise to* 2·4 *cubic inches of carbonic anhydride* (condensed by the addition of ammonia) *and* 5·1 *cubic inches of nitrogen*, whilst the other 4·8 cubic inches were unchanged and could be dissolved out by means of boiled water. Knowing the proportion of oxygen in the carbonic anhydride, and the densities of nitrogen and of nitrous oxide, Davy was able to conclude:

"that 100 grains of nitrous oxide are composed of 37 oxygen and 63 nitrogen: existing in a much more condensed form than when in their simple forms."

It is, however, a simpler matter to deduce the composition of the gas by volume. Priestley and Lavoisier had shown that charcoal burns in oxygen without producing any change in the volume of the gas; 2·4 cubic inches of carbonic anhydride would thus contain 2·4 cubic inches of oxygen derived from nitrous oxide. The 5·2 cubic inches of nitrous oxide, therefore, contained 5·1 cubic inches of nitrogen, and 2·4 cubic inches of oxygen; or, speaking approximately, *nitrous oxide contains its own volume of nitrogen and half its volume of oxygen.*

Composition of nitrous air or nitrous gas (nitric oxide).—Davy next turned his attention to the gas which Mayow had prepared by the action of iron on nitric acid, and Priestley had described under the name of "nitrous air." This gas was described by Davy in 1800, and by Gay-Lussac in 1809 and in 1816 as "nitrous gas." The modern name of NITRIC OXIDE was introduced about the year 1818.

It had been shown by Priestley in 1786 (*Experiments and Observations*, 1786, VI. 304) that iron increased in weight when heated by means of a lens in a jar of nitrous air; at the same time the volume of gas was diminished about one half, the residue consisting of an inactive gas resembling atmospheric nitrogen. Charcoal heated in the same way produced carbonic anhydride and nitrogen (*loc. cit.* p. 434), but the results were less trustworthy. Davy repeated the experiment with charcoal and found that, after applying the burning glass for four hours, 15·4 cubic inches of nitrous gas gave 8·7 cubic inches of carbonic anhydride and 7·4 cubic inches of nitrogen. From these figures he calculated "that 100 grains of nitrous gas contain 56·5 oxygen and 43·5 nitrogen" (Davy's *Works*, III. 77–79). The composition by volume may be deduced by assuming that the carbonic anhydride contained its own volume of oxygen derived from the nitrous gas. The 15·4 volumes of nitrous gas would then contain

8·7 volumes of oxygen and 7·4 volumes of nitrogen, *i.e. one volume of nitrous gas contained* rather more than *half its volume of oxygen and* rather less than *half its volume of nitrogen.* It was left for Gay-Lussac in 1809 to show that the ratios $1 : \frac{1}{2} : \frac{1}{2}$ represent the composition of the gas by volume more accurately than the figures given by Davy. In doing this he had the advantage of being able to use the very inflammable metal "potassium" which Davy had prepared in 1807 by the action of an electric current on potash. Gay-Lussac found that :

"On burning the new combustible substance from potash in 100 parts by volume of nitrous gas, there remained over exactly 50 parts of nitrogen, the weight of which, deducted from that of the nitrous gas (determined with great care by M. Bérard at Arcueil), yields as result that this gas is composed of equal parts by volume of nitrogen and oxygen" (A.C.R. IV. 14).

Composition of nitrous fumes (nitrogen peroxide).— The composition of the brown fumes of nitrogen peroxide could not be determined by the methods employed in the cases of nitrous oxide and nitric oxide, since it was impossible to collect the gas over water or over mercury. By admitting nitric oxide, oxygen, and water successively into an exhausted globe and weighing at each stage, Davy was able to calculate that the 100 parts of the gas contained 70 parts by weight of oxygen, and 30 parts by weight of nitrogen (*Works*, III. 15). But the experiment was rendered complex by leakage of air into the globe through the stopcocks, and by other sources of error for which corrections had to be applied ; it will therefore be convenient to describe in its place the more exact experiments on the admixture of nitric oxide and oxygen which were made by Gay-Lussac in 1816. Gay-Lussac measured the contraction which took place when oxygen, confined over mercury in a graduated tube, was admitted into a bulb con-

taining a known volume of nitric oxide, and conversely. He describes his experiments as follows:

"The apparatus consists of a small bulb united to a graduated tube by means of a capillary tube 6 centimetres in length, divided into two equal parts by a tap . . . ."

"The manner of procedure is as follows: Knowing that the little bulb holds 170 parts of the graduated tube, I introduced into it, after having made a vacuum, 160 parts of nitrous gas; I put then into the tube a definite volume of oxygen, for example, 200 parts, and having opened the tap, I find that 158 parts have entered the bulb. This has then received 160 + 158 = 318 of gas: but its capacity being only 170, there must have disappeared a volume equal to 318 – 170 or 148. Working thus and taking the mean of several results, I found that for 100 parts of nitrous gas the contraction is 94.

"One cannot deduce from this experiment the quantity of oxygen that is combined with the nitrous gas; but if one makes another experiment in which the oxygen disappears, because the nitrous gas is in excess, and if one observes the contraction, one will know the relationship in which the oxygen and the nitrous gas are combined in each experiment, assuming that the same product is formed, and consequently that the contractions are the same in each case. For example, I found that using 100 parts of oxygen and an excess of nitrous gas, the contraction was 192. But since in the first experiment a contraction of 94 corresponded with 100 parts of nitrous gas, in the second experiment the contraction of 192 should correspond with 204 of the same gas. According to this, 100 parts of oxygen are combined with 204 of nitrous gas, or, in round numbers, 200; and I fix the contraction at 200 instead of 192, that is to say, I make it equal to the volume of the nitrous gas or double that of the oxygen." ("On the Combinations of Azote with Oxygen," *Ann. de Chimie*, 1816, **1**, 401—402).

Gay-Lussac's figures showed that:

100 parts of oxygen combining with
204 parts of nitrous gas contract to the extent of
192 parts and give rise to 304 – 192 =
112 parts of the brown nitrous fumes.

Gay-Lussac believed that these should be taken as round numbers and concluded that 100 *parts of oxygen combine with* 200 *parts of nitrous gas to form* 100 *parts of the brown fumes.*

It is now known that the relative volume of the product varies very greatly with the temperature; at temperatures above 150° C. 200 volumes are produced, but at atmospheric temperatures the quantity may be only a little above 100 volumes. The gas resulting from the admixture is now called NITROGEN PEROXIDE. Since it is formed by the combination of one volume of oxygen with two volumes of nitric oxide (containing 1 volume oxygen and 1 volume nitrogen) it follows that *nitrogen peroxide is a compound of nitrogen with oxygen in the ratio of one volume of nitrogen to two volumes of oxygen.*

C. NITRIC AND NITROUS ACIDS.

Two varieties of nitric acid.—Although Cavendish had discovered in 1784 the nature of the characteristic constituents of nitric acid, it was not until 1816 that the quantitative composition of the acid was finally determined. This delay was due, mainly, to the fact that the name was applied to acids which varied widely in composition and properties.

During the earlier alchemistic period nitric acid was prepared by throwing a mixture of green vitriol and nitre into a retort or on a charcoal fire and condensing the brown fumes in a receiver containing cold water. In this way a red, fuming acid was produced.

On the other hand, the acid which Glauber prepared by distilling saltpetre with oil of vitriol in glass vessels at a low temperature was almost colourless. But it was not possible to distinguish the two varieties sharply from one another, and the whole range of acids, from the least to the most highly coloured, were described under a single name as

"the nitrous acid." The name NITRIC ACID, now used to distinguish the colourless acid prepared by Glauber's method, was not introduced until 1787.

Nitric and nitrous acids.—It was recognised both by Priestley and by Scheele that pure nitric acid is colourless, but becomes red when reduced or deoxidised by contact with inflammable substances. Thus Scheele in his *Treatise on air and fire* (1777) asserts that :

"The colours of the acid of nitre are accidental. When a few ounces of fuming acid of nitre are distilled by a very gentle heat, the yellow separates itself from it and goes into the receiver, and the residuum in the retort becomes white and colourless like water. This acid has all the chief properties of acid of nitre, except that the yellow colour is wanting. This I call the pure acid of nitre ; as soon, however, as it comes into contact with an inflammable substance, it becomes more or less red. This red acid is more volatile than the pure, hence heat alone can separate them from one another ; and, for exactly the same reason the volatile spirit must go over first in the distillation of Glauber's spirit of nitre. When this has gone over, the colourless acid follows" (A.C.R. VIII. 20–21).

The gradual reduction of the acid is described (A.C.R. VIII. 21) as producing :

(1) Red nitrous vapours (nitrogen peroxide).

(2) A weak, volatile PHLOGISTICATED ACID OF NITRE (nitrous acid).

(3) Colourless nitrous air (nitric oxide).

(4) Complete destruction of the acid (production of nitrogen).

Scheele examined in detail the properties of the phlogisticated acid of nitre, prepared by the action of inflammable substances upon the colourless acid. He made the important discovery that a salt of the phlogisticated acid was produced by heating common nitre or saltpetre until it ceased to "boil." In addition to collecting the gas

(oxygen) set free during this action, Scheele noted that :

"Nitre maintained in red-hot fusion in a glass retort for half an hour, becomes moist in the open air, and deliquesces after cooling, and still does not show any trace of alkali."

"This liquefied nitre permits its volatile acid to escape immediately, when rubbed or mixed with the vegetable acids" (A.C.R. VIII. 28–29).

A further distinction was discovered by Cavendish, who found that nitre after heating in an earthenware retort acquired the property of forming a precipitate when mixed with nitrate of silver (A.C.R. III. 46), the silver salt of the "phlogisticated" acid being almost insoluble in water (see above, p. 191).

The name NITRIC ACID was given to the acid of common nitre by the French chemists in 1787. The traditional name of NITROUS ACID was transferred by them to the "phlogisticated" or deoxidised acid of Scheele's ignited salt.[1] Thus they write :

"We have not hesitated to make the authority of the rule prevail over that of custom, by naming for example, *nitric acid* that in which the azote is impregnated with all the oxygen it is capable of containing, and reserving the appellation of *nitrous acid* for that much weaker acid where the same base is mixed to a much less quantity of oxygen" (*Chemical Nomenclature*, tr. 1788, p. 35).

The salts of nitric acid were called NITRATES, whilst those derived from nitrous acid were called NITRITES.

Composition of nitric and nitrous acids.—The first attempts to determine the composition of nitric acid were made by Lavoisier in 1776 (*Mem. Acad. Sci.*, 1776, 671 ; *Works*, II. 129) eight years before Cavendish had discovered

[1] Saltpetre which has been heated with metallic lead consists almost entirely of potassium nitrite, the potassium salt of nitrous acid, but the red fuming "acid of nitre" contains both nitric and nitrous acids.

in atmospheric "nitrogen" the principle from which the acid is derived. Lavoisier's experiments were therefore restricted to measuring the proportions in which nitrous air (nitric oxide) and oxygen are united in the acid.

Lavoisier's analysis of nitric acid.—Lavoisier first attempted to analyse nitric acid by acting upon it with mercury in such a way that the mercury was recovered unchanged, whilst the acid was resolved into a series of gaseous constituents. For this purpose two ounces of acid of density 1·316 were heated with two ounces of mercury and the gaseous products were collected as they were set free,

(1) during the dissolution of the mercury in the acid,

(2) during the decomposition of the nitrate to oxide (red precipitate),

(3) during the decomposition of the oxide into mercury and oxygen.

At the end of the experiments 226 cubic inches of nitrous air and 238 cubic inches of oxygen had been collected, in addition to a considerable quantity of water, whilst the mercury was recovered intact. The experiment failed to give correct results because nitrous fumes, produced at various stages of the action, were absorbed and lost in the water over which the gases were collected; but the method was so ingenious as to be well worthy of notice.

Lavoisier's synthesis of nitric acid.—Lavoisier also attempted in 1776 to synthesise nitric acid by combining together known quantities of nitrous air and oxygen in presence of water. He found that $7\frac{1}{3}$ measures of nitrous air, mixed with 4 measures of oxygen over water,

"were reduced to about $\frac{1}{3}$ of a measure, that is to say to $\frac{1}{34}$ of their original volume."

"The water in the tube was acid at the end of this operation, or rather was nothing but a weak [nitric] acid; on saturating it with an alkali, I obtained from it by evaporation a true saltpetre" (*Works*, II. 135).

The result of this experiment, in which nitrous air combined with only half its volume of oxygen, did not agree with those obtained by the analytical method, in which the volumes were approximately equal. The discrepancy led Lavoisier to suggest that the acid prepared from nitre, which he had used for analysis, differed essentially from the acid synthesised from nitrous air, and that it was considerably richer in oxygen.

Later investigators found that the proportions in which nitric oxide and oxygen combined were not definite, but varied widely with the conditions under which the experiment was carried out; the problem which Lavoisier had attacked was indeed of altogether exceptional difficulty, and forty years elapsed before the correct solution was given by one of the brilliant group of Frenchmen who, in the early years of the nineteenth century, resumed at Arcueil, near Paris, the work which was so tragically interrupted by the untimely death of Lavoisier.

Combination of nitric oxide with oxygen to form nitric and nitrous acids.—When nitric oxide is added in suitable proportions to common air or to oxygen confined over water, the whole of the oxygen is removed and the water becomes inpregnated with nitric or nitrous acid. The method is fairly trustworthy as a means of absorbing or estimating oxygen, but great variations were found in the quantity of nitric oxide required to remove a given volume of oxygen, and consequently also in the proportions of nitrous air and oxygen in the resulting acid. Thus:

Lavoisier found:	*oxygen* : *nitric oxide* =	100 : 187
Dalton found:	*oxygen* : *nitric oxide* =	100 : 130 to 360
Davy found:	*oxygen* : *nitric oxide* =	100 : 133 to 300

Such variations were not difficult to understand in view of Cavendish's observation that when water impregnated with the mixed gases was distilled in a glass retort:

"The first runnings were very acid, and smelt pungent, being nitrous acid much phlogisticated; what came next had no sensible taste or smell; but the last runnings were very acid, and consisted of nitrous acid not phlogisticated" (A.C.R. III. 11).

Similar mixtures of nitric and nitrous acids were invariably obtained, until Gay-Lussac in 1816 succeeded in obtaining first one acid and then the other as the sole product of the admixture of the gases, and gave the correct limiting proportions as follows:

Oxygen : *nitric oxide* = 100 : 133. Product, *nitric acid.*
Oxygen : *nitric oxide* = 100 : 400. Product, *nitrous acid.*

Gay-Lussac in his paper "On the Combinations of Azote with Oxygen" writes:

"I come now to the combinations of nitrous gas with oxygen: they seem to vary with the slightest change in the conditions; but I shall prove that there are three distinct combinations which, by their mixing, can explain all those which are not in definite proportions."

"When nitrous gas and oxygen are mixed, the absorption varies according to the diameter of the tube, the rapidity of mixing, and the order in which the gases are introduced into the tube. Wishing to work over mercury, with water to absorb the acid, but fearing that the mercury would be attacked, I added potash to the water, and thus obtained constant absorptions, independent of the conditions I have just mentioned. I made a great many experiments, and concluded that 100 parts of oxygen absorb 400 of nitrous gas: provided that the solutions of potash are strong, the absorptions are almost all comprised between 495 and 500, and are rarely below 490. This combination of oxygen and nitrous gas, which had not been distinguished, so far as I know, and which I will call provisionally *pernitrous acid*,[1] cannot be obtained free; as soon as one saturates the potash with an acid, nitrous gas is liberated, and ordinary

[1] Now called nitrous acid.

nitrous acid [1] is produced, which remains dissolved in the water. Reducing the nitrous gas to its elements, one finds that the proportion of 100 of oxygen to 400 of nitrous gas reduces to :

Nitrogen 100,
Oxygen 150"

(*Annales de Chimie*, 1816, **1**, 399—400).

"It remains now to consider nitric acid, and to determine by what proportion of oxygen and nitrous gas it should be represented . . . I worked at first, like Dalton, in tubes of 5 millimetres diameter, using an excess of oxygen, and obtained almost exactly the results that he gives, that is to say, an absorption of 134 to 136 parts of nitrous gas for 100 of oxygen ; but I found also that tubes of twice this diameter can be used, provided that one does not shake the water, and that one waits some minutes. The absorption obtained by Dalton being only 130, I will adopt the figure 133, which is also adopted by Davy, and it only remains to determine to what acid it belongs. The red sulphate of manganese,[2] which I have already recommended as a reagent to test when a body is saturated with oxygen, will fulfil our purpose admirably ; for it is at once decolorised by nitrous acid, but not at all by nitric acid."

"I began by producing an absorption of 180 parts of nitrous gas and 100 of oxygen, and found that the acid formed . . . . decolorised the red sulphate of manganese immediately. This salt was also decolorised when the absorption of nitrous gas was 160, 150, and even 138 ; but it no longer took place in the experiment in which only 134 parts of nitrous gas were absorbed. It is thus proved that [the product] is ordinary nitric acid, and that it is formed by the proportion of 100 of oxygen gas to 133 of nitrous gas, which reduces to

Nitrogen 100,
Oxygen 250"

(*Annales de Chimie*, 1816, **1**, 403—404).

[1] Yellow nitric acid saturated with nitric oxide.

[2] A red oxidising agent, probably a permanganate.

Composition of the oxides and acids of nitrogen.—Gay-Lussac had now determined the composition of the two acids derived from saltpetre as well as of the three gaseous oxides which could be prepared from it. He summarised his results in a table which, on substituting modern names for the different compounds, reads as follows:

	Nitrogen.	Oxygen.
Nitrous oxide	100	50
Nitric oxide	100	100
Nitrous acid	100	150
Nitrogen peroxide	100	200
Nitric acid	100	250

This table, the sequence of which was anticipated in a remarkable way by Scheele in 1777, affords an exceptionally good illustration of the laws of chemical combination, the proportions of oxygen in the five compounds being in the ratios 1 : 2 : 3 : 4 : 5.

Summary and Supplement

A. Nitrogen.

Cavendish, in 1781, found nitric acid in the water obtained by exploding hydrogen with an excess of oxygen and concluded that it had been produced by oxidation of atmospheric azote. In 1784, by sparking over potash a mixture of three parts of air with five parts of oxygen, he succeeded in absorbing almost the whole of the gas and obtained 1·4 grains of nitre. By sparking with an excess of oxygen, which was afterwards absorbed by liver of sulphur, he oxidised the whole of the azote except about $\frac{1}{120}$; the azote therefore consists almost entirely of a gas from which nitre can be prepared and to which Chaptal in 1790 gave the name *nitrogen*; the residue was shown by Rayleigh and Ramsay in 1895 to contain an inactive gas which they called *argon*.

The oxidation of nitrogen in presence of potash may be represented by the equations :

$$2N_2 + 5O_2 + 4KOH \rightarrow \underset{\text{(Potassium nitrate.)}}{4KNO_3} + 2H_2O$$

$$2N_2 + 3O_2 + 4KOH \rightarrow \underset{\text{(Potassium nitrite.)}}{4KNO_2} + 2H_2O$$

The fact that a part of the nitre produced in this way was "phlogisticated," *i.e.* in the "reduced" form as nitrite, was noticed by Cavendish.

B. Oxides of Nitrogen.

Davy, in 1800, determined the composition by weight of the three gases which Priestley prepared from nitric acid, as follows :

	Oxygen	:	Nitrogen.
"Diminished nitrous air (Nitrous oxide, N_2O)	37	:	63
"Nitrous air" (Nitric oxide, NO)	56·5	:	43·5
Brown Fumes (Nitrogen peroxide, NO_2 or N_2O_4)	70	:	30

In the case of the two colourless oxides, he burned charcoal in the gas and measured the quantities of nitrogen and of carbonic anhydride which were produced. These are as follows :

Nitrous oxide $2N_2O + C \rightarrow 2N_2 + CO_2$ (containing O_2, $\frac{1}{2}$ *vol.*)
1 *vol.* 1 *vol.* $\frac{1}{2}$ *vol.*

Nitric oxide $2NO + C \rightarrow N_2 + CO_2$ (containing O_2, $\frac{1}{2}$ *vol.*),
1 *vol.* $\frac{1}{2}$ *vol.* $\frac{1}{2}$ *vol.*

whence we have as the composition by volume :

Nitrous oxide. *Nitrogen* : *oxygen* = 1 : $\frac{1}{2}$
Nitric oxide. *Nitrogen* : *oxygen* = $\frac{1}{2}$: $\frac{1}{2}$.

The composition of the brown gas was determined, but not very accurately, by mixing known quantities of nitric oxide and oxygen.

Gay-Lussac, in 1807, determined more accurately the composition of nitric oxide (which does not readily part with its oxygen) by burning metallic potassium in it :

$$2NO + 4K \rightarrow N_2 + 2K_2O.$$
$$1\ vol. \qquad \tfrac{1}{2}\ vol.$$

In 1816, he determined the composition of nitrogen peroxide by measuring the contraction produced on adding oxygen to a known volume of nitric oxide, and conversely. He found that the same contraction (192 volumes) was produced by adding nitric oxide to 100 volumes of oxygen, or oxygen to 204 volumes of nitric oxide. Oxygen and nitric oxide therefore combined in the ratio of 100 volumes of oxygen to 204 volumes of nitric oxide, or very nearly one volume of oxygen to two of nitric oxide. As two volumes of nitric oxide contained one volume of nitrogen and one volume of oxygen, the composition of the product was as follows :

Nitrogen peroxide. *Nitric oxide* : *oxygen* = 2 : 1
Nitrogen : *oxygen* = 1 : 2.

The combination of the two gases may be represented by the equation :

$$2NO + O_2 \rightarrow N_2O_4 \text{ or } 2NO_2.$$
$$2\ vols.\ \ 1\ vol.\ \ 1\ vol.\ \ 2\ vols.$$

At low temperatures the product consists mainly of the colourless oxide N_2O_4, and the volume is reduced, as Gay-Lussac found, almost to one-third. Above 150° it consists entirely of the brown oxide NO_2, and occupies two-thirds of the original volume.

R. W. Gray, in 1905 (*Trans. Chem. Soc.*, 1905, **87**, 1601–1620), heated nickel in nitric oxide, and by using modern methods was able to weigh both the nitrogen and the oxygen present in a known weight of nitric oxide. The flask A (Fig. 40) was provided with a glass stopper, B, leading through a stopcock to a capillary ground-glass joint, D. A small platinum boat, H, containing finely-divided nickel was surrounded by a coil of platinum wire, which could be heated to any desired temperature by an electric current, supplied through the stout platinum electrodes, EE. The bulb M, containing

charcoal, and provided with a stopcock, could be connected with the bulb A, through the capillary ground-glass joints at K and D. Air could be pumped out or nitric oxide admitted through the stopcock P.

The bulb A was weighed (1) empty, and (2) filled with nitric oxide. After burning the nickel in the boat H, the nitrogen left in the bulb A was transferred to the bulb M by opening the

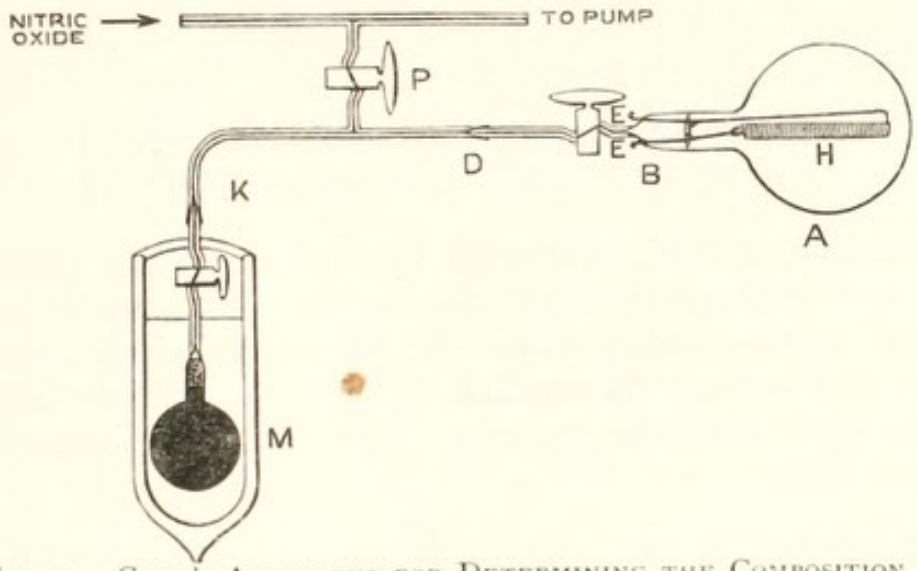


FIG. 40.—GRAY'S APPARATUS FOR DETERMINING THE COMPOSITION OF NITRIC OXIDE.

two stopcocks (after pumping out the air between K and D) and then cooling the charcoal in M by liquid air. The whole of the nitrogen was thus condensed on the charcoal and a vacuum was produced in the rest of the apparatus. A third weighing of the bulb A gave the weight of oxygen which had been taken by the nickel from the nitric oxide; the increase in the weight of the bulb M gave the weight of the nitrogen that had been set free, thus:

$$2NO + 2Ni \rightarrow N_2 + 2NiO.$$

In a typical experiment,

0·62103 gram nitric oxide gave { 0·33103 gram oxygen
0·28998 gram nitrogen,

whence 14·013 grams of nitrogen combine with 16 grams of oxygen to form 30·013 grams nitric oxide.

C. NITRIC AND NITROUS ACIDS.

The existence of two "acids of nitre," one strong and the other weak, was recognised by Priestley, Scheele, Cavendish,

and Lavoisier. The strong acid from which saltpetre is derived was distinguished in 1787 as *nitric acid* and its salts as *nitrates*; the weak acid, present in ignited saltpetre, was distinguished as *nitrous acid* and its salts as *nitrites*; the name nitrous acid was, however, also applied to nitrogen peroxide and to the red fuming variety of nitric acid. Typical formulæ are as follows:

$$\left.\begin{matrix}\text{Nitric acid, } HNO_3\\ \text{Nitrous acid, } HNO_2\end{matrix}\right\} \quad \left.\begin{matrix}\text{Saltpetre (potassium nitrate), } KNO_3\\ \text{Ignited } \text{„} \text{ (} \text{„} \text{ nitrite), } KNO_2\end{matrix}\right\}$$

$$\left.\begin{matrix}\text{Silver nitrate, } AgNO_3 \text{ (soluble in water)}\\ \text{Silver nitrite, } AgNO_2 \text{ (sparingly soluble)}\end{matrix}\right\}$$

Lavoisier, in 1776, attempted to analyse strong nitric acid with the help of mercury, as in the case of sulphuric acid (p. 168). He also synthesised a weak acid by mixing nitric oxide and oxygen over water. **Cavendish**, in 1781, showed that the latter process gives both the ordinary (nitric) and the phlogisticated (nitrous) acid.

Gay-Lussac, in 1816, finally determined the composition of the two acids by mixing nitric oxide and oxygen: (*a*) over potash, producing a pure nitrite; (*b*) in a narrow tube over water, producing pure nitric acid.

The action is shown by the following equations:

$$(a)\quad \underset{4\ vols.}{4NO} + \underset{1\ vol.}{O_2} + 4KOH \rightarrow \underset{\text{(Potassium nitrite.)}}{4KNO_2} + 2H_2O.$$

$$(b)\quad \underset{4\ vols.}{4NO} + \underset{3\ vols.}{3O_2} + 2H_2O \rightarrow \underset{\text{(Nitric acid.)}}{4HNO_3}.$$

Since nitric oxide contains half its volume of nitrogen and half its volume of oxygen, the four volumes of nitric oxide shown in each of the above equations contain two volumes of nitrogen and two volumes of oxygen; the anhydrides of the two acids therefore have the following composition:

Nitrous acid	*Nitric oxide*	: *oxygen* = 4 : 1
	Nitrogen	: *oxygen* = 2 : 3
Nitric acid	*Nitric oxide*	: *oxygen* = 4 : 3
	Nitrogen	: *oxygen* = 2 : 5.

The composition by volume of the whole series of oxides investigated by Gay-Lussac is as follows :

		Nitrogen	:	Oxygen.
Nitrous oxide	N_2O	100	:	50
Nitric oxide	NO	100	:	100
Nitrous anhydride	N_4O_6 or N_2O_3	100	:	150
Nitrogen peroxide	N_2O_4 or NO_2	100	:	200
Nitric anhydride	N_2O_5	100	:	250

CHAPTER XI

MURIATIC ACID AND CHLORINE

A. The Discovery of Chlorine

Scheele's investigation of pyrolusite (1771–1774).—During the years from 1771 to 1774 Scheele was occupied, at the request of Bergman, in the investigation of a Swedish mineral to which the name of "Brunsten" or "Manganese"[1] was given. This mineral is now generally known as PYROLUSITE, whilst the name MANGANESE has been transferred to the metal which it contains. This mineral was a black powder which resembled the metallic calces in appearance, but differed from them in being insoluble in dilute oil of vitriol and in nitric acid; it dissolved, however, in presence of various inflammable substances, such as sugar and gum, and had the curious quality of dissolving in the weak acids (sulphurous and nitrous acids) which are produced by reducing or "phlogisticating" oil of vitriol and nitric acid. The mineral could also be rendered soluble by baking it with oil of vitriol, when a gas was given off identical in its properties with the "fire air," or oxygen, which Scheele had prepared by heating nitre.

Pyrolusite was thus shown to have the properties of a calx combined with oxygen. Such compounds of a calx with

[1] "On Manganese, Manganesium, or Magnesia Vitrariorum," Scheele's *Essays*, tr. 1786, repr. 1901, pp. 52–104.

oxygen are now generally described as PEROXIDES; thus pyrolusite is sometimes called PEROXIDE OF MANGANESE, but is more often distinguished by its colour as BLACK OXIDE OF MANGANESE. The composition of pyrolusite as a compound of a calx or earth with oxygen is very similar to that of chalk as a compound of lime with fixed air. But whilst the fixed air contained in chalk is set free even by the weakest acids, the oxygen of pyrolusite is only driven off by heating strongly with oil of vitriol. Another method of separating oxygen from pyrolusite was described in 1785 by Berthollet (A.C.R. XIII. 16), who heated the mineral (compare the burning of chalk to lime) and thus extracted from it "a large quantity of vital air"; in this process the pyrolusite "lost an eighth of its weight."

Scheele's discovery of chlorine (1774).—The behaviour of "manganese" towards spirit of salt differed from its behaviour with other acids, in that the mineral dissolved in the cold acid without the addition of any reducing agent to take away the oxygen. In the cold solution, as Scheele pointed out, "the manganese has here attached itself so loosely to the acid that water can precipitate it, and this precipitate behaves like ordinary manganese." But when the mixture was warmed, a pungent gas was liberated, and a colourless solution was obtained, similar to those produced by other acids with the help of a reducing agent. Scheele describes his discovery of the new gas as follows:

"One ounce of pure spirit of salt was poured on half an ounce of finely-ground manganese. After this mixture had stood one hour in the cold, the acid had assumed a dark brown colour. Part of this solution was poured into a bottle, which was left open in a warm place. The soiution gave off a smell like warm aqua regis, and after a quarter of an hour it was clear and colourless as water, and the smell was gone."

"The remainder of the brown mixture was set to digest, in order to see whether the marine[1] acid would saturate itself with manganese. As soon as the mixture became warm, its smell of aqua regis became considerably augmented, and an effervescence also arose, which continued until the following day, when the acid was found to be saturated. On the residue which it had been unable to dissolve, there was again poured one ounce of spirit of salt, whereupon all the above-mentioned phenomena occurred, and the manganese became completely dissolved, except a little siliceous earth."

"In order clearly to apprehend this novelty I took a retort containing a mixture of manganese and spirit of salt. In front of the neck I bound a bladder emptied of air, and set the retort in hot sand. The bladder became distended by the effervescence in the retort. When the acid no longer effervesced, which was an indication of its saturation, I removed the bladder, and found that this air had coloured it yellow, as if by aqua fortis, but did not contain any trace of fixed air; it had, however, a quite characteristically suffocating smell, which was most oppressive to the lungs. It resembled the smell of warm aqua regis. The solution in the retort was clear, inclining to yellow, which last-mentioned colour was caused by its containing iron" (A.C.R. XIII. 5–7).

The gas which Scheele had thus prepared, he regarded as "marine acid, deprived of phlogiston," and called it "dephlogisticated marine acid," but when the theory of phlogiston was overthrown, Davy gave to it the name CHLORINE (Greek χλωρὸς greenish-yellow) on account of its characteristic colour. Although this name was not introduced until 1810, it is used, on account of its simplicity and convenience, throughout the chapter in place of the cumbrous and misleading names given to it during the intervening period.

The properties of chlorine.—In addition to describing its suffocating smell and yellow colour, Scheele states that

[1] Marine acid = muriatic acid, the acid derived from brine.

the gas "unites with water in very small quantity; and gives to water a slightly acid taste; but as soon as it comes in contact with a combustible matter it becomes again a proper marine acid." As usually prepared it contained a certain quantity of acid vapour, but this could be got rid of by collecting it in wet bottles; the acid was then dissolved by the water, whilst the greater part of the chlorine remained as a gas, into which various substances could be plunged. The following properties were noticed:

"The corks in the bottles became yellow, as from aqua fortis."

"Blue litmus paper became almost white; all vegetable flowers—red, blue, and yellow—became white in a short time; the same thing also occurred with green plants. In the meantime the water in the bottle became changed to a weak and pure marine acid. The former colours of these flowers, as well as those of the green plants, could not be restored either by alkalis or by acids."

"Iron filings were put into the same bottle and they dissolved. This solution was evaporated to dryness and distilled with an addition of oil of vitriol, when a pure marine acid, which did not dissolve gold, again passed over."

"All metals were attacked, and with gold it is noteworthy that its solution in this dephlogisticated marine acid forms with volatile alkali a fulminating gold."[1]

"Insects immediately died in the vapours; and fire was immediately extinguished by them" (A.C.R. XIII. 8–9).

Berthollet (1785) regards chlorine as an oxygen compound.—Chlorine was next investigated by the French chemist Berthollet (*Mem. Acad. Sci.*, 1785, 276–295; A.C.R. XIII. 11–31), who made a special study of the properties of CHLORINE-WATER. This was prepared by passing the gas through a series of bottles; the first bottle, empty and cold, served to condense and remove the acid vapours;

[1] See Chapter XII.

three others almost filled with water were used to dissolve the gas. By surrounding the bottles with ice, Berthollet obtained yellow crystals which he considered to be the solidified gas (A.C.R. XIII. 13–14); these have since been shown to be a compound of the gas with water.

Berthollet found that solutions of chlorine in water were decomposed by exposure to light, oxygen being liberated and muriatic acid reproduced. Scheele had regarded chlorine as muriatic acid which had "lost one of its constituents," namely, phlogiston; he would therefore have interpreted this experiment as a decomposition in which water was robbed of its phlogiston by the chlorine, whilst the oxygen which it contained was set free. This view may be expressed by the equation:

$$\underset{\text{(Hydrogen+oxygen.)}}{\text{Chlorine + water}} \rightarrow \underset{\text{(Chlorine+hydrogen.)}}{\text{muriatic acid}} + \text{oxygen.}$$

Berthollet preferred, however, to regard the change as a simple decomposition of chlorine into muriatic acid and oxygen:

$$\underset{\text{(Muriatic acid+oxygen.)}}{\text{Chlorine}} \rightarrow \text{muriatic acid} + \text{oxygen}$$

The fundamental weakness of Berthollet's theory lay in the fact that chlorine *by itself* could not be decomposed into muriatic acid and oxygen even by the most drastic treatment. This was in direct contradiction to his own view that in chlorine

"the vital air . . . . adheres so feebly to the marine acid that the action of light suffices to disengage it promptly" (A.C.R. XIII. 20).

Berthollet shows that chlorine is not an acid.—Another difficulty in regarding chlorine as a compound of muriatic acid with oxygen arose when Berthollet himself discovered that chlorine was not an acid. He points out that "Scheele

and Bergman were unable to recognise this essential quality, as in the process which they employed the water of the vessels in which they received the gas" was contaminated with "a portion of marine acid which always passed over in the distillation." In Berthollet's apparatus this acid was "retained in the first bottle," which was left empty and surrounded with ice or cold water; if by chance any acid passed forward it was absorbed in the first of the three bottles of chlorine-water (A.C.R. XIII. 15).

Chlorine-water purified in this way was found to have the following properties:

"It has a harsh taste which does not resemble that of the acids."

"It destroyed vegetable colours . . . . without any red tint becoming apparent."

"It does not cause an effervescence with solution of fixed alkali, even when the latter is saturated with fixed air" (A.C.R. XIII. 14).

The fact that chlorine was not an acid was in direct contradiction to Lavoisier's conception of oxygen as the acid-producer. Lavoisier had concluded that muriatic acid, like carbonic, nitric, sulphuric, and phosphoric acids, must be a compound of oxygen; if chlorine contained more oxygen than muriatic acid it should have been a stronger acid; actually it was not an acid at all.

This difficulty was realised by the French chemists who drew up the new system of chemical nomenclature in 1787; in proposing to describe chlorine as an "oxygenated muriatic acid" they say of muriatic acid that "it is an acid of a particular nature, because it imbibes an excess of oxygen, and because in this state its acidity seems rather to decrease than to augment" (*Chemical Nomenclature*, p. 33).

Gay-Lussac and Thenard (1809) prove that muriatic acid gas contains hydrogen.—That muriatic acid gas (1) con-

tains hydrogen and (2) is the sole product of the combination of hydrogen with chlorine was proved by the French chemists Gay-Lussac and Thenard in 1809. The presence of hydrogen was shown by the fact that this gas was liberated freely when the muriatic gas was acted upon by metals.[1] Thus they write:

"We have also examined the action of the metal of potash on muriatic gas. At the ordinary temperature this action is very slow; but as soon as the metal is fused there is combustion with disengagement of light, and there result muriate of potash and hydrogen gas."

"The quantity of hydrogen collected in this experiment is precisely the same as that which the metal would give in contact with water."

"We passed a current of muriatic gas over well-cleaned iron turnings at a dull red heat. Much hydrogen gas was disengaged, without sensible admixture of muriatic gas; much muriate of iron was at the same time obtained; the residual turnings were not oxidised" (A.C.R. XIII. 34 and 38).

Hydrogen, combined with oxygen in the form of water, was also collected "by passing muriatic acid gas at a moderate heat over litharge which had been fused and then reduced to coarse powder."

Muriatic acid gas a compound of hydrogen and chlorine.—Gay-Lussac and Thenard observed further that equal volumes of hydrogen and chlorine combined together to form muriatic gas (*a*) by keeping the mixture for several days, (*b*) by gently heating it, (*c*) by exposure to light. They found

"that a mixture, in equal parts, of [chlorine] gas and hydrogen gas changes, in the course of several days, into ordinary muriatic gas, and that no water is deposited."

"If a mixture of equal parts of these two gases is made and a small piece of iron heated in mercury to 150° intro-

[1] These were now generally recognised as elementary substances.

duced, there is a violent inflammation, and formation of muriatic acid."

"We made two mixtures, each consisting of about ½ litre of [chlorine] gas with the same volume of hydrogen gas, which we knew acted only slowly on one another; one of them we placed in complete darkness, and exposed the other to the light of the sun, which was that day very feeble. At the end of several days the first mixture was still coloured green, and appeared to have undergone no change; the second, on the contrary, had been completely decolorised in less than a quarter of an hour, and was almost entirely decomposed."

"Being no longer able, after these experiments, to doubt as to the influence of light on the combination of the two gases, and judging from the rapidity with which it had operated, that if the light had been much more vivid it would have operated much more quickly, we made new mixtures . . . . and placed them in complete darkness, awaiting some moments of bright light. Two days after having made the mixtures, we were able to expose them to the sun. Scarcely had they been exposed when they suddenly inflamed with a very loud detonation, and the jars were reduced to splinters, and projected to a great distance. Fortunately we had provided against such occurrences, and had taken precautions to secure ourselves against accidents" (A.C.R. XIII. 38, 41, 43).

These experiments proved conclusively that muriatic gas was a compound of hydrogen and chlorine, and was, in fact, the only substance produced by the combination of these gases. The composition of the gas must therefore be represented by the equation:

$$\text{Chlorine} + \text{hydrogen} \rightarrow \text{muriatic gas},$$

instead of

$$\text{Chlorine} - \text{oxygen} \rightarrow \text{muriatic gas}.$$

This view is expressed in the modern system of nomenclature, in which muriatic acid gas is described as HYDROGEN

CHLORIDE and its solution in water as HYDROCHLORIC ACID,[1] the muriates derived from the acid being described as CHLORIDES.[1]

B. CHLORINE AN ELEMENT.

Gay-Lussac and Thenard regard chlorine as the oxide of an imaginary radical.—The French chemists were so obsessed with the idea that all acids must contain oxygen, that they refused to abandon this view, even when chlorine had been proved to be a simpler substance than muriatic acid. Thus, instead of admitting that chlorine might be an element, they regarded it as the oxide of an unknown radical, analogous with nitrogen, carbon, sulphur, or phosphorus. Muriatic acid, formed by the union of chlorine with hydrogen, was regarded as a ternary compound of this radical with hydrogen and oxygen, or perhaps with water. According to this new view:

Chlorine = X + oxygen.
Muriatic acid = chlorine + hydrogen
= X + oxygen + hydrogen.

It will be seen that this theory merely substituted for chlorine the symbol (X + oxygen), where X was an imaginary radical which had never been isolated. To prove the correctness of their theory, it was necessary for Gay-Lussac and Thenard to extract oxygen from chlorine, or water from muriatic acid, without making use of substances in which oxygen was already present. The experiment of passing muriatic gas over litharge was obviously invalid (as Davy pointed out in 1810), since the formation of water

[1] The name "hydrochloric acid" was proposed by Gay-Lussac in 1814 (*Ann. d. Chimie*, 1814, **91**, 9). The term "chloride" was introduced by Davy in 1816 (*Works*, V. 516), as a substitute for the word "chlorure" suggested by Gay-Lussac.

could be accounted for by the combination of the hydrogen of the acid with the oxygen of the litharge, quite independently of the existence of any oxygen in chlorine.

The difficulty of decomposing chlorine. Chlorine as an agent for purifying charcoal.—Gay-Lussac and Thenard made many attempts to separate oxygen from chlorine and thus to set free its other hypothetical constituent. But all their efforts were unsuccessful, since neither the metals, nor phosphorus, nor any of the well-known absorbents of oxygen were capable of separating oxygen from the gas.

"Finally, as a last method, we tried to decompose [chlorine] by charcoal ignited at the extreme heat of the forge. To avoid the presence of the smallest quantity of water, we made the gas pass slowly through a large glass tube a metre and a half in length, filled with muriate of lime. This tube communicated with a porcelain tube in which the charcoal was exposed to a red heat. The first portions of the . . . . gas were completely converted into ordinary muriatic gas. This effect diminished gradually in spite of a very great elevation of temperature, and soon the gas passed without alteration, mixed only, towards the end of the experiment, with one thirty-third of an inflammable gas, which we believe to be carbonic oxide gas. This result clearly showed us that [chlorine] is not decomposed by charcoal, and that the muriatic gas which we had obtained at the commencement of the operation was due to the hydrogen of the charcoal. . . . In fact, on taking ordinary charcoal without igniting it, muriatic gas was disengaged during a lengthened period, even at a temperature only slightly elevated. . . . According as the charcoal lost its hydrogen, however, the quantity of muriatic acid went on diminishing, and finally nothing was obtained but [chlorine]" (A.C.R. XIII. 39–40).

In this passage Gay-Lussac and Thenard disclose incidentally a very efficient method of purifying charcoal. The charcoal which Stas used in determining the composition of carbonic anhydride (p. 149) was purified by heating it

in a current of chlorine, and the same method is still in general use.

A striking contrast was observed on comparing the effect of heat alone on dry and on moist chlorine. The dry gas resisted all attempts to decompose it, but the introduction of moisture was followed by the immediate production of oxygen and muriatic acid. In this experiment chlorine "alone or mixed with the vapour of boiling water" was introduced "into a porcelain tube exposed to a red heat. In the first case the gas did not suffer any alteration; but as soon as the vapour of water was introduced, oxygen gas and muriatic acid were obtained. It is not necessary for this decomposition that the temperature should be very high, as it still takes place below a red heat." When hydrogen was used in place of water the formation of muriatic acid took place even more readily "at a temperature only a little higher than that of boiling water" (A.C.R. XIII. 41).

At the conclusion of their experiments Gay-Lussac and Thenard were obliged to admit that since chlorine "is not decomposed by charcoal . . . it might be supposed . . . that this gas is a simple body," and agreed that "the phenomena which it presents can be explained well enough on this hypothesis" (A.C.R. XIII. 48). But they were not prepared to abandon the view that it contained oxygen and preferred to regard it still as a compound. It was therefore left for Davy to adopt and to advocate the view that chlorine was a simple or elementary substance, and finally to win general recognition for a conception that gave the death-blow to Lavoisier's oxygen theory of acids.

Davy (1810) regards chlorine as an element.—At the time when Gay-Lussac and Thenard were making their experiments on chlorine, Davy was engaged in similar researches on this gas. During the early part of 1810, the failure of all attempts to decompose chlorine, even by the

action of charcoal heated to whiteness by a Voltaic battery, led him:

"to doubt of the existence of oxygen in that substance, which has been supposed to contain it above all others in a loose and active state; and to make a more rigorous investigation than had been hitherto attempted for its detection" (A.C.R. IX. 23).

He repeated the experiments of Gay-Lussac and Thenard on the combination of hydrogen and chlorine, and confirmed their observation that the product was muriatic acid gas free from any other substance except perhaps a mere trace of water.

But he could not discover any evidence of the presence of oxygen in muriatic acid gas or in chlorine, and at the close of the year he expressed his belief:

"that the body improperly called in the modern nomenclature of chemistry, *oxymuriatic acid gas* has not as yet been decompounded; but that it is a peculiar substance, elementary as far as our knowledge extends, and analogous in many of its properties to oxygen gas."

"To call a body, which is not known to contain oxygen, and which cannot contain muriatic acid, oxymuriatic acid, is contrary to the principles of that nomenclature in which it is adopted."

"After consulting some of the most eminent chemical philosophers in this country, it has been judged most proper to suggest a name founded upon one of its obvious and characteristic properties—its colour—and to call it CHLORINE or Chloric gas."

"Should it hereafter be discovered to be a compound, and even to contain oxygen, this name can imply no error, and cannot necessarily require a change" (A.C.R. IX. 40, 59).

Elements and compounds.—The controversy as to the elementary nature of chlorine was of value in fixing clearly

the conception of an ELEMENT. The four elements of Aristotle :

earth, *air*, *fire*, and *water*,

and the three principles of the alchemists :

mercury, *sulphur*, and *salt*,

served rather to describe the qualities than the actual composition of the bodies in which their presence was implied. The first conception of an element as a substance which cannot be decomposed into simpler substances was given by Boyle. But no clearer statements of this view can be found in the whole of the literature of chemistry than those made by Davy in his controversy with the French chemists, and afterwards with Berzelius. Two of these may be quoted :

"Some authors continue to write and speak with scepticism on the subject, and demand stronger evidence of chlorine being undecompounded. These evidences it is impossible to give. It has resisted all attempts at decomposition. In this respect it agrees with gold, and silver, and hydrogen, and oxygen. Persons may doubt whether these are elementary bodies ; but it is not philosophical to doubt whether they have not been resolved into other forms of matter" (A.C.R. IX. 73).

"It is possible that oxymuriatic gas may be compound, and that this body and oxygen may contain some common principle ; but at present we have no more right to say that oxymuriatic gas contains oxygen than to say that tin contains hydrogen ; . . . and till a body is decompounded, it should be considered as simple" (A.C.R. IX. footnote, p. 61).

Davy (1810) determines the composition by volume of hydrogen chloride.—Until the year 1810 muriatic acid gas was regarded either as a simple substance (Berthollet) or as a compound of the unknown muriatic radical with one-third or one-fourth of its weight of water (Davy ; Gay Lussac ; A.C.R. XIII. 49).[1] In that year, however, Davy, having proved it

[1] Berzelius (*Chemical Proportions*, 1819, 125) assumed that 442·65 parts of chlorine contained 142·65 parts of the muriatic radical and 300 parts of oxygen.

to be a binary compound of two simple gases, hydrogen and chlorine, succeeded also in establishing its composition by volume. Davy states that Cruikshank had shown that chlorine and hydrogen, when mixed in equal proportions, gave a product almost entirely condensible by water; Gay-Lussac and Thenard showed that the product was muriatic acid, but did not make any measurements of volume. These could not be made in the ordinary way either over water (which dissolved the acid gas) or over mercury (which was acted on by chlorine). In Davy's experiments the two gases "were mixed in equal volumes over water, and introduced into an exhausted vessel and fired by the electric spark." As the gases were moist, "there was always a deposition of a slight vapour, and a condensation of from one-tenth to one-twentieth of the volume; but the gas remaining was muriatic acid gas." The contraction was reduced when the gases were dried, "by introducing them into vessels containing muriate of lime, and by suffering them to combine at common temperatures." Although Davy was never "able to avoid a slight condensation," he found that "in proportion as the gases were free from oxygen or water, this condensation diminished." It was therefore reasonable to suppose that the pure gases would unite in equal volumes without contraction (A.C.R. IX. 26).

Davy also mixed together equal volumes of chlorine and sulphuretted hydrogen, both dried: "in this instance the contraction was not $\frac{1}{40}$; sulphur . . . . was formed on the side of the vessel, but no vapour was deposited. The residual gas contained about $\frac{19}{20}$ of muriatic acid gas, and the remainder was inflammable" (A.C.R. IX. 26)

These experiments proved that hydrogen and chlorine combine together in equal volumes and without any marked contraction, as shown by the equation:

Hydrogen	+ chlorine	→ hydrogen chloride.
1 *vol.*	1 *vol.*	2 *vols.*

In the case of sulphuretted hydrogen, which was known to contain its own volume of hydrogen, the volume changes were similar:

Sulphuretted hydrogen	+ chlorine	→ hydrogen chloride	+ sulphur.
1 *vol.*	1 *vol.*	2 *vols.*	*solid*

Davy showed further that hydrogen chloride liberates half its volume of hydrogen when the chlorine which it contains is absorbed by a metal. Thus in:

"the decomposition of muriatic acid gas, by heated tin and zinc, hydrogen equal to about half its volume was disengaged, and metallic muriates the same as those produced by the combustion of tin and zinc in [chlorine] resulted" (A.C.R. IX. 28).

"With potassium, in experiments made over very dry mercury, the quantity of hydrogen is always from 9 to 11, the volume of the muriatic acid gas used being 20" (A.C.R. IX. 27).

"When mercury is made to act upon 1 in volume of muriatic acid gas, by Voltaic electricity, all the acid disappears, calomel is formed, and about 0·5 of hydrogen evolved" (A.C.R. IX. 27).

This decomposition of the gas by sparking in presence of mercury was discovered by Priestley (*Experiments on Air*, 1775, II. 239) and studied in detail by Henry in 1800 (*Phil. Trans.* 1800, 191). It is of special interest as an example of a reversible change. Usually the action proceeds as shown by the upper arrow in the equation:

$$\text{Hydrogen} + \text{chlorine} \rightleftharpoons \text{hydrogen chloride.}$$

But chlorine acts upon mercury so strongly that a very slight decomposition of the hydrogen chloride, as shown by the lower arrow, is sufficient to corrode the mercury and ultimately to remove the whole of the chlorine from the gas, leaving a residue of pure hydrogen. The compound formed

by the action of chlorine on an excess of mercury is an insoluble white powder known as CALOMEL. It contains more mercury and less chlorine than the CORROSIVE SUBLIMATE which is formed when the chlorine is in excess.

Compounds of chlorine with the metals.—Davy's view that chlorine was an element involved also a new conception as to the nature of the muriates, or chlorides. Most of the salts that had been investigated contained a fixed, earthy BASE, usually a metallic oxide, in combination with a volatile ACID, usually the oxide of a non-metal such as carbon, nitrogen, sulphur or phosphorus. These salts were, therefore, BINARY COMPOUNDS of the two oxides or TERNARY COMPOUNDS of metal, non-metal and oxygen, thus:

$$\text{CHALK} = \begin{cases} \text{LIME} = \begin{cases} \text{METAL} \\ \text{OXYGEN} \end{cases} \\ \text{FIXED AIR} = \begin{cases} \text{CARBON} \\ \text{OXYGEN} \end{cases} \end{cases}$$

$$\text{SULPHATE OF COPPER} = \begin{cases} \text{COPPER OXIDE} = \begin{cases} \text{COPPER} \\ \text{OXYGEN} \end{cases} \\ \text{SULPHURIC ANHYDRIDE} = \begin{cases} \text{SULPHUR} \\ \text{OXYGEN} \end{cases} \end{cases}$$

The muriates on the other hand, as Scheele had observed, were formed by the direct combination of chlorine with the metals.

In order to maintain the analogy with the sulphates, phosphates, etc., the French chemists assumed a further sub-division of the chlorine, thus:

$$\text{MURIATE OF LEAD} = \begin{cases} \text{LEAD} = \text{LEAD} \\ \text{CHLORINE} = \begin{cases} \text{OXYGEN} \\ \text{UNKNOWN MURIATIC RADICAL} \end{cases} \end{cases}$$

Davy showed that this view was not justified by any experimental evidence. He suggested, as a more reasonable hypothesis, that chlorine "may possibly belong to the same class of bodies as oxygen" (A.C.R. IX. 33), and that

the compounds of chlorine with lead, silver, mercury, potassium and sodium might "be considered as a class of bodies related more to the oxides" than to the ordinary salts (A.C.R. IX. 34)." Gay-Lussac recognised a still closer analogy between chlorine and sulphur, and between the chlorides and sulphides. According to these views a true analogy is supplied by comparing the muriates or chlorides with binary compounds, such as :

$$\text{LITHARGE (OXIDE OF LEAD)} = \begin{cases}\text{LEAD}\\ \text{OXYGEN}\end{cases}$$

$$\text{GALENA (SULPHIDE OF LEAD)} = \begin{cases}\text{LEAD}\\ \text{SULPHUR}\end{cases}$$

and not with ternary compounds, such as :

$$\text{SULPHATE OF LEAD} = \begin{cases}\text{LITHARGE} = \begin{cases}\text{LEAD}\\ \text{OXYGEN}\end{cases}\\ \text{SULPHURIC ANHYDRIDE} = \begin{cases}\text{SULPHUR}\end{cases}\end{cases}$$

Displacement of sulphur and oxygen by chlorine.—The analogy between chlorine, sulphur, and oxygen is shown by the readiness with which these elements can be interchanged in their compounds with the metals. Thus Scheele, in his first description of chlorine, stated that by contact with the gas "cinnabar became white on the surface, and when the piece was washed in water a pure sublimate solution was obtained, but the sulphur was not altered" (A.C.R. XIII. 9). This action may be represented by the equation :

$$\underset{\text{(Mercury + sulphur)}}{\text{Cinnabar}} + \text{chlorine} \rightarrow \underset{\text{(Mercury + chlorine)}}{\text{corrosive sublimate}} + \text{sulphur}$$

A similar process is now used on a large scale for converting sulphide ores of zinc, lead, and silver into chlorides.

The conversion of oxides into chlorides was described by Davy, who thus obtained a direct proof of the presence of oxygen in the earths. Davy found that :

"When baryta, strontia, or lime, is heated in [chlorine] to

redness, a body precisely the same as a dry muriate is formed, and oxygen is expelled from the earth. I have never been able to effect so complete a decomposition of these earths by [chlorine], as to ascertain the quantity of oxygen produced from a given quantity of earth. But in three experiments made with great care I found that one of oxygen was evolved for every two in volume of [chlorine] gas absorbed" (A.C.R. IX. 47).

The displacement of oxygen by chlorine is effected even more easily by the action of muriatic acid gas or hydrogen chloride. This gas being a HYDRIDE, *i.e.* a compound of hydrogen with another element, interacts with metallic oxides to form muriates or chlorides *and water*, thus:

LITHARGE	+	MURIATIC ACID GAS	→	MURIATE OF LEAD	+	WATER
(Lead + oxygen)		(Hydrogen + chlorine)		(Lead + chlorine)		(Hydrogen + oxygen)

Under similar conditions an acidic OXIDE, such as fixed air or sulphuric anhydride, unites with the metallic oxide to form a ternary salt *and nothing else*.

Berthollet (1788) prepares chlorate of potash.— Although the muriates, like the sulphides, were found to be binary compounds containing no oxygen, oxidised muriates (ternary compounds analogous with the sulphates) were discovered at an early date. The most important of these, now known as CHLORATE OF POTASH or POTASSIUM CHLORATE, was first prepared in a pure state by Berthollet in 1788, by passing chlorine gas into hot aqueous potash. (*Journ. de Physique*, 1788, **33**, 217–224). After crystallising out a great deal of muriate of potash (potassium chloride) the new salt was obtained in hexagonal plates with a lustre like mica. These did not taste like muriate of potash, but produced in the mouth "a feeling of freshness closely resembling that of nitre." The salt detonated with charcoal; after the detonation nothing was left but ordinary muriate of potash · the salt was therefore an "oxygenated

muriate of potash." On heating it, oxygen was liberated more easily and in much larger quantity than from nitre; 100 grains of salt gave 75 cubic inches or nearly 37 grains of oxygen; the salt could therefore be used very conveniently for the preparation of oxygen and has been employed for that purpose ever since. On account of the readiness with which its oxygen was set free and the brilliancy of its detonation with charcoal, Berthollet predicted that "the powder which I propose to prepare with this salt, will have remarkable properties"; the experiment was carried out shortly afterwards but produced a disastrous and fatal explosion. The acid from which the oxidised muriate is derived was prepared by Gay-Lussac in 1814 (*Ann. de Chimie*, 1814, **91**, 107–110). He described the acid (*ibid.* p. 9) as CHLORIC ACID, and its salts CHLORATES.

Berthollet (1788) prepares bleaching solutions, containing alkaline hypochlorites.—By passing chlorine into a cold aqueous solution of a mild or caustic alkali, Berthollet obtained a liquid which possessed all the bleaching qualities of chlorine-water, and decomposed slowly (like chlorine-water exposed to sunlight) with liberation of oxygen gas. When the liquid was heated, these properties disappeared and nothing was left but the chloride and chlorate. The bleaching properties are due to the presence of a salt (derived from an unstable HYPOCHLOROUS ACID), which contains less oxygen than the chlorate and is distinguished as a HYPOCHLORITE. Hypochlorite solutions were used by Berthollet as a convenient source of chlorine in the experiments in which he laid the foundations of the bleaching industry (*Ann. de Chimie*, 1789, **2**, 151–190).

Tennant (1799) **prepares bleaching powder.**—A somewhat similar compound, prepared by the direct union of chlorine with lime, and widely known as BLEACHING POWDER, was introduced by the English chemist **Tennant** in 1799 as a substitute for hypochlorite of potash or soda.

Summary and Supplement

A. The Discovery of Chlorine

Scheele, in 1774, described the properties of the mineral "manganese," now known as *pyrolusite* or *black oxide of manganese*, MnO_2. It is insoluble in dilute nitric or sulphuric acid, but liberates oxygen and is converted into a sulphate by baking with oil of vitriol.

$$\underset{\text{(Manganese dioxide.)}}{MnO_2} + H_2SO_4 \rightarrow \underset{\text{(Manganous sulphate.)}}{MnSO_4} + H_2O + \tfrac{1}{2}O_2$$

It also liberates oxygen when heated (Berthollet, 1785), giving rise to an oxide analogous with smithy scale, Fe_3O_4.

$$3MnO_2 \rightarrow Mn_3O_4 + O_2.$$

It dissolves in cold muriatic acid to a dark solution, which contains an unstable manganic salt and from which the black oxide can be recovered by dilution; this reversible action may perhaps be represented by the equation :—

$$MnO_2 + 4HCl \rightleftharpoons MnCl_4 + 2H_2O,$$

but no chloride of the formula $MnCl_4$ has yet been isolated. When the liquid is heated, a pungent, green gas escapes, to which **Davy**, in 1810, gave the name *chlorine*.

$$MnO_2 + 4HCl \rightarrow \underset{\text{(Manganous chloride.)}}{MnCl_2} + \underset{\text{(Chlorine)}}{Cl_2} + 2H_2O.$$

The gas bleaches coloured flowers, extinguishes flame, and unites directly with nearly all metals, thus :—

Lead $Pb + Cl_2 \rightarrow \underset{\text{(Lead chloride.)}}{PbCl_2}.$

Iron $2Fe + 3Cl_2 \rightarrow \underset{\text{(Ferric chloride.)}}{2FeCl_3}.$

Gold $2Au + 3Cl_2 \rightarrow \underset{\text{(Auric chloride)}}{2AuCl_3}.$

Berthollet, in 1785, collected chlorine-water free from muriatic acid and showed that the gas is not an acid. From the

solutions he froze out *chlorine hydrate*, Cl_2+8H_2O. He found that chlorine water was decomposed by light, liberating oxygen and reproducing muriatic acid ; he therefore regarded chlorine as a compound of oxygen with muriatic acid and called it "oxymuriatic gas." The action is really a decomposition of water by chlorine :

$$Cl_2+H_2O \rightleftarrows 2HCl+\tfrac{1}{2}O_2 ;$$

the action is reversible, as shown by the double arrows, since muriatic acid exposed to air and light becomes impregnated with chlorine.

Gay-Lussac and Thenard, in 1809, proved that muriatic gas was a compound of hydrogen with chlorine, a fact that is expressed by the modern name *hydrogen chloride*, HCl, for the gas and *hydrochloric acid* for the solution. They separated the hydrogen from it by the action of metals, thus :

Potassium $2K+2HCl \rightarrow \underset{\text{(Potassium chloride.)}}{2KCl}+H_2$

Iron $Fe+2HCl \rightarrow \underset{\text{(Ferrous chloride.)}}{FeCl_2}+H_2$

It should be noted that the *ferrous chloride*, $FeCl_2$, produced in this way contains less chlorine than the *ferric chloride*, $FeCl_3$, produced by the direct action of chlorine upon iron.

Hydrogen, in the form of water, was also separated from muriatic gas and litharge :

$$\underset{\text{(Hydrogen chloride.)}}{2HCl} + \underset{\text{(Litharge.)}}{PbO} \rightarrow \underset{\text{(Lead chloride.)}}{PbCl_2} + \underset{\text{(Water.)}}{H_2O}$$

They united hydrogen and chlorine to form hydrogen chloride : (*a*) slowly by keeping in diffused daylight ; (*b*) rapidly by heating ; (*c*) with a violent explosion by exposure to bright sunlight. Although they could not extract oxygen from chlorine even by red-hot charcoal, they contended that chlorine gas was the oxide of an unknown radicle and that muriatic gas was a ternary compound of this radical with oxygen and hydrogen, thus :

Chlorine = X + oxygen
Muriatic gas = X + oxygen + hydrogen.

B. Chlorine an Element.

Davy, in 1810, being quite unable to separate oxygen from chlorine, suggested that the gas was an element and gave to it the name *chlorine*. He determined the volumetric composition of hydrogen chioride, which is formed without change of volume when chlorine acts upon hydrogen or upon sulphuretted hydrogen.

$$\underset{1\ vol.}{H_2} + \underset{1\ vol.}{Cl_2} \rightarrow \underset{2\ vols.}{2HCl}$$

$$\underset{1\ vol.}{H_2S} + \underset{1\ vol.}{Cl_2} \rightarrow \underset{2\ vols.}{2HCl} + \underset{solid.}{S}$$

He showed that half its volume of hydrogen is liberated when the hydrogen chloride is acted on by metals, thus :

Tin $Sn + \underset{2\ vols.}{2HCl} \rightarrow \underset{\text{(Stannous chloride.)}}{SnCl_2} + \underset{1\ vol.}{H_2}.$

Zinc $Zn + \underset{2\ vols.}{2HCl} \rightarrow \underset{\text{(Zinc chloride.)}}{ZnCl_2} + \underset{1\ vol.}{H_2}.$

Potassium $2K + \underset{2\ vols.}{2HCl} \rightarrow \underset{\text{(Potassium chloride.)}}{2KCl} + \underset{1\ vol.}{H_2}.$

Mercury (By sparking.) $2Hg + \underset{2\ vols.}{2HCl} \rightarrow \underset{\text{(Calomel.)}}{Hg_2Cl_2} + \underset{1\ vol.}{H_2}.$

It should be noted that the *stannous chloride*, $SnCl_2$, prepared in this way contains less chlorine than the *stannic chloride*, $SnCl_4$, prepared by the action of chlorine on tin and that *calomel* or *mercurous chloride*, Hg_2Cl_2, contains a smaller proportion of chlorine than the *corrosive sublimate* or *mercuric chloride*, $HgCl_2$, prepared by the action of chlorine on mercury or its sulphide. In the case of zinc and potassium the products are identical with those obtained by the action of chlorine on the metal.

All these chlorides are binary compounds of metal and chlorine analogous with the sulphides and oxides, rather than with ternary salts such as the sulphates and carbonates. This

analogy is illustrated by the mutual displacement of chlorine, sulphur and oxygen, for instance :

$$\underset{\text{(Cinnabar.)}}{HgS} + Cl_2 \rightarrow \underset{\text{(Corrosive sublimate.)}}{HgCl_2} + S.$$

$$\underset{\text{(Lime.)}}{CaO} + Cl_2 \rightarrow \underset{\text{(Muriate of lime.)}}{CaCl_2} + \tfrac{1}{2}O_2.$$

Berthollet, by the action of chlorine on potash, prepared ternary salts, containing metal, chlorine and oxygen :

$$2KOH + Cl_2 \rightarrow KCl + \underset{\text{(Potassium hypochlorite.)}}{KClO} + H_2O.$$

$$6KOH + 3Cl_2 \rightarrow 5KCl + \underset{\text{(Potassium chlorate.)}}{KClO_3} + 3H_2O.$$

The *potassium hypochlorite* prepared from cold potash liberates chlorine when acted on by acids, and was used as a convenient source of chlorine for bleaching ; but it was soon displaced by the *bleaching powder*, $CaOCl_2$, which **Tennant** prepared by the direct action of chlorine on slaked lime. The *potassium chlorate*, which Berthollet prepared by the action of chlorine on hot potash, is a crystalline salt, is readily decomposed by heat and forms a convenient source for the preparation of small quantities of oxygen :

$$2KClO_3 \rightarrow 2KCl + 3O_2.$$

CHAPTER XII

THE HALOGENS.

A. FLUORINE.

Fluorine.—In 1813 and 1814 Davy published two papers on "Fluor Spar" and the "Fluoric Compounds" (*Works*, V. 408—424, 425—436). In these he recognised the existence of an element, resembling chlorine, which he proposed to call FLUORINE. The origin of these fluoric compounds is described in his "Elements of Chemical Philosophy" (1812), as follows:

"There is a substance found abundantly in nature called FLUOR SPAR; it is usually either blue, green, yellow, or white, transparent, and crystallised in cubes. It is a common product of the mines in Derbyshire.

"When this substance, in fine powder, is mixed with oil of vitriol and distilled in retorts of silver or lead, connected with receivers of the same metal artificially cooled, an intensely active fluid is produced. It has the appearance of sulphuric acid, but is much more volatile, and sends off white fumes when exposed to air. It must be examined with great caution, for when applied to the skin it instantly disorganises it, and produces very painful wounds. When potassium is introduced into it, it acts with intense energy upon it, and produces hydrogen gas and a neutral salt: when lime is made to act upon it, there is a violent heat produced, water is given off, and the same substance as fluor spar is produced. When it is dropped into water a hissing noise is

produced with much heat, and an acid fluid not disagreeable to the taste is formed if the water be in sufficient quantity. It instantly corrodes and dissolves glass" (*Works*, IV. 347—348).

Hydrofluoric acid.—The acid vapour prepared by the action of oil of vitriol on fluor spar had been used since 1670 at Nuremberg for etching glass. The liquid acid was discovered in 1771 by Scheele (*Essays*, pp. 1–51), who called it "fluor acid"; but it was first obtained in its pure form in 1809

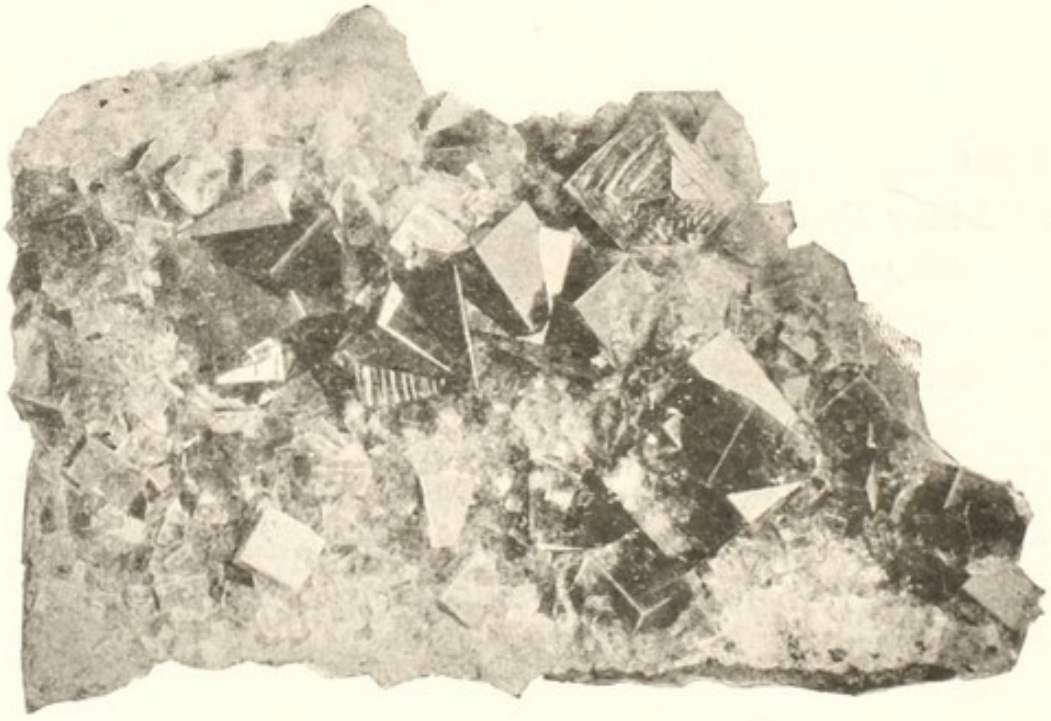


FIG. 41.—TWINNED CUBES OF FLUOR SPAR.
British Museum (Natural History).

by Gay-Lussac and Thenard, who distilled the acid in metal vessels in order to avoid contamination by glass. Davy at first regarded the liquid acid as a compound of water with an anhydrous oxy-acid, strictly analogous with sulphuric acid. But, after recognising chlorine as an element, he "was forcibly struck by the analogy" between the chlorine compounds and those prepared from fluor spar. After many fruitless attempts to isolate oxygen from them, Davy concluded:

"That there exists in the fluoric compounds a peculiar substance, possessed of strong attractions for metallic bodies and hydrogen, . . . and which, in consequence of its strong affinities and high decomposing agencies, it will be very difficult to examine in a pure form, and, for the sake of avoiding circumlocution, it may be denominated FLUORINE, a name suggested to me by M. Ampère" (*Works*, V. 423).

Davy concluded further that:

"Fluor spar and other analogous substances, . . . must be regarded as binary compounds of metals and fluorine" (*Works*, V. 424), and

"That the pure liquid fluoric acid consists of hydrogen united to a substance, which, from its strong powers of combination, has not as yet been procured in a separate form, but which is detached from hydrogen by metals" (*Works*, V. 425).

This acid, composed of hydrogen and fluorine, is now known as HYDROFLUORIC ACID.[1] Davy made many attempts to decompose the acid by the electric current, but did not succeed in isolating fluorine. The element was, however, prepared by this method by Moissan in 1886.

B. IODINE.

Iodine discovered by Courtois (1811).—The view that chlorine was an element was greatly strengthened by the isolation, in 1811 (*Hist. Acad. Sci.*, 1813, p. cxxiv), of a substance which resembled chlorine in its properties, and like chlorine could not be decomposed into simpler constituents.

[1] This name was first suggested by Davy (*Works*, IV. 350) in 1812 to express the view that the liquid was a hydrated oxy-acid, but was abandoned by him in the following year in favour of the older name "fluoric acid." It was introduced again by Gay-Lussac, in 1814, to express the fact that the acid contained, not water as Davy had suggested, but hydrogen.

Davy, writing in 1814, says:

"This substance was accidentally discovered about two years ago by M. Courtois, a manufacturer of saltpetre at Paris. In his process for procuring soda from the ashes of sea-weeds, he found the metallic vessels much corroded; and in searching for the cause of this effect, he made the discovery. The substance is procured from the ashes after the extraction of the carbonate of soda, with great facility, and merely by the action of sulphuric acid:—when the acid is concentrated, so as to produce much heat, the substance appears as a vapour of a beautiful violet colour, which condenses in crystals having the colour and the lustre of plumbago" ("On a New Substance which becomes a violet-coloured Gas by Heat," Davy's *Works*, V. 437).

The properties of iodine.—The new substance which Courtois had discovered was described by Désormes and Clément, at a meeting of the Paris Academy of Sciences on November 29, 1813. Their paper was not published in the Memoirs of the Institute, but a summary was given in the *Annales de Chimie* under Courtois's name. The properties of iodine are there described as follows:

"The new substance, which has been called *iodine* on account of the beautiful violet colour of its vapour, has the appearance of a metal. Its specific gravity is about four times that of water. It is very volatile; its odour is analogous to that of [chlorine]; it imparts a red-brown stain to paper and to the hands, but this disappears after a short time; it is neither acid nor alkaline; on putting it into a retort and heating, it vaporises at a very gentle heat, about 75° C. It boils under water and produces a magnificent violet vapour; when sublimed in considerable quantity, large, brilliant plates are produced, but these are not massive; it is little soluble in water, more in alcohol and much in ether.

A red heat does not change the nature of iodine; it traverses a red-hot porcelain tube without alteration.

It is the same with iodine vapour in oxygen; it is not changed at all by a red heat. The violet vapour escapes

from the action of the oxygen as if it were alone, and the whole of the iodine is found again in the vessels in which it is condensed" (*Ann. de Chimie*, 1813, **88**, 305-306).

Iodine examined by Gay-Lussac and by Davy (1813–1814). Iodine an element.—At the request of Clément, iodine was examined more completely by **Gay-Lussac**[1] and by **Davy**,[1] between whom a strong and healthy rivalry had arisen.

The two chemists agreed in regarding iodine as an element. Thus Davy writes:

"The new substance, I find, is not decomposed when voltaic sparks are taken in it in its gaseous state from ignited points of charcoal: at first there are white fumes, probably from the action of moisture or hydrogen in charcoal, on the substance; but these fumes soon cease, and when the tube in which the experiment is made is cooled, the substance appears unaltered.

"From all the facts that have been stated there is every reason to consider this new substance as *an undecompounded body*. In its specific gravity, lustre, . . . and colour, it resembles the metals; but in all its chemical agencies it is more analogous to oxygen and chlorine" (Davy's *Works*, V. 452—453).

The new element had been described in France as "ione" or "iode" (Greek, *ἰώδης*, violet) Davy proposed to describe it in English as IODINE as this "name will be more analogous to chlorine and fluorine" (Davy's *Works*, V. 454—455).

[1] **Davy's** first paper was sent from Paris on December 10, 1813. His "Further Experiments and Observations on Iodine" (*Works*, V. 457–477) were dated from Florence on March 23, 1814, whilst a third paper, "On a Solid Compound of Iodine and Oxygen" (*Works*, V. 492–502), was dated from Rome, February 10, 1815. **Gay-Lussac** read two memoirs to the Paris Academy of Sciences on December 6 and December 20, 1813; his completed "Researches on Iodine" were read on August 1, 1814 (*Annales de Chimie*, 1814, **91**, 5–96; Ostwald's *Klassiker*, No. IV).

Gay-Lussac expressed his opinion as follows :—

"Iodine is not inflammable ; it cannot even be combined directly with oxygen. I consider it as a simple substance, and I place it . . . . between sulphur and chlorine, because it has stronger affinities than the former, and weaker than the latter" (*Ann. de Chimie*, 1814, **91**, 8 ; *Klassiker*, IV. 5).

The iodides.—Iodine combines directly with a large number of metals, forming compounds which Davy describes as IODIDES. Thus Clément, describing the discovery of Courtois, writes :—

"With metallic mercury it forms in the cold, by shaking, a beautiful red powder resembling vermilion.

"Iodine readily attacks, in the cold, iron, zinc, tin, and antimony. . . . These compounds are soluble in water. Those with lead and silver are not soluble ; the former is of a beautiful yellow colour" (*Ann. de Chimie*, 1813, **88**, 308—309).

Davy found that it formed a salt-like substance by combination with the metal potassium :—

"I heated some potassium in a little glass tube, and passed some of the substance in vapour over it ; at the moment the vapour came in contact with the potassium, there was an inflammation and the potassium burnt slowly with a pale blue light. The substance formed by the action of potassium was white, fusible at a red heat, and soluble in water. It had a peculiar acrid taste" (Davy's *Works*, V. 441).

Iodine combined with chlorine to form a yellow solid, volatile by heat. Although it did not combine directly with oxygen, a solid oxide was prepared by Davy in 1815 :—

"The compound of oxygen and iodine appears as a white semi-transparent solid ; it has no smell, but a strong astringent sour taste. . . . When strongly heated it decomposes, undergoing fusion at the moment, and is entirely converted into gaseous matter and iodine, leaving no

residuum whatever. . . . The gas formed is found to be pure oxygen, and the solid sublimate produced is pure iodine" (Davy's *Works*, V. 494).

Clément also records (*Ann. de Chimie*, 1813, **88**, 509) the formation by the action of ammonia on iodine of an explosive black powder, which Gay-Lussac (*Ann. de Chimie*, 1814, **91**, 29; *Klassiker*, IV. 15) recognised as an iodide of nitrogen.

Hydriodic acid.—Désormes and Clément found that iodine (like chlorine) is capable of uniting directly with hydrogen to form an acid :—

"Iodine is not acted on by passing it over red hot charcoal; but hydrogen effects a complete change in the appearance of this substance.

"If a mixture of hydrogen with dry or moist iodine vapour is passed through the red-hot tube, the violet colour disappears, scarcely any trace of it can be seen, and a colourless gas is collected, of which one part is promptly absorbed by water and the other part is pure hydrogen.

"The water in which the soluble gas was collected was very acid; it acquired a red colour and became perceptibly warm" (*Ann. de Chimie*, 1813, **88**, 306—307).

This experiment was repeated by Gay-Lussac, who made the further discovery, that

"Hydriodic acid gas is partially decomposed at a red heat; the decomposition is complete if it is mixed with oxygen; water is formed, and iodine reappears. On the other hand, I have found that on passing water and iodine vapour through a porcelain tube at a red heat, there was no decomposition. There is here a great difference between iodine and chlorine, for the latter removes hydrogen from oxygen; but there is also a resemblance between sulphur and iodine, since oxygen removes the hydrogen from both" (*Ann. de Chimie*, 1814, **91**, 18).

The partial decomposition of hydriodic acid by heat is an excellent example of a balanced action—

hydriodic acid $\rightleftharpoons$ *hydrogen* + *iodine.*

In presence of oxygen the action proceeds to completion—

oxygen + *hydriodic acid* → *water* + *iodine.*

This complete decomposition of the acid is directly contrary to the main course of the action which Berthollet had discovered in chlorine water exposed to sunlight—

oxygen + *hydrochloric acid* ← *water* + *chlorine.*

The properties of hydriodic acid.—Gay-Lussac found that hydriodic acid was prepared more readily by combining iodine with phosphorus and decomposing the iodide with water. In this action water is decomposed; the oxygen unites with phosphorus to form phosphorous acid, whilst the hydrogen unites with iodine to form hydriodic acid. Gay-Lussac made a careful study of the acid and records its properties as follows:—

"Hydriodic gas decomposes as soon as it comes into contact with mercury; the surface of the metal becomes covered with a yellow-green substance, which is the iodide of mercury, and if the contact is sufficiently prolonged, or if it is shaken, the hydriodic acid is promptly decomposed; the iodine combines completely with the metal, and there remains a volume of hydrogen gas which is exactly the half of that of the hydriodic gas. I passed the gas over zinc and potassium, and the product was always hydrogen and an iodide. Thus, according to this analysis . . . there can remain no doubt as to the nature of hydriodic gas.

"This gas is colourless; its odour resembles that of hydrochloric gas; its taste is very acid; it contains half its volume of hydrogen, and saturates its own volume of ammonia. Chlorine removes its hydrogen instantly; a beautiful violet vapour is produced, and hydrochloric gas is formed" (*Ann. de Chimie*, 1814, **91**, 14—15).

C. Bromine.

Balard (1826) discovers bromine.—In a memoir "On a peculiar substance contained in sea-water" (*Ann. Chim. Phys.*, 1826, **32**, 337), **Balard**, a young French chemist,

described the discovery of a new member of the group of halogens :

"I have observed several times that, on treating with chlorine-water the extract of the iodine-containing ashes of seaweed, after having added a solution of starch, there appears not only a blue zone due to iodine, but above this a zone of bright yellow."

"This orange-yellow colour was shown also when I treated the mother-liquor of sea-salt in the same way. . . . The appearance of this hue was accompanied by a strong, peculiar smell."

"The saline mother-liquor, treated thus with chlorine, loses its colour and its characteristic smell by exposure to air during one or two days" (*loc. cit.* p. 337).

"The yellow saline liquor, submitted to distillation, liberated, during the first moments of boiling, thick, red vapours which condensed on cooling to a liquid, which retained most of the properties of the coloured liquor; but these properties were much more pronounced."

"In order to obtain this substance in a pure state, . . . I passed the red vapours over calcium chloride. They condensed in a small receiver, in volatile, deep-red drops, filling the little vessel in which they were contained with vapours comparable in colour with nitrous vapour" (*loc. cit.* pp. 338–339).

The aqueous liquid was decolorised by the action of alkalis, and by reducing agents such as zinc and sulphuric acid, sulphurous acid, hydrogen sulphide, and ammonia, but the colour could be restored by the addition of more chlorine. The properties of the substance suggested that it might be a new chloride of iodine, but it gave none of the usual tests for this element, and could not be decomposed, even by the electric arc. It appeared, indeed, to be an element, closely resembling chlorine and iodine, forming a series of analogous compounds, but clearly to be distinguished from these elements both in its physical properties and in its chemical actions.

On account of its odour the new element was described (*loc. cit.* p. 341) as BROMINE (Greek, *βρώμος*, a stink).

Liebig fails to recognise bromine as an element.—The German chemist **Liebig** (1803–1873), in a candid piece of autobiography, wrote in 1838:—

"I know a chemist who, while at Kreuznach, many years ago, undertook an investigation of the mother-liquor from the salt-works. He found iodine in it; he observed, moreover, that the iodide of starch turned of a fiery yellow by standing overnight. The phenomenon struck him; he procured a large quantity of the mother-liquor, saturated it with chlorine, and obtained by distillation a considerable amount of a liquor colouring starch yellow, and possessing the external properties of chloride of iodine, but differing in many of its reactions from the latter compound. He explained, however, every discrepancy most satisfactorily to himself; he contrived for himself a theory on it."

"Several months later he received the splendid paper of M. Balard, and, on the very same day, he was in a condition to publish a series of experiments on the behaviour of bromine with iron, platinum, and carbon, for Balard's bromine stood in his laboratory, labelled liquid chloride of iodine. Since that time, he makes no more theories unless they are supported and confirmed by unequivocal experiments; and I can positively assert that he has not fared badly by so doing" (*Ann. Chem. Pharm.*, 1838, **25**, 29–30; quoted by Hofmann, *Trans. Chem. Soc.*, 1875, **28**, 1098.)

D. CYANOGEN.

Scheele (1782) prepares prussic acid from prussian blue.—Prussian blue, or Berlin blue, was first described in 1710, as a product obtained by mixing *lixivium sanguinis*[1] with a salt of iron. Scheele, in 1782, distilled both Prussian blue itself and the *lixivium* from which it was made with vitriolic acid in a glass retort. The distillate was a watery liquor with a "peculiar smell and taste" (*Essays*, p. 237).

[1] An extract of calcined blood containing potassium ferrocyanide

When re-distilled from powdered chalk to free it from traces of oil of vitriol, the liquid appeared to be "neither acid nor alkaline," since it neither reddened paper dyed with litmus, nor restored the blue colour to a paper which had been reddened by acids. It combined with ammonia and with potash to form salts, but these were "decomposed by all acids," even by carbonic acid (*Essays*, p. 280). It formed salts with lime and magnesia, but was not able to liberate carbon dioxide from chalk.

On account of its origin and its power of forming salts, the French chemists, in 1787, described the liquid as PRUSSIC ACID, and its salts as PRUSSIATES (*Chemical Nomenclature*, tr. 1788, pp. 58 and 73).

Berthollet (1787) determines the composition of prussic acid.—Scheele found that the vapour of prussic acid was inflammable, and after combustion gave a precipitate with lime-water (*Essays*, p. 285). Ammonia could also be separated in many ways from the prussic compounds. Bergman therefore thought "that prussic acid is composed of carbonic acid, of volatile alkali, and of phlogiston."

Berthollet, in 1787 (*Mem. Acad. Sci.*, 1787, 148–162; compare *Ann. de Chimie*, 1789, **1**, 30–39), made a careful study of the acid, and especially of the action of chlorine upon it, and expressed his views as to its composition as follows:—

"I conclude from this, that hydrogen and azote exist in prussic acid, that they are combined with charcoal, and that, when oxygen is added, all the principles necessary for the formation of carbonate of ammonia are present together; but in order that they may take the form of ammonia and of carbonic acid, the concurrence is needed of alkali or of lime which tend to combine with the carbonic acid. . . ."

"It would seem to me then that there remains no doubt as to the composition of prussic acid. . . It is a compound of azote, of hydrogen, and of pure charcoal or carbon" (*loc. cit.*, p. 159; compare *Ann. de Chimie*, 1789, **1**, 37 and 38).

Gay-Lussac (1815) prepares and analyses anhydrous prussic acid.—Gay-Lussac, in 1811, (*Ann. de Chimie*, 1811, **77**, 128) prepared anhydrous prussic acid by distilling its mercury salt with concentrated hydrochloric acid. In his memoir "On Prussic Acid" (*Ann. de Chimie*, 1815, **95**, 136–231), he describes it as follows:—

"It is a colourless, odorous liquid, with a taste at first fresh, then burning . . . and a true poison. Its density at 7° is 0·7058; at 18°, 0·6969: it boils at 26·5°, and solidifies about 15° below the temperature of melting ice; it then crystallises regularly and sometimes assumes the fibrous form of nitrate of ammonia. The cold which it produces in vaporising, even in air at 20°, is sufficient to freeze it. This phenomenon is easily produced by putting a drop at the end of a slip of paper or a tube of glass. Although I rectified the acid several times over powdered marble, it always kept the property of reddening blue litmus paper slightly: the red colour disappeared as the acid evaporated" (*Ann. de Chimie*, 1815, **95**, 145–146).

The anhydrous acid was vaporised into oxygen and exploded in a Volta's eudiometer. It gave an equal volume of carbonic anhydride and half its volume of nitrogen; one and a quarter volumes of oxygen were used, of which one volume was required to produce one volume of carbonic anhydride, whilst the one-quarter volume was used in burning one-half a volume of hydrogen.

Gay-Lussac concluded that the acid "contained one volume of carbon-vapour, one-half volume of azote and one-half volume of hydrogen," but no oxygen. The correctness of this analysis was proved (1) by the density of the gas, (2) by passing it over iron heated in a porcelain tube, when carbon was deposited and a gaseous mixture of equal volumes of hydrogen and nitrogen was set free (*Ann. de Chimie*, 1815, **95**, 147–152).

Gay-Lussac regards prussic acid as a hydracid.—After completing his analyses, Gay-Lussac writes:—

"This acid, compared with the animal substances, is distinguished by the great quantity of azote which it contains, by less hydrogen, and above all by the absence of oxygen. Its acidifying properties cannot depend on hydrogen, which has an alkaline influence, but on carbon and nitrogen. It must be considered as a true hydracid, in which carbon and nitrogen replace the chlorine in hydrochloric acid, the iodine in hydriodic acid and the sulphur in hydrosulphuric acid"[1] (*Ann. de Chimie*, 1815, **95**, 155).

Gay-Lussac regards prussic acid as a derivative of the "compound radical" cyanogen.—**Gay-Lussac** found that prussic acid, when acted on by potassium, liberated half its volume of hydrogen and gave a salt, just as hydrochloric and hydriodic acids did in similar circumstances. He therefore suggested that it contained a COMPOUND RADICAL, CYANOGEN, which acted the part of the simple radicals, chlorine and iodine:

"There is, then, a very great analogy between prussic acid and hydrochloric and hydriodic acids: like them, it contains half its volume of hydrogen, and like them it has a radical which combines with potassium, and forms a compound quite analogous with the chloride and iodide of potassium: only this radical is compound, where chlorine and iodine are simple."

"It seemed to me to be necessary to create a new name to designate the radical of prussic acid. That of *cyanogen*[2] having seemed most suitable to the chemists of this capital, I have adopted it and shall use it in this memoir. Ordinary prussic acid will then receive the name of *hydrocyanic* acid and the prussiates that of *hydrocyanates*. The compounds of cyanogen with simple substances, when it plays the same rôle as chlorine in the chlorides, will be designated by the name of *cyanides*" (*Ann. de Chimie*, 1815, **95**, 161, and 162–163).

Gay-Lussac's view of the nature of the cyanogen-compounds was vindicated by the discovery of CYANOGEN GAS, which he

[1] *i.e.*, sulphuretted hydrogen. [2] Greek κύανος, blue.

obtained by heating mercuric cyanide (*loc. cit.* pp. 172–199). As one of the first examples of a "compound radical," it became of dominant importance in the development of structural chemistry during the ensuing forty years.

E. Hydracids and Halogens.

Gay-Lussac (1814) abandons the oxygen-theory of acids.—The discovery of hydriodic acid, confirming Davy's contention that muriatic acid was a simple hydride, containing no oxygen, made it necessary to abandon the limitations imposed by Lavoisier's oxygen-theory of acids. Gay-Lussac was impressed by the fact that sulphur, chlorine, and iodine could form acids by combining either with oxygen or with hydrogen. He suggested that these compounds should be distinguished as follows:

Oxygen-Acids	*Hydrogen-Acids*
SULPHURIC ACID	HYDROSULPHURIC ACID[1]
CHLORIC ACID	HYDROCHLORIC ACID
IODIC ACID	HYDRIODIC ACID.

"Like [sulphur and chlorine, iodine] forms two acids, the one by combining with oxygen, and the other by combining with hydrogen. . . . The compounds of chlorine, of iodine and of sulphur with hydrogen, which show the properties of the acids formed by oxygen, must be included in the same class under the same name of acid; but to distinguish them, I propose to add to the specific name of the acid, the generic word *hydro*; so that the acid compounds of hydrogen with chlorine, iodine and sulphur, would bear the name of hydrochloric acid, hydriodic acid, and hydrosulphuric acid; and the acid compounds of oxygen with the same substances, would have, according to the recognised principles of nomenclature, the names of chloric acid, iodic acid, etc." (*Ann. de Chimie*, 1814, **91**, 8–9).

[1] *i.e.*, sulphuretted hydrogen.

Gay-Lussac on Hydracids.—In a section on Acidity and Alkalinity, appended to his "Researches on Iodine," Gay-Lussac urged, as a general proposition, that the name "acid" must be extended to include a series of acidic hydrides, the HYDRACIDS, in addition to the well-known OXYACIDS.

"For a long time I have regarded an acid, in the most general sense of the word, as merely a substance, containing oxygen or not, which neutralises alkalinity, and an alkali likewise is only a body which neutralises acidity.

"Whatever may be the definition of acids at which one arrives, they must be formed into several groups, because they do not derive their acid character from the same substance. We have:

"1. The acids properly so-called, in which oxygen may be considered as the acidifying principle, and which contain only two elements; such as . . . sulphuric, sulphurous, . . . carbonic acids.[1]

"2. Acids formed by hydrogen and another substance: this group includes the hydrochloric, hydriodic, and hydrosulphuric[2] acids. It is probable that in these acids, chlorine iodine and sulphur are the acidifying principles; but as hydrogen is present in all of them, I thought it was more convenient to derive their generic name from it. These different acids can be designated by the name of *hydracids*" (*Ann. de Chimie*, 1814, **91**, 145, 147, 148).

Berzelius (1825) on halogens and haloid-salts.—Gay-Lussac's dual classification of the acids was accepted by Berzelius. It carried with it the recognition of two types of salts, since the union of two oxides produced a *ternary* salt, whilst the interaction of an acidic hydride with a basic oxide gave rise to a *binary* salt *and water*. He therefore proposed in 1825[3] to describe the binary compounds as HALOID SALTS, and their non-metallic components as HALOGENS.

[1] *i.e.*, sulphuric, sulphurous, and carbonic anhydrides.
[2] *i.e.*, sulphuretted hydrogen.
[3] The Swedish paper was translated into French in 1826.

"What we call a *salt* must be defined according to a certain electro-chemical relation and without any regard to the number of the constituent elements. Thus we say that the compound of chlorine with sodium is a salt, because these two substances completely neutralise the electro-chemical properties of one another. . . .

"According to this view, electro-negative substances may be divided into three classes. First: those which form salts by neutralising the electro-positive metals: I call these *halogens* (salt-producers); they are chlorine, iodine, and fluorine. . . ."

"Salts may be divided into two classes: those which result from the combination of a halogen with an electro-positive metal, and those which are formed by the union of an acid with a base: I will call the first *haloid-salts*, and the second *amphi-salts*" ("Memoir on Sulpho-salts," *Ann. Chim. Phys.*, 1826, **32**, 62—63 and 65).

In the second class of salts Berzelius included not only *oxy-salts* formed from two oxides, but *sulpho-salts* formed from two sulphides, etc. The discovery of bromine in the following year completed the series of four halogen-elements (fluorine, chlorine, bromine and iodine), and added a new group of haloid-salts, but did not lead to any further theoretical developments.

The hydrogen-theory of acids.—The uniformity of composition, which was implied in Lavoisier's oxygen-theory of acids, was destroyed by the discovery of the hydracids. It was restored later by a theory which regarded all acids as hydrogen compounds.

The "hydrogen theory" of acids was foreshadowed, in 1816, by Davy (*Works*, V. 514—515), who regarded it as "a simple statement of facts to say that liquid nitric acid is a compound of . . . hydrogen . . . azote and . . . oxygen," and suggested that "hydrogen in [an] acid, may be considered as acting the part" played by a metal in the salts derived from it.

A very clear statement was made by **Auguste Laurent** (1807—1853), who regarded all acids as salts of hydrogen, strictly analogous with the salts of silver or zinc, but differing from them in taste and volatility.

After considering the general resemblance between the compounds of zinc and those of an element **X**, which turns out to be hydrogen, he writes:—

"If hydrogen had been a comparatively fixed body, and its oxide fixed and solid, no one would have thought of excluding it from the metals. . . .

"Dumas has even gone so far as to conceive, that if we could but condense hydrogen, it would present a metallic aspect.[1] . . .

"For my part I do not see any difference between acids (meaning thereby the salts of hydrogen) and ordinary salts; neither do I recognise any difference between these two kinds of bodies, and the group of oxides in general" (*Chemical Method*, Cavendish Society Reprints, 1854, 41).

In Laurent's opinion, there is a profound difference between the acids as salts of hydrogen and the oxides from which many of them are derived by the addition of water.

"Having thus associated certain compounds, which chemists separate, I proceed now to separate certain other compounds which they associate. The anhydrous and the hydrated acids are always confounded and employed, theoretically at least, the one for the other. Nevertheless, these bodies do not present any analogy; under no circumstances whatever, do they comport themselves in the same manner: their functions are entirely different. Take for example the anhydrous sulphuric acid and the sulphate of hydrogen. The first does not combine with metals; the second does combine with them, at the same time liberating hydrogen. The first unites directly with the metallic oxides;

[1] Liquid hydrogen, which Dumas described as "hydrogenium" to indicate its metallic character, is not a metal, but resembles the paraffins, to which series it really belongs.

the second gives rise to a double decomposition. The first does not decompose chlorides, and even combines with some of them; whereas the second decomposes them. . . .

"The anhydrous and the hydrated acids, then, have not any analogy with one another, and ought to be placed in two perfectly distinct classes. . . .

"The anhydrous and the hydrated sulphuric acid have this in common: they both contain sulphur and oxygen; but with regard to analogy of properties, they do not manifest any whatever" (*Chemical Method*, 44 and 45).

Acids and acid anhydrides.—At the close of his "Chemical Method" (pp. 376—377) Laurent describes the acidic oxides as ANHYDRIDES, derived from the acids directly or indirectly by the removal of water. Laurent's views on the nature of acids were soon accepted; thus, in 1864, the following footnote was added to the third edition of Miller's "Elements of Chemistry" (Part II. p. 4):

"The term acid has been employed by chemical writers up to a late period, to designate indifferently either the anhydrous bodies formed by the union of oxygen with the non-metallic elements . . . (now more commonly called *anhydrides* . . .) or the hydrated compounds produced by the action of water upon the anhydrides, such as . . . oil of vitriol or sulphuric acid. To avoid this confusion, produced by the application of the same term to two substances essentially distinct, it will be convenient to follow the practice of many later authors, and to limit the term acid to those hydrated bodies which are really salts of hydrogen."

The system of nomenclature introduced by Laurent has persisted to the present day. The oxides of sulphur are described as SULPHUROUS ANHYDRIDE and SULPHURIC ANHYDRIDE, whilst the names SULPHUROUS ACID and SULPHURIC ACID are restricted to the hydrated acids formed by combining the oxides with water to form hydrogen sulphite and hydrogen sulphate respectively. So too the acidic oxide

of carbon is called CARBONIC ANHYDRIDE instead of carbonic acid, whilst the name CARBONIC ACID is applied to an unstable hydrate, hydrogen carbonate, which is produced when the gas is dissolved in water.

SUMMARY AND SUPPLEMENT

A. FLUORINE

Davy in 1813–14 recognised the presence in *fluorspar* (calcium fluoride, CaF_2) and in *hydrofluoric acid* (hydrogen fluoride, HF; described by Scheele in 1771 as "fluor acid") of an element *fluorine*, closely resembling chlorine. The analogy between hydrofluoric acid and hydrochloric acid appears in its physical properties, in its method of preparation :

$$\underset{\text{(Fluor-spar.)}}{CaF_2} + H_2SO_4 \rightarrow CaSO_4 + \underset{\text{(Hydrofluoric acid.)}}{2HF}.$$

$$\underset{\text{(Rock-salt.)}}{2NaCl} + H_2SO_4 \rightarrow Na_2SO_4 + \underset{\text{(Hydrochloric acid.)}}{2HCl}.$$

and in the action of metals upon it :

$$2HF + 2K \rightarrow 2KF + H_2,$$
$$2HCl + 2K \rightarrow 2KCl + H_2;$$

but mainly in the fact that no oxygen can be extracted from any of the fluoric compounds. The acid acts readily on the silica present in glass :

$$\underset{\text{(Silica.)}}{4HF + SiO_2} \rightleftharpoons \underset{\text{(Silicon tetrafluoride.)}}{SiF_4} + 2H_2O,$$

giving rise to a gas, silicon tetrafluoride, SiF_4, which is decomposed again by water, somewhat in the manner indicated by the lower arrow in the above equation; the actual product of the decomposition by water is, however, a *hydrosilicofluoric acid* :

$$(SiF_4 + 2HF = H_2SiF_6)$$

formed according to the equation :

$$2SiF_4 + 2H_2O = H_2SiF_6 + SiO_2 + 2HF,$$

(Hydrosilicofluoric acid.)

Davy attempted to isolate fluorine by passing an electric current through hydrofluoric acid. This method was used successfully by **Moissan** in 1886 (*Ann. Chim. Phys.* 1887, [vi], **12**, 473). An electric current was passed through a

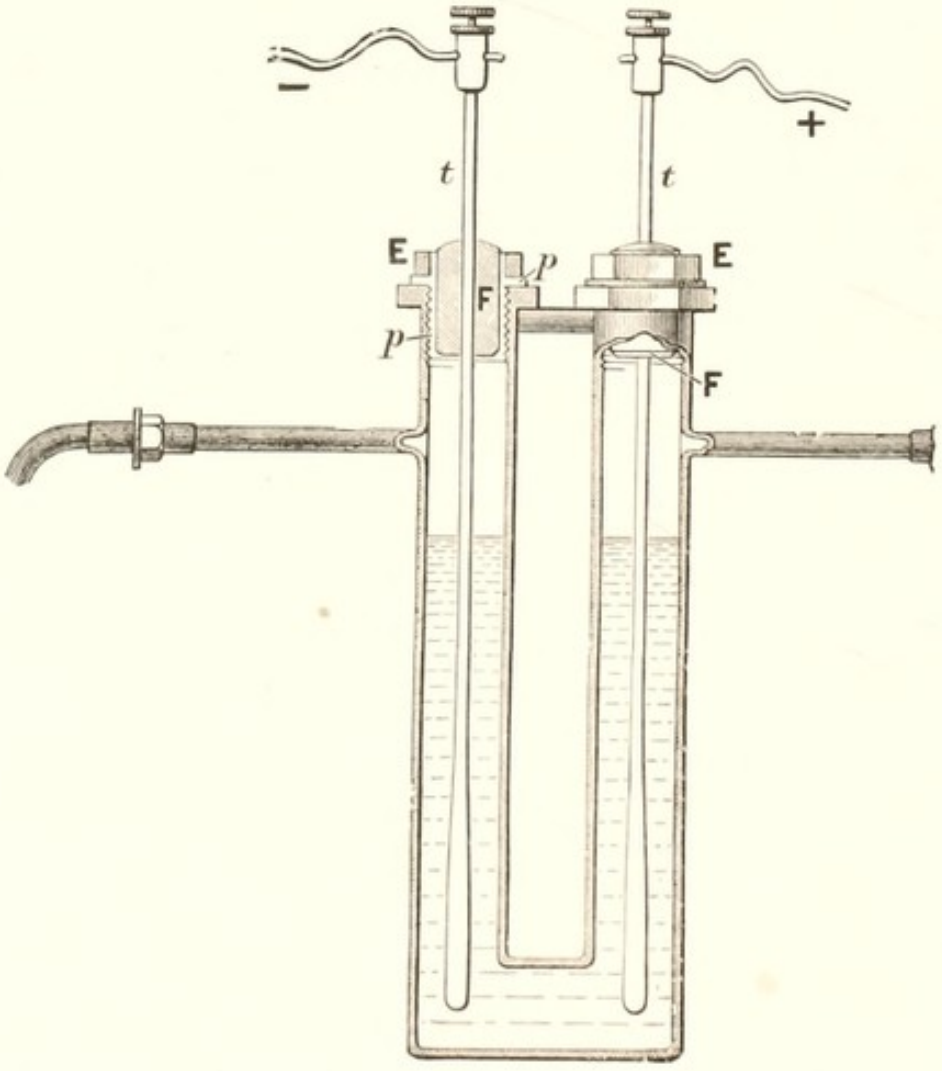


FIG. 42.—MOISSAN'S APPARATUS FOR PREPARING FLUORINE.

mixture of hydrogen fluoride and potassium fluoride, contained in a platinum U-tube (Fig. 42), and cooled to −23° C. by the evaporation of methyl chloride. The electrodes, *tt*, of platinum iridium alloy, were insulated from the U-tube by stoppers, FF, of fluorspar, the joints being made

air-tight by leaden washers, *p*, screwed down by brass caps, E. Hydrogen was liberated at the negative and fluorine at the positive electrode. It is a light-yellow gas, condensing to a liquid at $-187°$ C., and crystallising to a pale yellow solid at $-233°$C. It is a very active gas, unites explosively with hydrogen, and at once decomposes water, forming hydrofluoric acid, ignites charcoal, combines vigorously with phosphorus, liberates chlorine from potassium chloride, and unites directly with nearly all the metals, but has no marked action on dry glass.

B. Iodine

Iodine, discovered by **Courtois** in 1811 in the ashes of seaweed, resembles chlorine in its properties, and in its resistance to all efforts to effect its decomposition. It was examined by **Clément**, by **Gay-Lussac**, and by **Davy**, four memoirs on iodine being published within a fortnight at the close of 1813. The beautiful violet vapour is not decomposed by passing through a red-hot tube, alone or with oxygen, nor by the action of white-hot charcoal. But it unites directly with the metals to form fusible *iodides*. It also unites with sulphur and phosphorus ; with chlorine it forms a solid yellow chloride ICl. It unites directly at a red heat with hydrogen to form gaseous *hydrogen iodide* or *hydriodic acid*, but this action is reversible as the acid is decomposed partially by the same treatment :

$$H_2 + I_2 \rightleftarrows 2HI.$$
(Hydrogen iodide.)

Hydriodic acid is prepared more easily by the action of water on iodide of phosphorus :

$$2PI_3 + 6H_2O \rightarrow 2H_3PO_3 + 6HI,$$
(Phosphorous acid.) (Hydriodic acid.)

or by the action of sulphuretted hydrogen on iodine suspended in water :

$$SH_2 + I_2 \rightarrow S + 2HI.$$

The gas is intensely soluble in water, giving rise to a fuming

acid. It is decomposed by metals, liberating half its volume of hydrogen, *e.g.* :

$$2Hg + 2HI \rightarrow \underset{\text{(Mercurous iodide.)}}{Hg_2I_2} + H_2.$$

With ammonia, iodine interacts to form an explosive black compound, *nitrogen iodide*, NH_3,NI_3. With potash it gives a mixture of *potassium iodide* and *potassium iodate* (compare the preparation of potassium chlorate) :

$$3I_2 + 6KOH \rightarrow \underset{\text{(Potassium iodide.)}}{5KI} + \underset{\text{(Potassium iodate.)}}{KIO_3} + 3H_2O$$

When this mixture is acidified iodine is reproduced,

$$\underset{\text{(Hydriodic acid.)}}{5HI} + \underset{\text{(Iodic acid.)}}{HIO_3} \rightarrow 3I_2 + 3H_2O,$$

but *iodic acid*, HIO_3, can be prepared by the action of sulphuric acid on barium iodate,

$$Ba(IO_3)_2 + H_2SO_4 \rightarrow BaSO_4 + 2HIO_3$$

or by dissolving iodine in nitric acid :

$$3I_2 + 10HNO_3 \rightarrow 6HIO_3 + 10NO + 2H_2O\ ;$$

when dried at 200° iodic acid loses water and is converted into *iodic anhydride*, I_2O_5. A stable *periodic acid*, $HIO_4,2H_2O$, and a very unstable *hypoiodous acid*, HIO, are also known.

C. Bromine

Bromine, discovered by **Balard** in 1826, is a volatile red-brown liquid, intermediate in its properties between chlorine and iodine.

D. Cyanogen

Scheele (1782), by the action of oil of vitriol on Prussian blue, obtained a volatile acid, weaker than carbonic acid, to which the French chemists in 1787 gave the name *prussic acid*. He

showed that it was inflammable and gave carbon dioxide when burnt.

Berthollet (1787), by acting on prussic acid successively with chlorine and an alkali, oxidised prussic acid to carbonic acid and ammonia, and concluded that it was a compound of hydrogen, carbon, and nitrogen. The action is expressed by the following equations :

$$\underset{\text{(Prussic acid.)}}{HCN} + Cl_2 \rightarrow \underset{\text{(Cyanogen chloride.)}}{CNCl} + HCl$$

$$CNCl + KOH + H_2O \rightarrow CO_2 + NH_3 + KCl.$$

Gay-Lussac (1811), by distilling the mercury salt of the acid with hydrochloric acid, obtained anhydrous prussic acid as a liquid boiling at 26·5° C. and freezing at −15° C. In 1815, he exploded the vapour with oxygen and found that it gave 1 *vol.* carbonic anhydride, and $\frac{1}{2}$ *vol.* nitrogen, and that an additional $\frac{1}{4}$ *vol.* of oxygen was used to burn $\frac{1}{2}$ *vol.* of hydrogen to water. The actual figures for 100 *vols.* of vapour were :

Contraction	= 78·5 vols.
Contraction by potash	= 101·0 vols.
Nitrogen	= 46·0 vols.
Oxygen used	about 125 vols.

These numbers agree approximately with those required by the equation :

$$\underset{4\ vols.}{4HCN} + \underset{5\ vols.}{5O_2} \rightarrow \underset{4\ vols.}{4CO_2} + \underset{2\ vols.}{2N_2} + \underset{liquid}{2H_2O} \quad \underset{= 3\ vols.}{Contraction}$$

Gay-Lussac was struck by the analogy of prussic acid with hydrochloric and hydriodic acids and suggested that it contained a "compound radical" *cyanogen* which acted the part of the simple radicals chlorine and iodine. Prussic acid was therefore called *hydrocyanic acid* and its salts became known as *cyanides*. Typical formulæ are :

Hydrocyanic acid (compare HCl),	HCN
Potassium cyanide (sol. like KCl),	KCN
Silver cyanide (insol. like AgCl),	AgCN
Mercuric cyanide (compare $HgCl_2$),	HgC_2N_2.

These formulæ are often written, HCy, KCy, AgCy, $HgCy_2$, to bring out their close analogy with HCl, KCl, AgCl, $HgCl_2$,

the symbol Cy being used as an abbreviation for the cyanogen radical CN. Gay-Lussac prepared *cyanogen gas* by heating mercuric cyanide :

$$HgC_2N_2 \rightarrow Hg + C_2N_2.$$

E. Hydracids and Halogens

Iodine was recognised as an element both by Davy and by Gay-Lussac ; its acid hydride was therefore a binary compound, containing no oxygen. **Gay-Lussac** (1814) proposed to divide the acids into two groups, namely :—

(1) the *oxy-acids* (SO_2, SO_3, CO_2, etc.), and

(2) the *hydro-acids*, including in the latter group *hydrochloric acid* (HCl), *hydriodic acid* (HI), and "*hydrosulphuric acid*" (sulphuretted hydrogen, H_2S) ; *hydrofluoric acid* (HF) and *hydrocyanic acid* (prussic acid, HCN) were soon added to the second group of acids.

Berzelius (1825) recognised the existence of two corresponding series of salts, namely :—

(1) *amphi-salts*, which were ternary compounds, formed by the union of an acidic and a basic oxide, sulphide or selenide, and

(2) *haloid-salts* (*e.g.* common salt, NaCl), which were binary compounds of a metal with a *halogen*, fluorine, chlorine,[1] iodine, etc.

Laurent (1854), following **Davy** (1816), regarded all acids as salts of hydrogen ; sulphuric acid was then *hydrogen sulphate*, H_2SO_4, whilst the oxide (SO_3) which had been regarded previously as sulphuric acid was now called *sulphuric anhydride* ; so, too, *carbonic acid* was H_2CO_3 (compare Na_2CO_3) whilst the oxide (CO_2) was called *carbonic anhydride*.

[1] Bromine was not discovered until the following year.

CHAPTER XIII

THE DECOMPOSITION OF THE ALKALIS

A. The Composition of Ammonia

Alkalis regarded as elements.—At the time when Priestley succeeded in collecting "acid air" and "alkaline air" over mercury as permanently-elastic gases, there was no reason for supposing that either of these gases was other than a simple substance. The fixed alkalis were also still undecomposed and were generally thought to be simple, or elementary, substances.[1] Thus Higgins, in a treatise, "On Bleaching," published in 1799 (p. 18), writes:

"Pure pot-ash, according to our present knowledge of chemistry, is a simple elementary substance."

The first alkali to be decomposed was the volatile alkali which Priestley called "Alkaline air," and Bergman "Ammonia." The decomposition was effected almost simultaneously by Priestley himself and by Scheele, Bergman's illustrious pupil.[2]

Priestley (1775) decomposes "alkaline air."—Priestley, in 1773, found that "alkaline air" was inflammable. In

[1] Lavoisier, however, suspected that they might be compound (see below, p. 280).

[2] "It was well observed to me by a near relation of Bergman that *the greatest of Bergman's discoveries* was the discovery of Scheele" (Thomas Beddoes, 1786).

1775 he discovered further that it was decomposed by electric sparks, increasing largely in volume, and was thus converted into an inflammable gas which was insoluble in water.

"I dipped a lighted candle into a tall cylindrical vessel, filled with alkaline air, when it went out three or four times successively; but at each time the flame was considerably enlarged, by the addition of another flame, of a pale yellow colour; and at the last time this light flame descended from the top of the vessel to the bottom. At another time, upon presenting a lighted candle to the mouth of the same vessel, filled with the same kind of air, the yellowish flame ascended two inches higher than the flame of the candle. The electric spark taken in alkaline air is red, as it is in common inflammable air" (Priestley, *Experiments on Air*, I. 175).

"I took the electric explosion in a small quantity of *alkaline air*, in the same manner as in the two preceding experiments, and observed that every stroke added considerably to the quantity of air; and when water was admitted to it, just as much remained unabsorbed as had been added by the explosions. I then took about an hundred explosions of the same jar, in a larger quantity of alkaline air; after which, so much of it remained unabsorbed by water, that I could examine it with the greatest certainty. It neither affected common air, nor was affected by nitrous air, and was as strongly inflammable as any air that I had ever produced" (*Experiments on Air*, II. 239–240).

Scheele (1774) oxidises ammonia by means of "manganese."—The inflammable nature of ammonia was also recognised by Scheele in his essay "On Manganese" (1774). It has been shown in a preceding chapter (p. 210) that this mineral dissolves in dilute acids only in presence of reducing or deoxidising agents, substances "rich in phlogiston," as Scheele described them. Amongst these substances was the volatile alkali ammonia, the salts of which were able to dissolve the mineral when acids alone failed to act upon it.

The ammonia was, therefore, a "phlogisticated" or combustible substance.

Scheele also collected the non-inflammable constituent of ammonia, and showed that it was an inert gas resembling "phlogisticated air" or azote.

"If finely powdered manganese be exposed with pure [nitric] acid, and some volatile alkali, to digestion for several weeks, you will observe a great number of air bubbles rise to the surface. This kind of air, collected in a bladder tied to the neck of the flask, is not aerial acid [*i.e.* carbonic anhydride], but of a quite different nature. During the digestion, the volatile alkali is entirely decomposed; for if the solution be mixed and distilled with a sufficient quantity of quicklime, not the least smell of volatile alkali appears in the receiver. In this process, the phlogiston, one of the constituent parts of volatile alkali, has combined with the manganese, and thus rendered the acid of nitre capable of acting upon the manganese. The elastic fluid, collected in the bladder, has been either separated from the volatile alkali, and is then its other constituent part, or it is a product arising from its decomposition. That the nitrous acid has no share here is clearly proved by the following process:

"I repeated the very same distillation with manganese and sal-ammoniac. . . . It happened here as I expected; I obtained the same kind of air in the bladder as in the preceding experiment" (Scheele's *Essays*, p. 83).

Scheele (1777) oxidises ammonia by the calx of gold.—Scheele prepared the same inert gas by detonating FULMINATING GOLD. This substance is a compound of the volatile alkali with calx of gold, prepared by adding the volatile alkali to a solution of gold in aqua regia. It had been known from the time of Basil Valentine to possess the property of detonating violently when heated. Bergman determined its composition by precipitating the calx of gold by means of a fixed alkali, and then converting it into "aurum fulminans" by the action of ammonia, or of one of its salts

("On the Fulminating Calx of Gold," Bergman's *Essays*, II., 134–165; pp. 155, 156). He also drove off the volatile alkali by gentle heat, when the gold lost its power of detonating (*loc. cit.* p. 145), and remained in the form of an inert calx, the "aurum mutum" of the alchemists. When the fulminate is detonated, the oxygen of the calx combines with the inflammable constituent of the ammonia, the inert, gaseous constituent is suddenly set free, and a residue of metallic gold remains.

Scheele in the course of his *Experiments on Air and Fire* confirmed Bergman's observations and actually extracted a small quantity of ammonia from the fulminate. Following Bergman he detonated half a drachm of fulminating gold over water and obtained six ounce-measures of a gas, which had the following properties:

"(1) It was not miscible with water.
"(2) It did not precipitate lime-water.
"(3) It extinguished immediately the flame of a burning candle; and was consequently air, in every respect, similar to that generated by the destruction of volatile alkali" (*Experiments on Air and Fire*, tr. J. R. Forster, 1780, pp. 142–143).

The liberation of gas by the action of chlorine on ammonia is noted in his essay "On Manganese" (*Essays*, p. 71).

Berthollet (1785) proves that ammonia is a compound of hydrogen and nitrogen.—To the French chemist Berthollet belongs the credit of proving definitely in 1785 that the inflammable constituent of ammonia is hydrogen, and the inert constituent nitrogen. He also made an accurate quantitative analysis of the gas.

The nature of the inflammable constituent was determined by neutralising the ammonia with nitric acid and heating the crystalline nitrate thus produced. Nitrous oxide was set free, and a considerable volume of water was condensed.

The formation of water was attributed to the oxidation of the inflammable constituent of the ammonia by the oxygen of the acid. Berthollet concluded from this experiment that "the inflammable gas of water is a constituent part of the volatile alkali" (*Mem. Acad. Sci.*, Paris, 1785, **99**, 319).

The inert constituent was first examined as a product of the action of chlorine on ammonia.

"The gas obtained from a mixture of volatile alkali and [chlorine] showed all the negative properties which characterise phlogisticated air or atmospheric [azote].[1] . . . It follows that the volatile alkali is a compound of inflammable air and [azote], and this result will be confirmed by the experiments which will follow" (*ibid.* p. 320).

A more careful study of the gas from fulminating gold proved that this gas was actually nitrogen.

"I made use of the gas which is set free in the detonation of fulminating gold, in order to assure myself that it is really [azote] that is contained in the volatile alkali; to obtain it pure I filled a small glass retort with boiled water, in which I placed the fulminating gold; I distilled this water at the pneumatic trough; when the retort was dry, most of the fulminating gold detonated, and although there were seven grains of it, the retort was not broken, because the mouth was free; by plunging the retort into water I collected the gas which had been set free; I mixed it with the proportions of vital air indicated by Cavendish; I submitted this mixture to the action of electricity, and the diminution which it experienced was similar to that which one obtains when dealing with atmospheric [azote]" (*ibid.* pp. 321—322).

"One can now explain the properties of fulminating gold: the gold is there present as a calx, that is to say, united with vital air; it is also combined with volatile alkali, as Bergman has so well shown; the inflammable gas of the volatile alkali forms water with the vital air, its

[1] "Mofette" is the word used in the original paper.

[azote] is suddenly liberated and the metal is revived" (*ibid.* p. 321).

Although the actual conversion into nitre of the nitrogen of the volatile alkali was not realised in this experiment, Berthollet was able to quote two cases in which the converse change had been effected, since ammonia had actually been prepared by the action of zinc on a solution of nitre, and by the action of a fixed alkali on the products of interaction of tin and nitric acid. "It is necessary to note that in each case nitric acid was present which must have provided the [azote]" (*ibid.* p. 326).

Berthollet's analysis of ammonia.—In a paper published in the *Journal de Physique* for April, 1786, vol. **28**, p. 273, Berthollet compared the weight of ammonia driven off by gentle heat from fulminating gold, with the weight of water produced when the fulminate was detonated; he "concluded that the inflammable gas formed almost one-sixth by weight . . . of the volatile alkali," the proportion now accepted as correct being 3/17 instead of 3/18. In 1785[1] he carried out a volumetric analysis which showed that two volumes of ammonia gas were increased to four volumes by sparking, and that these four volumes consisted of nearly three parts of hydrogen with one part of nitrogen.

"We made some alkaline gas from a mixture of one part of sal-ammoniac and three to four parts of freshly-burnt lime, so that it should be free from water . . .: we introduced it into a glass tube provided with an exciter; the space which it occupied was . . . 1·7 cubic inches. It was electrified until an increase in volume was no longer perceptible; after that, a little water was introduced into the tube, and no absorption was perceived, although it was shaken, so that the alkaline gas was completely decomposed; the increase of its volume was 1·6 cubic inches; then the

[1] The paper was not published till 1788.

gas was introduced into a Volta eudiometer, mixing each measure successively with vital air, and detonating after each addition, in the following manner :

"(1) Two measures of vital air.
One measure of decomposed alkaline gas.
(2) One measure of vital air.
One measure of gas.
(3) Two measures of vital air.
One measure of gas.
(4) One measure of gas.
Total : five measures of vital air and four measures of gas.

"These nine measures were reduced to 4·6 measures, so that 4·4 measures were destroyed. Care was taken, in this experiment, to put an excess of vital air in order to be sure of destroying all the combustible part ; but one knows that combustion causes 145 measures of inflammable gas to disappear for 74 of vital air. It follows then that the 4·4 measures destroyed represent 2·9 measures of inflammable gas and 1·5 measures of vital air. The four measures of electrified gas which were tested, would then represent 2·9 measures of inflammable gas and 1·1 of [azote]" (*Mem. Acad. Sci.*, Paris, 1785, **99**, p. 324).

St. Claire Deville in 1865 showed that the decomposition of ammonia into nitrogen and hydrogen is not quite complete (*see* Chapter XX). The decomposition is, in fact, another example of a balanced action, as may be indicated by the reversible equation,

$$\text{Ammonia} \rightleftharpoons \text{nitrogen} + \text{hydrogen}.$$

The proportion of ammonia which persists is so small that Berthollet failed to detect any contraction of volume on adding water to the gas.[1]

The composition of sal-ammoniac.—When Priestley had prepared "acid air" and "alkaline air," he tried the experi-

[1] The evaporation of water into the dry gas would produce an increase of volume which would compensate for the decrease of volume due to the absorption of a little undecomposed ammonia.

ment of mixing them, expecting that common air might be produced. Instead, he obtained a crystalline deposit of sal-ammoniac. This salt is, therefore, a compound of the two gases with one another. In 1809, Gay-Lussac showed (A.C.R. IV. 10) that sal-ammoniac is formed by the union of ammonia and of hydrogen chloride in equal volumes.

Both gases, although regarded as simple substances when they were first prepared, were afterwards shown to be compounds containing hydrogen. Sal-ammoniac is, therefore, a ternary compound of nitrogen, hydrogen and chlorine:

$$\text{SAL-AMMONIAC} = \begin{cases} \text{AMMONIA} = \begin{cases} \text{NITROGEN} \\ \text{HYDROGEN} \end{cases} \\ \text{MURIATIC ACID GAS} = \begin{cases} \text{HYDROGEN} \\ \text{CHLORINE} \end{cases} \end{cases}$$

It is analogous with the oxygen-salts such as:

$$\text{SULPHATE OF COPPER} = \begin{cases} \text{COPPER OXIDE} = \begin{cases} \text{COPPER} \\ \text{OXYGEN} \end{cases} \\ \text{SULPHURIC ANHYDRIDE} = \begin{cases} \text{OXYGEN} \\ \text{SULPHUR} \end{cases} \end{cases}$$

but differs from them in being formed by the union of two hydrides instead of two oxides. Such salts were described as hydrogen- or HYDRO-SALTS, in contrast with the better-known oxygen- or OXY-SALTS (see, for instance, Turner's "Chemistry," 1847, I. 566).

Davy (1807) suspects the presence of oxygen in ammonia.—Davy's success in isolating metals from the fixed alkalis (see below, pp. 273–280) led him, in 1807, to suspect that the volatile alkali might also contain a metallic constituent in combination with oxygen and hydrogen.

"As the two fixed alkalies contain a small quantity of oxygen united to peculiar bases, may not the volatile alkali likewise contain it? was a query which soon occurred to me in the course of inquiry; and in perusing the accounts of the various experiments made on the subject, some of which I had carefully repeated, I saw no reason to consider the circumstance as impossible" (Davy's *Works*, V. 92).

He made many attempts to prepare oxygen from nitrogen or water from ammonia, but concluded at last that these could not be produced from the pure dry gases. The presence of oxygen in nitrogen was, however, accepted by Berzelius up to about 1820, both chlorine and nitrogen being tabulated as oxides in his essay on "Chemical Proportions" in 1819. Davy (1812) also suspected the presence of hydrogen in sulphur and phosphorus and, by analogy, in inflammable substances and metals generally (*Works*, IV. 358–359). These tentative hypotheses are of interest as showing the great difficulty of establishing the elementary character of any given substance.

Seebeck (1808) prepares an amalgam from ammonia.— Davy's views as to the composition of ammonia led him to attach great importance to the discovery of a metallic amalgam prepared from it by the action of an electric current. Berzelius and Hisinger had found (*Ann. de Chimie*, 1804, **51**, 167) that concentrated aqueous ammonia was decomposed into nitrogen and hydrogen by passing an electric current through it, between platinum wires. Seebeck at Jena and Berzelius and Pontin (Gilbert's *Annalen*, 1810, **6**, 247–280) at Stockholm, discovered early in 1808 that an amalgam was produced, instead of hydrogen, when mercury was substituted for platinum. The amalgam was examined immediately by Davy, who included a section "On the production of an Amalgam from Ammonia" (*Works*, V. 122) in a paper on the Decomposition of the Earths, read before the Royal Society on June 30, 1808. Davy describes its preparation and properties as follows:

"When a globule of pure mercury is negatively electrified by a Voltaic apparatus of 100 pairs of plates, it being in contact with solution of ammonia in a cavity made in a piece of muriate of ammonia, or any ammoniacal salt, moistened in such a manner, and so placed on a disc of platina, that the circuit is completed; the globule increases

rapidly in volume, the quicksilver loses its fluidity, and at length becomes of the consistency of soft butter, and arborescent crystallisations shoot from it, which are quite solid. The amalgam so formed has perfectly metallic properties. It effervesces copiously when thrown into water, hydrogen gas is given off, and a solution of ammonia is found in the water. When exposed to the air it gradually loses its consistence; it emits a strong odour of ammonia, and reddens paper tinged with turmeric held above it; and at last is found merely quicksilver.

"I found a still more easy mode of making the amalgam by employing mercury combined with a minute quantity of potassium, sodium or barium.[1] When a compound of this kind is placed in contact with a solution of ammonia, or any moistened ammoniacal salt, it enlarges to eight or ten times its bulk, and becomes a soft solid, and may be preserved for a much longer time than the amalgam formed by electrical powers; it changes very slowly even under water" (*Works*, IV. 353–354; the quotation is from Davy's "Elements of Chemical Philosophy," published in 1812).

Composition of the amalgam from ammonia.—Davy thought at first that the amalgam might have been formed by deoxidation of ammonia and "attempted to procure a peculiar metallic substance from it by distillation out of the contact of air, but without success; . . . on the application of heat, hydrogen and ammonia were always evolved, and the mercury recovered its former state. . . . In the most accurate experiments the proportions of ammonia and hydrogen were two to one by volume" (*Works*, IV. 355).

As these products were formed, even from carefully-dried amalgam, he was obliged to adopt the alternative view of Gay-Lussac and Thenard that "the amalgam consists of mercury united to azote and hydrogen, the hydrogen being in larger proportion than in ammonia" (*Works*, IV. 354). Since two volumes of ammonia contained one volume of nitrogen and three volumes of hydrogen, the compound

[1] See below, pp. 275, 278, 281.

present in the amalgam (which contained two volumes of ammonia in combination with one volume of hydrogen) was composed of one volume of nitrogen united to four volumes of hydrogen.

Davy (1808) suggests the name "Ammonium."—In suggesting the name AMMONIUM for the substance present in the amalgam Davy writes :

"The more the properties of the amalgam obtained from ammonia are considered, the more extraordinary do they appear.

"Mercury by combination with about $\frac{1}{12000}$ part of its weight of new matter, is rendered a solid, yet has its specific gravity diminished from 13·5 to less than 3, and it retains all its metallic characters ; its colour, lustre, opacity, and conducting power remain unimpaired.

"It is scarcely possible to conceive that a substance which forms with mercury so perfect an amalgam, should not be metallic in its own nature ; and on this idea to assist the discussion concerning it, it may be conveniently termed *ammonium*" (*Works*, V. 130–131).

Ampère (1816) and Berzelius (1823) on the ammonium radical.—The discovery of ammonium amalgam had the effect of emphasising the close analogy of the compounds of ammonia with those of the alkali metals. Ampère in 1816 pointed out that the salts of the fixed and volatile alkalies would be strictly analogous if the "ammonium" of Seebeck's amalgam were regarded as the metallic base of the salts of ammonia.

"This difficulty would disappear by admitting that . . . the compound of one volume of nitrogen and four volumes of hydrogen, which is united to mercury in the amalgam discovered by Seebeck, and to chlorine in the hydrochloride of ammonia, behaves as a metal in all the compounds which it forms ; in such a way that a volume of ammonia gas combined with half a volume of water-vapour would be considered as a sort of oxide ; with half a volume of

sulphuretted hydrogen as a sulphide . . .; finally with a volume of hydrochloric or hydriodic gas, as a chloride or iodide of this compound metal" ("On a Natural Classification of Simple Substances," *Ann. Chim. Phys.*, 1816, **2**, 16, footnote).

According to Ampère's view the composition of sal-ammoniac should be represented as follows:

$$\text{SAL-AMMONIAC} = \begin{cases} \text{AMMONIA} = \begin{cases} \text{NITROGEN} \\ \text{HYDROGEN} \end{cases} = \text{AMMONIUM} \\ \text{MURIATIC GAS} = \begin{cases} \text{CHLORINE} = \text{CHLORINE} \end{cases} \end{cases}$$

This view was supported by the analogy of cyanogen (p. 245), a poisonous gas containing nitrogen and carbon, which "although a compound substance, shows all the properties of the simple substances [chlorine, iodine, sulphur, etc.] capable of acidifying hydrogen."

Berzelius, convinced at last that ammonia contained no oxygen, adopted Ampère's view, and in 1823 (*Jahresbericht*, 1823, **2**, 57) proposed to represent the composite metal ammonium by a symbol *Am*, analogous with those which he had already proposed for the metallic elements (p. 295).

Absorption and liberation of water in salt-formation.—For many years confusion prevailed in reference to the composition of salts, because no attention was paid to the appearance or disappearance of water; this water cost nothing, and, even when not in use as a solvent, could only be excluded by very careful drying.

It was recognised that salts can be formed by the direct combination of two oxides, two sulphides or two hydrides, *e.g.*

Two oxides: litharge + sulphuric anhydride $\longrightarrow$ lead sulphate.

Two hydrides: ammonia + muriatic gas $\longrightarrow$ sal-ammoniac.

But when a basic oxide combines with an acid hydride, *water is formed* in addition to the salt, *e.g.*

litharge + muriatic gas —→ lead chloride + water.

On the other hand, when a basic hydride combines with an acid oxide *water is absorbed*[1] in the formation of the salt. Thus ammonia does not unite with sulphuric anhydride to form a salt, but

ammonia + water + sulphuric anhydride —→ ammonium sulphate.

The water is needed to convert the ammonia into ammonium oxide, which can then unite with the acid oxide to form a salt: alternatively, it might be used to convert the acid oxide (sulphuric anhydride) into a hydro-acid (sulphuric acid) which can then unite directly with ammonia to form a salt, thus:

Two oxides: ammonium oxide + sulphuric anhydride —→ ammonium sulphate.

Two hydrides: ammonia + sulphuric acid —→ ammonium sulphate.

It is evident from these considerations that the ammonium salts of oxy-acids are *quaternary* compounds, containing both hydrogen and oxygen, in addition to nitrogen and (*e.g.*) sulphur.

The case of ammonium nitrate is specially interesting, as the acid oxide and basic hydride are both compounds of nitrogen. When the salt is heated, the hydrogen of the "ammonium" unites with oxygen from the acid to form water, and the nitrogen escapes in the form of nitrous oxide. In the case of ammonium nitrite the decomposition is almost explosive, the salt being decomposed completely into water and nitrogen.

[1] Sal-volatile, which Priestley prepared from ammonia and carbonic anhydride, is an exception; the product is not ammonium carbonate, but ammonium *carbamate*, which forms a carbonate only when dissolved in water.

Daniell (1840), regards salts as binary compounds of two radicals.—Gay-Lussac, in 1815, had recognised in cyanogen a compound-radical which could act the part of a non-metallic element, such as chlorine, iodine or sulphur. Ampère, in 1816, recognised in ammonium a compound radical which could act the part of a metal. The way was thus opened up for a final unification of all the different types of salts. The binary salts formed by the union of metal and halogen now became the type instead of the exception. In the ammonium salts, the metal was replaced by a compound-radical: in the cyanides, the halogen was replaced by a compound-radical. It only remained to include the oxygen salts in the same category by regarding the sulphates as compounds of a metal, with a compound SULPHATE-RADICAL. This radical was composed of sulphuric anhydride united with the oxygen of the base, thus:

$$\text{LEAD SULPHATE} = \begin{cases} \text{LEAD OXIDE} = \begin{cases} \text{LEAD} \\ \text{OXYGEN} \end{cases} = \text{LEAD.} \\ \text{SULPHURIC ANHYDRIDE} = \begin{cases} \\ \text{SULPHUR} \end{cases} \end{cases} = \text{SULPHATE.}$$

just as the ammonium of sal-ammoniac (p. 268) was composed of ammonia united with the hydrogen of the acid.

This view of the nature of salts was generally adopted when **Daniell**, in 1840, showed that the first action of an electric current on salt solutions was to decompose the salt into metal and non-metal, if the radicals were simple, or if the radicals were compound, into "metallic" and "non-metallic" compound-radicals.

B. Decomposition of the Alkalies and Earths.

Volta (1790) produces an electric current by means of the voltaic pile.—The Italian physicist Volta discovered in 1790 that insulated discs of zinc and copper, when brought into contact for a moment and then separated, acquired

respectively a positive and a negative charge of electricity. This method of producing electric charges was much improved in the VOLTAIC PILE,[1] which he described in the *Philosophical Transactions* for 1800 (pp. 403–431). This consisted of a series of pairs of zinc (or tin) and silver (or copper) discs, separated by cards, which were soaked in brine to render them conducting (Fig. 43). The voltaic pile had the advantage that the electric charges were replenished as quickly as they were drawn off, so that a continuous ELECTRIC CURRENT could be obtained. The

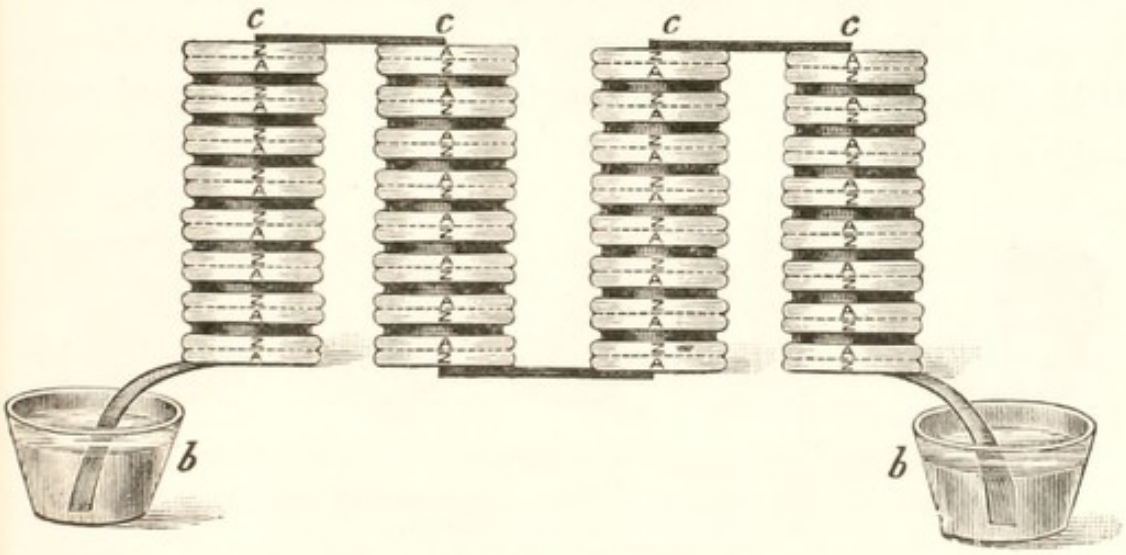


FIG. 43.—THE VOLTAIC PILE.
It is composed of 32 discs of copper or silver, A A (*e.g.* silver coins) and 32 discs of zinc, Z Z, separated by cards soaked in brine and terminating in two basins of water, *b b*.

current was not sufficiently intense to produce sparks, except with the help of a Leyden jar, and would only produce a severe electric shock when the hands were moistened, or, better, dipped into bowls of water, *bb*; but even a small pile was capable of producing a far greater *quantity* of current than the largest of the electrical machines then in use. The power of the pile could be increased almost indefinitely by augmenting the number of

[1] A voltaic pile presented by Volta to Davy is still preserved in the Library of the Royal Institution.

pairs of discs, whilst the efficiency of each unit was much improved by replacing the wet cards by vessels of wood, earthenware or glass, arranged side by side and filled with brine, or with dilute alkali (Fig. 44); each CELL of the BATTERY contained a zinc and a copper plate separated by a layer of solution, the zinc and copper plates of *adjacent* cells being soldered together.

Nicholson and Carlisle (1801) decompose water by the electric current.—Nicholson and Carlisle discovered in 1801 that two platinum wires, attached to the terminal plates of a voltaic pile and dipped in a glass of water, became covered with bubbles of gas. Closer examination showed that the gas collected from the positively-charged wire

FIG. 44.—THE VOLTAIC BATTERY OR "CROWN OF CUPS."
Plates of zinc, Z Z, and copper or silver, A A, are soldered together at *a a* and immersed in cups of brine.

attached to the zinc plate of the pile, was *oxygen*, and that *hydrogen* was liberated from the negatively-charged wire attached to the silver plate of the pile. At the end of 13 hours, 72 grain-measures of oxygen and 142 grain-measures of hydrogen were collected, *i.e.* "nearly the proportions in bulk of what are stated to be the component parts of water" (*Nicholson's Journal*, 1801, IV. 186). The electric current had thus been able to overcome the affinity of oxygen and hydrogen for one another, and had caused both gases to be liberated in the free state. The discovery of the decomposing power of the electric current was of great importance because compounds had been decomposed previously only by heat, or by the action of some

substance which combined very strongly with one constituent and thus set the other free.

Berzelius and Hisinger (1803) decompose salts by the electric current.—Berzelius and Hisinger in 1803 made the further discovery that dissolved salts were also decomposed by the current, the acid of the salt collecting with the oxygen round the positively-charged wire and the base with the hydrogen round the negatively-charged wire (*Ann. de Chimie*, 1804, **51**, 172).

Davy constructs an electric battery.—On leaving the Pneumatic Institute at Bristol in 1801 to take up the Professorship of Chemistry at the Royal Institution, Davy at once took up the work of investigating the decomposing action of the electric current. He built up for this purpose a large battery "containing 24 plates of copper and zinc 12 inches square, 100 plates of 6 inches, and 150 of 4 inches square, charged with solutions of alum and [nitric] acid." After describing, in his Bakerian lecture of 1806, "a number of decompositions and chemical changes produced by electricity," he concluded "that the new methods of investigation promised to lead to a more intimate knowledge than had hitherto been obtained, concerning the true elements of bodies" which had not hitherto been decomposed (A.C.R. VI. 5).

Davy (1807) prepares a metal from potash.—During the autumn of the following year Davy used the experience gained in these researches in his brilliant and successful attempt to decompose the caustic alkalies. Although Black had demonstrated fifty years earlier the relation of these substances to the mild alkalies, nothing whatever was known of their nature. They had usually been regarded as elements. Davy himself, knowing that ammonia was a compound of nitrogen and hydrogen, expected that the caustic alkalies would prove to be compounds of nitrogen with other combustible substances, perhaps sulphur or phosphorus.

As the result of little more than a month's work, Davy found himself in a position to "demonstrate the decomposition and composition" of the caustic alkalies.

On applying the current to saturated solutions of potash and soda, Davy found that "the water of the solutions alone was affected, and hydrogen and oxygen disengaged with the production of much heat and violent effervescence" (A.C.R. VI. 7).

"The presence of water appearing thus to prevent any decomposition," Davy passed the current through "potash in igneous fusion," and found that "a most intense light was exhibited at the negative wire, and a column of flame, which seemed to be owing to the development of combustible matter, arose from the point of contact."

All attempts to isolate the combustible matter under these conditions failed, because the heat required to melt the potash was more than sufficient to ignite the inflammable product. But when Davy employed "electricity as the common agent for fusion and decomposition," metallic globules appeared at the negatively-charged surface; whilst oxygen was produced at the positive pole.

"A small piece of pure potash, which had been exposed for a few seconds to the atmosphere, so as to give conducting power to the surface, was placed upon an insulated disc of platina, connected with the negative side of the battery . . . and a platina wire, communicating with the positive side, was brought in contact with the upper surface of the alkali. The whole apparatus was in the open atmosphere."

"Under these circumstances a vivid action was soon observed to take place. The potash began to fuse at both its points of electrization There was a violent effervescence at the upper surface; at the lower, or negative surface, there was no liberation of elastic fluid; but small globules having a high metallic lustre, and being precisely similar in visible characters to quicksilver, appeared, some of which burnt with explosion and bright flame, as soon as they were formed,

and others remained, and were merely tarnished, and finally covered by a white film which formed on their surfaces" (A.C.R. VI. 8).

To the new metal thus produced, the "basis of potash," Davy gave the name POTASSIUM.

Davy describes the physical properties of potassium.—The new metal at ordinary temperatures is

"a soft and malleable solid, which has the lustre of polished silver," but "at about the freezing point of water it becomes harder and brittle, and when broken in fragments, exhibits a crystallised texture, which in the microscope seems composed of beautiful facets of perfect whiteness and a high metallic splendour."

"To be converted into vapour, it requires a temperature approaching that of red heat; and when the experiment is conducted under proper circumstances, it is found unaltered after distillation."

"It is a perfect conductor of electricity," and "an excellent conductor of heat."

"Resembling the metals in all these sensible properties it is however remarkably different from any of them in specific gravity; I found that it rose to the surface of naphtha distilled from petroleum, and of which the specific gravity was ·861 and it did not sink in double distilled naphtha,[1] the specific gravity of which was about ·770, that of water being considered as 1" (A.C.R. VI. 14).

Gay-Lussac and Thenard (*Physico-Chemical Researches*, 1811, I. 111) who prepared the metal in larger quantities by allowing molten potash to flow on to iron filings heated to whiteness in a gun-barrel jacketed with clay, found that the density of potassium at 15° C. relatively to water at the same temperature was 0·865. They also gave the melting point as 58°, the value now accepted being 62·5°.

The chemical properties of potassium.—(a) *Oxidation.*—Davy had considerable difficulty in preserving the new

[1] This statement made twice by Davy, is remarkable in that it makes the density of sodium less than 0·77.

substance, since the globules "acted more or less upon almost every body to which they were exposed." It could be preserved in "recently distilled naphtha"; but when exposed to the atmosphere its metallic lustre was immediately destroyed and a white crust formed upon it.

"This crust I soon found to be pure potash, which immediately deliquesced, and new quantities were formed, which in their turn attracted moisture from the atmosphere till the whole globule disappeared, and assumed the form of a saturated solution of potash."

When exposed to air or oxygen confined by mercury,

"an absorption of oxygen took place; a crust of alkali instantly formed upon the globule; but from the want of moisture for its solution, the process stopped, the interior being defended from the action of gas."

The new metal was readily combustible; when strongly heated in oxygen "a rapid combustion with a brilliant white flame was produced, and the metallic globules were found converted into a white and solid mass," which Davy was not able to distinguish from ordinary potash (A.C.R. VI. 11).

(b) *Combination with Chlorine, Sulphur, Phosphorus and the Metals.*—When introduced into chlorine gas, potassium "burns spontaneously with a bright red light, and a white salt, proving to be muriate of potash is formed" (A.C.R. VI. 16). Muriate of potash is, therefore, a binary compound of a metal with chlorine, of the same type as those prepared from lead, silver, and iron; this fact is expressed in the name POTASSIUM CHLORIDE which is now given to the salt.

Potassium also resembles the other metals in that it combines readily with sulphur and phosphorus.

It possesses the property of forming alloys with other metals. With mercury it forms an amalgam, "a substance exactly like mercury in colour"; "the compound is fluid at the temperature of its formation; but when cool it appears as

a solid metal, similar in colour to silver" even when containing only one part of potassium to seventy parts of mercury. When these amalgams are exposed to air, "they rapidly absorb oxygen ; potash which deliquesces is formed ; and in a few minutes the mercury is found pure and unaltered." "When a globule of the amalgam is thrown into water, it rapidly decomposes it with a hissing noise ; potash is formed, pure hydrogen disengaged, and the mercury remains free" (A.C.R. VI. 20).

(c) *Decomposition of Water.*—The strong affinity of potassium for oxygen was shown in a very striking manner by its violent action upon water even when quite cold :

"When it is thrown upon water, or when it is brought into contact with a drop of water at common temperatures, it decomposes it with great violence, an instantaneous explosion is produced with brilliant flame, and a solution of pure potash is the result."

"When water is made to act upon the basis of potash out of the contact of air and preserved by means of a glass tube under naphtha, the decomposition is violent ; and there is much heat and noise, but no luminous appearance, and the gas evolved when examined in the mercurial or water pneumatic apparatus is found to be pure hydrogen."

"So strong is the attraction of the basis of potash for oxygen, and so great the energy of its action upon water, that it discovers and decomposes the small quantities of water contained in alchol and ether, even when they are carefully purified."

"The basis of potash when thrown into solutions of the mineral acids, inflames and burns on the surface" (A.C.R. VI. 16, 17, 18).

(d) *Reduction of Oxides.*—Finally potassium was found to be an active reducing agent, removing the oxygen from metallic oxides and liberating the metal.

"When a small quantity of the oxide of iron was heated with it, to a temperature approaching its point of distillation,

there was a vivid action; alkali and grey metallic particles which dissolve with effervescence in muriatic acid, appeared. The oxides of lead and the oxides of tin were revived still more rapidly; and when the basis of potash was in excess, an alloy was formed with the revived metal" (A.C.R. VI. 22).

The decomposition of caustic soda.—Davy immediately examined caustic soda to see if he could decompose it as he had done potash. He found that:

"Soda, when acted upon in the same manner as potash exhibited an analogous result; but the decomposition demanded greater intensity of action in the batteries, or the alkali was required to be in much thinner and smaller pieces" (A.C.R. VI. 9).

The "basis of soda" was a white, metallic substance very similar to potassium.

To the metal thus prepared from soda Davy gave the name SODIUM.

Physical properties of sodium.—The properties of sodium were described as follows:

"The basis of soda . . . . is a solid at common temperatures. It is white, opaque, and when examined under a film of naphtha, has the lustre and general appearance of silver. It is exceedingly malleable, and is much softer than any of the common metallic substances."

"It conducts electricity and heat in a similar manner to the basis of potash; and small globules of it inflame by the voltaic electrical spark, and burn with bright explosions."

"Its specific gravity is less than that of water. It swims in oil of sassafras of 1·096, water being 1, and sinks in naphtha of specific gravity 0·861. This circumstance enabled me to ascertain the point with precision. I mixed together oil of sassafras and naphtha, which combine very perfectly, observing the proportions till I had composed a fluid, in which it remained at rest above or below; and this fluid consisted of nearly twelve parts naphtha, and five of oil of sassafras, which gives a specific gravity to that of water,

nearly as nine to ten, or more accurately as 0·9348 to 1" (A.C.R. VI. 23—24).

Gay-Lussac and Thenard found the density at 15° to be 0·972 relatively to water at the same temperature.

"The basis of soda has a much higher point of fusion than the basis of potash." Davy gave the melting point as 120° to 180° F., but the value now accepted is higher, viz. 98° C. He was not "able to ascertain at what degree of heat it is volatile; but it remains fixed in a state of ignition at the point of fusion of plate glass" (A.C.R. VI. 24).

Chemical properties of sodium.—In its chemical properties sodium resembled potassium, but was much less vigorous in its action on air, oxygen and water.

"When the basis of soda is exposed to the atmosphere, it immediately tarnishes, and by degress becomes covered with a white crust, which deliquesces much more slowly than the substance which forms on the basis of potash. It proves, on minute examination, to be pure soda.

"The basis of soda combines with oxygen slowly, and without luminous appearance at all common temperatures; and when heated, this combination becomes more rapid; but no light is emitted till it has acquired a temperature nearly that of ignition.

"The flame that it produces in oxygen gas is white, and it sends forth bright sparks, occasioning a very beautiful effect; in common air, it burns with light of the colour of that produced during the combustion of charcoal, but much brighter.

"Its operation upon water offers most satisfactory evidence of its nature. When thrown upon this fluid, it produces a violent effervescence, with a loud hissing noise; it combines with the oxygen of the water to form soda, which is dissolved, and its hydrogen is disengaged. In this operation there is no luminous appearance" (A.C.R. VI. 24—25).

"When introduced into [chlorine], it burnt vividly with numerous scintillations of a bright red colour. Saline matter was formed in this combustion, which, as might have

been expected, proved to be muriate of soda" (A.C.R. VI. 25).

Common salt was thus shown to be a binary compound of sodium and chlorine, a fact which is expressed by the name SODIUM CHLORIDE.

Sodium, like potassium, combined with non-metals such as sulphur and phosphorus, formed alloys with tin and other metals, and a solid amalgam with mercury.

The bases of potash and soda are metals.—"Should the bases of potash and soda be called metals?" This question Davy answered in the affirmative. "They agree with metals in opacity, lustre, malleability, conducting powers as to heat and electricity, and in their qualities of chemical combination. Their low specific gravity does not appear a sufficient reason for making them a new class; for amongst the metals themselves there are remarkable differences in this respect, platina being nearly four times as heavy as tellurium." Davy therefore decided "to adopt the termination which by common consent has been applied to other newly-discovered metals," and to call the new substances potassium and sodium. He added, "Whatever future changes may take place in theory, there seems, however, every reason to believe that the metallic bases of the alkalies, and the common metals, will stand in the same arrangement of substances; and as yet we have no good reasons for assuming the compound nature of this class of bodies" (A.C.R. VI. 33—35).

Davy (1808) separates new metals from the alkaline earths.—Although the nature of the caustic alkalies had scarcely even been conjectured[1] before their decomposition by Davy, the similarity between the alkaline earths, such as lime and baryta, and the metallic oxides, had long been

[1] Lavoisier, in 1789, regarded the alkalis as "evidently compound, although we are still ignorant of the nature of the principles which enter into their composition" (*Works*, I. 137).

recognised and had indeed led Lavoisier to suggest that they were of the same nature (*Works*, I. 122, 126, 137).

Fresh from his recent successes with potash and soda, Davy, in 1808, attacked the alkaline earths, and after some failures isolated their metals in the form of amalgams with mercury.

"The earths were slightly moistened, and mixed with one-third of red oxide of mercury, the mixture was placed on a plate of platina, a cavity was made in the upper part of it to receive a globule of mercury, of from fifty to sixty grains in weight, the whole was covered by a film of naphtha, and the plate was made positive, and the mercury negative, by a proper communication with the battery."

"The amalgams obtained in this way, were distilled in tubes of plate glass, or in some cases in tubes of common glass. These tubes were bent in the middle, and the extremities were enlarged, and rendered globular by blowing, so as to serve the purposes of a retort and receiver."

"The tube after the amalgam had been introduced, was filled with naphtha, which was afterwards expelled by boiling, through a small orifice in the end corresponding to the receiver, which was hermetically sealed when the tube contained nothing but the vapour of naphtha, and the amalgam."

"I found immediately that the mercury rose pure by distillation from the amalgam, and it was very easy to separate a part of it; but to obtain a complete decomposition was very difficult" (A.C.R. VI. 46—47).

In this manner Davy obtained metals from baryta, from lime, and from the earth now known as strontia; these metals he named BARIUM, CALCIUM, and STRONTIUM. He seems also to have obtained a specimen of the metal contained in magnesia; he first called this metal "magnium," but afterwards reverted to the name MAGNESIUM.

Properties of the metals of the earths.—Barium was described by Davy as "a white metal of the colour of silver," solid at ordinary temperatures but "fluid at a heat below

redness." "When exposed to air, it rapidly tarnished, and fell into a white powder, which was barytes. When this process was conducted in a small portion of air, the oxygen was found absorbed, and the nitrogen unaltered; when a portion of it was introduced into water, it acted upon it with great violence and sunk to the bottom, producing in it barytes; and hydrogen was generated" (A.C.R. VI. 49).

Strontium was described by Davy as closely resembling barium.

In reference to calcium, Davy writes:

"The metal from lime, I have never been able to examine exposed to air or under naphtha. In the case in which I was able to distil the quicksilver from it to the greatest extent, the tube unfortunately broke, whilst warm, and at the moment that the air entered, the metal, which had the colour and lustre of silver, instantly took fire, and burnt with an intense white light into quicklime" (A.C.R. VI. 50).

The metal is now manufactured on a considerable scale by passing an electric current through the muriate, CALCIUM CHLORIDE, to which fluor-spar (CALCIUM FLUORIDE) is added to render it more easily fusible.

"The metal from magnesia seemed to act upon the glass, even before the whole of the quicksilver was distilled from it. In an experiment in which I stopped the process before the mercury was entirely driven off, it appeared as a solid, having the same whiteness and lustre as the other metals of the earths. It sunk rapidly in water, though surrounded by globules of gas, producing magnesia, and quickly changed in air, becoming covered with a white crust, and falling into a fine powder, which proved to be magnesia" (A.C.R. VI. 50).

Composition of the earths.—Having isolated metals from the four alkaline earths, Davy was able to prove by

direct experiment that they were actually metallic oxides. Although he was not able to determine their composition by direct weighing, Davy satisfied himself:

"That when the metals of the earths were burned in a small quantity of air they absorbed oxygen, gained weight in the process, and were in the highly caustic or unslacked state; for they produced strong heat by the contact of water, and did not effervesce during their solution in acids."

Lime was thus proved to be CALCIUM OXIDE. Slaked lime, formed by combining lime with water, is sometimes regarded as HYDRATE OF LIME, but is more usually described as CALCIUM HYDROXIDE, *i.e.* a ternary compound of calcium, hydrogen and oxygen. Similar names are given to the other earths.

Composition of the alkalis.—Davy at first regarded the alkalis as "highly combustible metallic bases united to oxygen" (A.C.R. VI. 43.), but he soon discovered that the oxides required to be combined with water in order to convert them into caustic alkalis. He also confirmed the observation of Gay-Lussac and Thenard that when the metals were burned in oxygen, PEROXIDES were formed, from which the excess of oxygen could be detached by further heating, or by the action of water in converting the peroxide into a common caustic.

These relationships were demonstrated very clearly in his experiments on the elementary nature of chlorine. He combined chlorine gas (1) with metallic potassium, (2) with the oxide and peroxide, (3) with the hydrated oxide (identical with ordinary caustic potash) and found that:

(1) In the direct combination of potassium with chlorine no water or oxygen was separated, the only product being a neutral muriate or chloride formed by the direct combination of about 1·1 cubic inch of chlorine with each grain of potassium.

(2) A grain of potassium burning in oxygen was found (after igniting the calx to decompose the peroxide) to produce an absorption amounting to $\frac{1}{2}$ cubic inch. By absorbing $1\frac{1}{8}$ cubic inches of chlorine the oxide was converted into chloride; exactly half a cubic inch of oxygen was regenerated, but "there was no separation of moisture," provided that the chlorine had been properly dried.

(3) Similar phenomena were observed in the action of chlorine on the peroxide, the whole of the absorbed oxygen being regenerated without liberating any water. But when chlorine was admitted to "a white sublimate of hydrate" formed by the action of moisture on the peroxide "it instantly became transparent from the evolution of water; and on heating the glass in contact with the sublimate, its opacity was restored, and water driven off." (A.C.R. IX. 41—43).

Caustic potash was, therefore, a binary compound of oxide of potassium with water, corresponding with slaked lime, or a ternary compound of potassium, oxygen and hydrogen. It is therefore described as POTASSIUM HYDROXIDE. Similar experiments show that caustic soda is correctly described as SODIUM HYDROXIDE.

SUMMARY AND SUPPLEMENT.

A. THE COMPOSITION of AMMONIA.

Priestley, in 1773, showed that ammonia was inflammable and in 1775 decomposed it by sparking. This method was used by **Berthollet** in 1785 to determine the composition of the gas. He found that

ammonia *gave* hydrogen + nitrogen
2 *vols.* 3 *vols.* 1 *vol.*

The action was shown by **St. Claire Deville**, in 1865, to be incomplete and reversible.

$$2NH_3 \rightleftarrows 3H_2 + N_2$$
(Ammonia.) (Hydrogen.) (Nitrogen.)

since the gas after sparking gave a cloud of sal-ammoniac when mixed with hydrogen chloride ; he was even able to recombine a mixture of hydrogen and nitrogen by sparking it in presence of hydrogen chloride.

$$3H_2 + N_2 + 2HCl \rightarrow \underset{\text{(Sal-ammoniac.)}}{2NH_4Cl}$$

The presence of an inflammable constituent in ammonia had already been recognised in 1774 by **Scheele** who found that the mineral "manganese" could be dissolved by acids when combined with ammonia, in the same way that it was dissolved in presence of combustible substances. In this process the non-inflammable constituent was liberated as an inactive gas :

$$\underset{\text{(Manganese dioxide.)}}{3MnO_2} + \underset{\text{(Ammonium nitrate.)}}{2NH_4NO_3} \rightarrow \underset{\text{(Manganous nitrate.)}}{Mn(NO_3)_2} + \underset{\text{(Manganous oxide.)}}{2MnO} + \underset{\text{(Water.)}}{4H_2O} + \underset{\text{(Nitrogen.)}}{N_2}$$

The same inert gas was liberated when ammonia was oxidised by the calx of gold during the detonation of *fulminating gold*, an explosive compound obtained by precipitating gold chloride with ammonia.

$$\underset{\text{(Fulminating gold.)}}{Au_2O_3,2NH_3} \rightarrow \underset{\text{(Gold.)}}{2Au} + \underset{\text{(Water.)}}{3H_2O} + \underset{\text{(Nitrogen.)}}{N_2}$$

The gas prepared from fulminating gold was used by Berthollet, when he sparked the inactive constituent of ammonia with oxygen, and showed that it was diminished in the same way as atmospheric nitrogen. Berthollet also showed that the inflammable constituent was really hydrogen ; he oxidised ammonia with nitric acid, by heating crystalline ammonium nitrate, and collected the water produced

$$\underset{\text{(Ammonium nitrate.)}}{NH_4NO_3} \rightarrow \underset{\text{(Water.)}}{2H_2O} + \underset{\text{(Nitrous oxide.)}}{N_2O} ;$$

the other product was pure nitrous oxide.

The discovery of the composition of ammonia, together with that of muriatic acid (hydrogen chloride) showed that *hydrosalts* could be produced by combining two hydrides, *e.g.*

$$\underset{\text{(Ammonia.)}}{NH_3} + \underset{\text{(Hydrogen chloride.)}}{HCl} \rightarrow \underset{\text{(Sal ammoniac.)}}{NH_4Cl}$$

in just the same way that *oxy-salts* were formed by combining two oxides, *e.g.*

$$\underset{\text{(Litharge.)}}{PbO} + \underset{\text{(Sulphuric anhydride.)}}{SO_3} \rightarrow \underset{\text{(Lead sulphate.)}}{PbSO_4}$$

In 1808, **Seebeck** at Jena, and **Berzelius** and **Pontin** at Stockholm, discovered that an amalgam could be produced by passing an electric current through ammonia in the presence of mercury. The amalgam is decomposed by heat into mercury, hydrogen (1 *vol.*) and ammonia (2 *vols.*). As ammonia (2 *vols.*) contains hydrogen (3 *vols.*) and nitrogen (1 *vol.*), the pseudo-metal in the amalgam contains nitrogen (1 *vol.*) combined with hydrogen (4 *vols.*) ; Davy in 1808, proposed to call it *ammonium*. **Ampère**, in 1816, showed that the salts of ammonia could be regarded as strictly analogous with the salts of the metals if ammonium were regarded as a "compound metal," which united directly with halogens to form salts such as sal-ammoniac or *ammonium chloride :*

$$\underset{\text{(Ammonia.)}}{NH_3} + \underset{\text{(Hydrogen chloride.)}}{HCl} = \underset{\text{(Sal-ammoniac.)}}{NH_4Cl} \text{ or } \underset{\text{(Ammonium chloride.)}}{(NH_4)Cl}$$

A compound of ammonia with half its volume of water vapour constituted an *ammonium oxide*, which could unite with oxy-acids (anhydrides) to form oxy-salts, thus :

$$2NH_3 + H_2O \rightarrow \underset{\text{(Ammonium oxide.)}}{(NH_4)_2O}$$

$$\underset{\text{(Ammonium oxide.)}}{(NH_4)_2O} + \underset{\text{(Sulphuric anhydride.)}}{SO_3} \rightarrow \underset{\text{(Ammonium sulphate.)}}{(NH_4)_2SO_4}$$

The oxy-salts of ammonia contain both oxygen and hydrogen. In some cases these may be driven off together in the form of water, *e.g.* :

$$\underset{\text{(Ammonium Nitrate.)}}{NH_4NO_3} \rightarrow \underset{\text{(Water)}}{2H_2O} + \underset{\text{(Nitrous oxide.)}}{N_2O}$$

$$\underset{\text{(Ammonium nitrite.)}}{NH_4NO_2} \rightarrow \underset{\text{(Water)}}{2H_2O} + \underset{\text{(Nitrogen.)}}{N_2}$$

The decomposition of ammonium nitrate, the "nitrum flammans" of the alchemists, had been known from an early period and was used by Berthollet in 1785 to prove the presence

of hydrogen in ammonia; the decomposition of ammonium nitrite takes place so readily that this salt was separated from its solutions in a crystalline form for the first time in 1909 (P. C. Rây, *Trans. Chem. Soc.*, **95**, 345).

Berzelius, in 1823, proposed to represent the compound radical ammonium, NH_4, by the symbol *Am*, thus:

ammonium chloride = NH_4Cl or AmCl.

Two compounds having the composition of

ammonium oxide, $2NH_3 + H_2O = (NH_4)_2O$ or Am_2O and
ammonium hydroxide, $NH_3 + H_2O = (NH_4)OH$ or AmOH,

were actually isolated in 1909 (*Annual Reports*, **6**, 14); it is remarkable that both compounds, like ammonia itself, melt at $-78°$ C.

Daniell, in 1840, proposed to regard all salts as binary compounds of two radicals. In the halogen salts of the metals both radicals are simple or elementary. In the ammonium salts the "metallic" radical is compound. In the cyanides, sulphates, nitrates, etc. the "non-metal" is replaced by a compound radical, *cyanogen* CN, *sulphate* SO_4, *nitrate* NO_3, etc. These radicals are the first products of the action of an electric current on the salts.

B. Decomposition of the Alkalis

Volta, in 1790, discovered that electric charges appeared on insulated discs of zinc and copper if brought into contact and then separated; in 1800, he devised a *Voltaic pile* in which the charges were constantly renewed and a continuous electric current was produced. The pile was soon developed into the *Voltaic battery* and very large batteries were constructed in England for Davy and in France for Gay-Lussac and Thenard.

Nicholson and Carlisle, in 1801, showed that water was decomposed by the electric current into oxygen and hydrogen

$$2H_2O \rightarrow 2H_2 + O_2$$

Berzelius and Hisinger, in 1803, showed that dissolved salts were decomposed into alkali and acid by the electric current, *e.g.*:

$$\underset{\text{(Sodium sulphate.)}}{Na_2SO_4} + 2H_2O \rightarrow \underset{\text{(Caustic soda.)}}{2NaOH} + \underset{\text{(Sulphuric acid.)}}{H_2SO_4}$$

These two actions were regarded by Daniell in 1840 as due to a decomposition of the salt into its two radicals, *e.g.*

$$Na_2SO_4 \rightarrow 2Na + SO_4 ;$$

the radicals then acted on the water, so that caustic soda and hydrogen were produced together at the negatively-charged electrode (Faraday's *kathode*) where the current left the liquid, whilst sulphuric acid and oxygen were produced together at the positively charged electrode (Faraday's *anode*) where the current entered the liquid, thus :

$$\textit{Kathode}: \quad 2Na + 2H_2O \rightarrow 2NaOH + H_2$$
$$\textit{Anode} \ : \quad SO_4 + H_2O \rightarrow H_2SO_4 + \tfrac{1}{2}O_2$$

Davy, in 1807, after having failed to separate a metal from aqueous caustic potash, passed an electric current across a piece of solid potash, slightly moistened on the surface. The potash was melted by the heat of the current andgave a light inflammable metal, which Davy called *potassium*. A similar metal, *sodium*, was separated from caustic soda. These metals were intensely active ; they combined directly with chlorine to form salt-like substances, and had so great an attraction for oxygen that they were able to decompose water at ordinary temperatures, liberating hydrogen and reproducing the caustic alkali ; they were used constantly during the succeeding years as the most powerful agents for extracting oxygen from substances in which its presence was suspected.

Thus *boron*, the characteristic non-metal of *borax* (sodium borate) and of *boric acid* (prepared by Homberg in 1702 and commonly known as "sedative salt"), was isolated in 1808, by Davy, and by Gay-Lussac and Thenard, by heating boric anhydride with potassium. *Silicon*, which exists as an oxide (*silica* or *silicic anhydride*) in quartz and sand, and in the mineral *silicates*, was prepared by Gay-Lussac and Thenard in 1809 by the action of potassium on the fluoride. *Aluminium*, the characteristic metal of alumina, of alum, and of clay, was isolated by Wöhler in 1827 by the action of potassium on the chloride.

Davy, in 1808, separated a new series of metals from the alkaline earths—magnesia, lime, strontia and baryta. The earths were mixed with oxide of mercury, covered with naphtha and submitted to the action of the electric current. Amalgams were obtained, from which the mercury was distilled off, more or

less completely, leaving behind a residue of metallic *magnesium*, *calcium*, *strontium* or *barium*. The metals oxidised rapidly and were converted into unslaked or caustic earths, which were thus shown to be metallic oxides:

Magnesia	=	magnesium oxide	MgO
Lime	=	calcium oxide	CaO
Strontia	=	strontium oxide	SrO
Baryta	=	barium oxide	BaO

The slaked oxides, formed by uniting the oxides with water, are called *hydroxides*, *e.g.*

slaked lime = lime + water
= calcium hydroxide, CaO,OH_2 or $Ca(OH)_2$

Davy at first regarded the caustic alkalis as oxides of potassium and sodium, but further experiments showed that they were really hydroxides like slaked lime, since
potassium and *chlorine* gave *potassium chloride* only

$$2K + Cl_2 \rightarrow 2KCl,$$

potassium oxide and *chlorine* gave *potassium chloride* and *oxygen*

$$K_2O + Cl_2 \rightarrow 2KCl + \tfrac{1}{2}O_2,$$
(1 *vol.*) ($\frac{1}{2}$ *vol.*)

potassium peroxide and *chlorine* gave *potassium chloride* and *oxygen*

$$K_2O_4 + Cl_2 \rightarrow 2KCl + 2O_2,$$

caustic potash and *chlorine* gave *potassium chloride*, *oxygen* and *water*

$$2KOH + Cl_2 \rightarrow 2KCl + \tfrac{1}{2}O_2 + H_2O.$$

PART II

CHEMICAL THEORIES

CHAPTER XIV

THE ATOMIC THEORY

A. Dalton's Atomic Theory

Theories as to the composition of matter.—From the time of the Greek philosophers there had existed two opposing theories of the constitution of matter (a) the *continuous*, according to which a void could not exist, and (b) the *atomic*, according to which all material substance consisted of particles separated by spaces.

The great English philosopher Isaac Newton gave his powerful support to the latter opinion, with the result that it became more and more prevalent, until at the close of the eighteenth century it was almost universal to think of substances as composed of minute particles, too small to be visible even by means of the microscope; these tiny particles were generally spoken of as "atoms," *i.e.* as indivisible. Newton's views as to the nature of atoms are set out in the following passage:

"It seems probable to me, that God in the beginning formed matter in solid, massy, hard, impenetrable, moveable particles; of such sizes and figures, and with such other properties, and in such proportions to space, as most conduced for the end for which he formed them; and that these primitive particles being solids, are incomparably harder than any porous bodies compounded of them; even

so very hard, as never to wear or break in pieces: no ordinary power being able to divide what God himself made One, in the first creation" (*Optics*, Book III; *Works*, 1782, IV. 260. Not included in the first edition of the Optics published in 1704).

Atoms and molecules.—The vague atomistic theory of the Greek philosophers was of little real value until Dalton showed that it could be used to explain the laws which govern chemical combination. The new ideas introduced into the Atomic Theory by Dalton may be summarised as follows:

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

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

(3) *The "compound atoms" of a chemical compound are formed by the union of two or more elementary atoms.*

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

In order to avoid the difficulty of describing a group of particles as an indivisible atom, it has become customary to reserve the name ATOM for the simple elementary atoms of which elements and compounds are alike composed. Groups of atoms, whether of the same kind or of different kinds, are distinguished as MOLECULES, *i.e.* little masses.

Dalton (1808) describes his atomic theory.—Dalton's views as to the nature and methods of combination of the atoms are set out clearly in his "*New System of Chemistry*," Vol. I., published in 1808:

"Whether the ultimate particles of a body, such as water, are all alike, that is, of the same figure, weight, etc., is a question of some importance. From what is known, we have no reason to apprehend a diversity in these particulars: if it does exist in water, it must equally exist in the elements constituting water, namely, hydrogen and oxygen. Now it

is scarcely possible to conceive how the aggregates of dissimilar particles should be so uniformly the same. If some of the particles of water were heavier than others, if a parcel of the liquid on any occasion were constituted principally of these heavier particles, it must be supposed to affect the specific gravity of the mass, a circumstance not known. Similar observations may be made on other substances. Therefore we may conclude that *the ultimate particles of all homogeneous bodies are perfectly alike in weight, figure, etc.* In other words, every particle of water is like every other particle of water; every particle of hydrogen is like every other particle of hydrogen, etc." (*New System*, 1808, I. 142; A.C.R. II. 28).

"Chemical analysis and synthesis go no farther than to the separation of particles one from another, and to their reunion. No new creation or destruction of matter is within the reach of chemical agency. We might as well attempt to introduce a new planet into the solar system, or to annihilate one already in existence, as to create or destroy a particle of hydrogen. All the changes we can produce, consist in separating particles that are in a state of cohesion or combination, and joining those that were previously at a distance" (A.C.R. II. 29).

"If there are two bodies, A and B, which are disposed to combine, the following is the order in which the combinations may take place, beginning with the most simple: namely,

1 atom of A + 1 atom of B = 1 atom of C, binary
1 atom of A + 2 atoms of B = 1 atom of D, ternary
2 atoms of A + 1 atom of B = 1 atom of E, ternary
1 atom of A + 3 atoms of B = 1 atom of F, quaternary
3 atoms of A + 1 atom of B = 1 atom of G, quaternary
etc., etc.

(*New System*, 1808, I. 212; A.C.R. II. 30.)

"From the application of these rules, to the chemical facts already ascertained, we deduce the following conclusions:

(1) That water is a binary compound of hydrogen and

oxygen, and the relative weights of the two elementary atoms are as 1 : 7, nearly.

(2) That ammonia is a binary compound of hydrogen and azote, and the relative weights of the two atoms are as 1 : 5, nearly.

(3) That nitrous gas is a binary compound of azote and oxygen, the atoms of which weigh 5 and 7 respectively; that [nitrogen peroxide][1] is a binary or ternary compound according as it is derived, and consists of one atom of azote and two of oxygen, together weighing 19; that nitrous oxide is a compound similar to [nitrogen peroxide], and consists of one atom of oxygen and two of azote, weighing 17. . .

(4) That carbonic oxide is a binary compound, consisting of one atom of charcoal, and one of oxygen, together weighing nearly 12; that carbonic acid is a ternary compound (but sometimes binary) consisting of one atom of charcoal, and two of oxygen, weighing 19; etc., etc. In all these cases the weights are expressed in atoms of hydrogen, each of which is denoted by unity" (A.C.R. II. 30–31).

Dalton's atomic symbols.—Much of the success of Dalton's atomic theory was due to the system of symbols which he introduced (A.C.R. II. 32), to represent the atoms of elements, and the molecules of compounds. Typical examples were:

Atoms.	Dalton's Symbol.	Berzelius's Symbol.
Hydrogen		H
Azote		N
Carbon		C
Oxygen		O
Sulphur		S

Molecules.	Dalton's Symbol.	Berzelius's Symbol.
Water		H + O
Ammonia		H + N

[1] "Nitric acid" in the original.

Molecules.	Dalton's Symbol.	Berzelius's Symbol.
Nitric oxide . . .		O + N
Nitrous oxide . . .		O + 2N
Nitrogen peroxide . .		2O + N
Carbonic oxide . . .		C + O
Carbonic anhydride . .		C + 2O

Berzelius's atomic symbols (1819)—Dalton's system of symbols was much improved by Berzelius, who, in his Essay *On the Theory of Chemical Proportions*, published in Paris in 1819, suggested that "Chemical symbols should be letters of the alphabet, in order to be easily drawn and printed without disfiguring the text"; he therefore "chose for this purpose the initial letter of the Latin name of each element"[1] (*loc. cit.*, p. 111). Since many elements had the same initial he proposed to use single letters to represent the chief non-metallic elements, and to add a second letter to distinguish the metals or other non-metals having the same initial. As examples he gives:

S = Sulphur.
Si = Silicium (silicon).
Sb = Stibium (antimony).
Sn = Stannum (tin).

C = Carbonicum (carbon.)
Co = Cobaltum (cobalt).
Cu = Cuprum (copper).

O = Oxygenium (oxygen).
Os = Osmium.

Compounds were distinguished by adding together the symbols of the constituent elements, *e.g.* the two oxides of copper were written Cu + O and Cu + 2O. Berzelius abbreviated his symbols by writing these two compounds as $\dot{C}u$ and $\ddot{C}u$, the dots representing atoms of oxygen. In the systems as used in the present day the two formulæ

[1] In a Swedish pamphlet published in 1814 Berzelius used initial letters to represent the *oxides* of the chief mineral-forming elements.

would be written CuO and CuO_2, but as the molecules of the two compounds are now regarded as containing only a single atom of oxygen the formulæ are actually written as Cu_2O and CuO.

Berzelius gave a list of fifty elements, with corresponding symbols. The majority of the symbols are easily-recognised abbreviations; exceptions are found in the case of:

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

The number of recognised elements has now grown to over 80.

The laws of chemical combination explained by the atomic theory.—One of the chief merits of Dalton's atomic theory was that it afforded a simple and obvious explanation of the three chief laws of chemical combination, namely:

(1) The law of fixed proportions.
(2) The law of multiple proportions.
(3) The law of reciprocal proportions.

B. Fixed Proportions.

The law of fixed proportions.—Throughout the alchemistic period very little attention was paid to the weights of the substances obtained in chemical processes. The study of chemical composition was confined to qualitative experiments, designed to find out the nature and not the

proportions of the constituent elements of various substances. A similar disregard of quantitative measurements prevailed during the vogue of the phlogiston theory, which became untenable as soon as the balance became a recognised tool of chemical science.

The credit of introducing quantitative conceptions into chemistry belongs mainly to Black, whose work on "Magnesia Alba" was a masterly demonstration of the possibilities of the new method. Black's methods were used with even greater effect by Lavoisier, the whole of whose work was carried out upon a quantitative basis.

The work of Black and of Lavoisier was based upon the tacit assumption of the LAW OF FIXED PROPORTIONS, that:

"*Chemical compounds are formed by the combination of their elements in fixed proportions by weight.*"

This law can be deduced at once from Dalton's theory that "the ultimate particles of all homogeneous bodies are perfectly alike in weight, figure, etc." Conversely, if the law of fixed proportions were not true, Dalton's theory would be a false hypothesis which could not stand the test of experiment.

Proust (1799-1802) formulates the law of fixed proportions.—The law of fixed proportions, which had been tacitly assumed by Black and Lavoisier, became a definite doctrine, to be tested and verified by experiment, in the hands of the French chemist **Joseph Louis Proust** (1755–1826), who carried out much analytical work bearing on this question whilst Professor of Chemistry at Madrid. Proust was impressed by the fact that the proportions in which the elements combine are "fixed by nature" and that the "power of augmenting or diminishing" these proportions "is not given to men" (*Journ. de Physique*, 1802, **55**, 325). Proust had already developed this view in 1799, when he found that there was no difference of composition between natural

and artificial carbonate of copper and that "in art as in nature copper never oxidises beyond 26%," whether the oxidation was brought about by fire, or by dissolving in nitric acid or by conversion into verdigris. Thus, in reference to the native carbonate of copper, he writes :

"If 100 parts of this carbonate, dissolved in nitric acid and thrown down by alkaline carbonates, give us 100 parts of artificial carbonate ; if the base of these two compounds is the black oxide, one must recognise an invisible hand which holds the balance in the formation of compounds and fashions their attributes at its will ; one must conclude that nature does not act otherwise in the depths of the earth, than on its surface, or in the hands of man" (*Ann. de Chimie*, 1799, **32**, 30).

In the case of iron and sulphur, Proust found an apparent exception to his rule ; iron pyrites was not identical with the artificial sulphide of iron (p. 175), but was "surcharged with an excess of sulphur," about 20% of which could be driven off by heating the mineral in a retort (*Nicholson's Journal*, 1802, **1**, 111 ; tr. from *Journ. de Physique*, 1801, **53**, 89–97). But in the course of the year 1802 he prepared an artificial sulphide, which appeared to have the same composition as iron pyrites, and concluded that iron and sulphur could combine in *two* fixed proportions.

"From the foregoing facts it follows, that iron can fix sixty per cent. of sulphur by a considerably elevated temperature. This proportion constitutes iron sulphurated to the minimum."

"By a lower heat it can also attract a [further] quantity which is equal to half of this weight ; and this result is iron sulphurated to the maximum, or with ninety parts of sulphur. If this last combination be exposed to the temperature which formed the first, it returns to that state ; that is to say, it returns to the minimum of sulphuration, by giving out all the sulphur it was capable of fixing above the proportion of sixty parts for each quintal of iron" (*Nicholson's*

Journal, 1802, **1**, 272; tr. from *Journ. de Physique*, 1802, **54**, 89-95).

These facts are only partially correct. The artificial sulphide contains 57 parts of sulphur combined with 100 of iron: in iron pyrites there are 114 (not 90) parts of sulphur combined with 100 parts of iron. When iron pyrites is heated it loses one-third of its sulphur, as Proust supposed, but the product is not identical with the artificial compound, ferrous sulphide.[1]

Berthollet (1803) challenges the law of fixed proportions.—In his *Essay on Chemical Statics*, published in 1803, Berthollet definitely challenged Proust's opinion that invariable proportions and constant attributes characterise all the true compounds of art or of nature, and that the chemist is no more able to control these proportions and attributes than he is able to control the affinities which the elements possess for one another (*Chemical Statics*, tr. 1804, II. 315–316). Berthollet maintained that the elements can combine in variable proportions, constancy of composition being secured only when some constituent crystallises out, or distils out from the mixture of interacting substances. In the special case of the oxides he proposed, in opposition to Proust, to show

"that the proportions of oxygen in the oxides depend on the same conditions as those which enter into the other combinations;

"that these proportions can vary, progressively, from the term at which the combination becomes possible, to that at which it acquires the highest degree;

"and, that when this effect does not take place, it is only because the conditions which I have pointed out become an obstacle to this progressive action" (*Chem. Statics, tr.* 1804, II. 316).

He suggested that metals like zinc, which oxidise by volatilising, take at once those proportions of oxygen which may be considered as constant; but that in the case of

[1] The equation, $3FeS_2 = Fe_3S_4 + S_2$, has already been given on p. 182.

metals such as tin and lead, which enter into a tranquil fusion, oxidation advances progressively from a minimum towards a maximum, producing a succession of colours and of other properties. Thus lead forms an oxide which begins by being grey; afterwards it passes to different shades of yellow, and finishes by becoming red. Iron also passes through different shades and acquires different properties as oxidation advances: similar effects may be observed in several metals (*loc. cit.* p. 317).

In the case of sulphur, Berthollet expresses the view that

"The metals can combine with sulphur in very various proportions, and the combinations which are thus formed have different properties according to their proportions: I am, in this case, again in opposition to the opinion of Proust, who asserts, that *by the invariable law of proportion, sulphur and iron are fixed at* $\frac{60}{100}$" (*loc. cit.* 372–373).

Proust (1804-1808) defends the law of fixed proportions; fixed proportions as a test of chemical combination. —Proust replied to the criticisms of Berthollet in a series of seven memoirs which appeared in the *Journal de Physique* during the last three months of 1804. It is not necessary to follow the controversy in detail: it will be sufficient to notice that Proust finished by using the law of fixed proportions as a test to distinguish chemical compounds from mere solutions of one compound or element in another. He was able to appeal to the general feeling of chemical workers to support the idea that there are in fact two different kinds of combination, that the dissolution of sugar in water is something different from the union of carbon, hydrogen and oxygen to form sugar, and so forth. It was no small service to point out that variable composition and fixed composition provide a test by which the two kinds of combination can be distinguished sharply from one another. These views were expressed by Proust, in 1806, as follows:

"The attraction which makes sugar dissolve in water,

may or may not be the same as that which makes a definite quantity of charcoal and of hydrogen dissolve in another quantity of oxygen, to form the sugar of our plants ; but we can see clearly, that the two sorts of attractions are so different in their results, that it is impossible to confound them."

"Thus the dissolution of nitre in water is for me quite distinct from that of nitrogen in oxygen which produces nitric acid, or from that of nitric acid in potash which produces saltpetre."

"The dissolution of ammonia in water is in my eyes not at all like that of hydrogen in nitrogen, which gives birth to ammonia."

"The dissolution of silver sulphide in antimony sulphide, which produces red silver ore,[1] is not at all like that of silver in sulphur which produces the sulphide of this metal."

"Finally, the dissolution of antimony sulphide in the lower oxide of antimony is, to my feeling, not at all like that of antimony in sulphur, and the reason of these distinctions seems to me to be evident, for the dissolution of sugar, of nitre, of ammonia in water, can be obtained in a range of proportions of which the extremes are infinitely separated ; but the dissolution, in one another, of the elements of nitric acid, of saltpetre, or of ammonia has only been permitted to us under the rigorous condition of a proportion of the two or more constituents" (*Journ. de Physique*, 1806, **63**, 369).

The distinction which Proust first made between a DISSOLUTION and a COMBINATION (*Journ. de Physique*, 1806, **63**, 370), and his description of the characteristics of a CHEMICAL COMPOUND, have become regular features of the chemical text-books of the hundred years which have elapsed since his memoirs were published.

Stas (1865) tests the accuracy of the law of fixed proportions.—The experiments of Proust were carried out before the introduction into chemistry of the methods of exact analysis which we owe to Berzelius ; they were therefore subject to errors varying from 1 per cent. to as much

[1] Proust, *Journ. de Physique*, 1804, **59**, 403.

as 20 per cent. in extreme cases. The exact analytical work of Berzelius and others showed that constancy of composition could be relied on within very narrow limits; but the suggestion was made, in 1860, by the Swiss chemist Marignac (Geneva *Archives*, 1860, **9**, 103) that small variations of composition might perhaps exist, even in the most stable and definite of chemical compounds. This suggestion was submitted to a most stringent test by Stas, who published a memoir on the subject in 1865 (*Works*, I. 445–481). Stas made a very careful comparison of the quantities of common salt required to convert different samples of silver into silver chloride. The standard was a sample of silver which had been distilled with the help of an oxy-hydrogen blowpipe. The relative quantities of salt were as follows:

Method of Preparation.	Salt used.
Distilled silver	100·000
Silver electrolysed from a cyanate solution; metal fused	99·998 99·999 99·997
Silver nitrate reduced by milk-sugar; metal fused	99·994 99·995 99·999
Silver nitrate reduced by sulphites; metal fused	99·997
Silver chloride reduced by fusing with sodium carbonate and nitrate	99·995
Silver chloride reduced by heating with charcoal and lime	99·991

In these experiments (*Works*, I. 466) the average deviation from the mean value amounted only to 0·002 per cent.

A similar series of experiments (*Works*, I. 478) was made on the precipitation of silver by means of different samples of ammonium chloride, both at atmospheric temperatures and at 100°. The results were as follows:—

Method of Preparation.	Quantity used to precipitate 100 parts of silver.
Chloride prepared from cold solutions of hydrochloric acid and ammonia. Ratio determined at ordinary temperature	49·600 49·599 49·598

Method of Preparation.	Quantity used to precipitate 100 parts of silver.
Chloride sublimed at ordinary pressure. Ratio determined at ordinary temperature . . .	49·598 49·597 49·593 49·597
Chloride sublimed at ordinary pressure. Ratio determined at 100°	49·597 49·602 49·597
Chloride sublimed in a vacuum. Ratio determined at ordinary temperature	49·598 49·592
Mean	49·997

In these experiments the average deviation from the mean was only 0·004 per cent.

The conclusion may be drawn that the law of fixed proportions is exact up to the extreme limit of experimental investigation.

Soddy and Hyman (*Trans. Chem. Soc.*, 1914, **105**, 1402—1408) have shown recently that different samples of "lead" may unite with quantities of chlorine which differ by one part in 225, a result that has been confirmed by Richards and Lembert (*J. Amer. Chem. Soc.*, 1914, **36**, 1329—1344). The difference is attributed to the presence in the metal of two elements, which are even more difficult to separate than NEODYMIUM and PRASEODYMIUM, which were regarded for a long time as a single element under the name of DIDYMIUM. The exceptional difficulty of resolving such mixtures cannot be regarded as affecting the validity of the law of fixed proportions, as it applies exclusively to pure chemical compounds.

C. MULTIPLE PROPORTIONS.

The law of multiple proportions.—The LAW OF MULTIPLE PROPORTIONS states that:

"*If several compounds be formed, the fixed proportions in which two elements combine together are in simple integral ratios to one another.*"

This law recognises that elements may combine together in different proportions, but adds (1) that each of these proportions is fixed and (2) that *the different fixed proportions are not independent of one another*, but are related in the simplest possible way. Thus, if hydrogen and oxygen unite together in the ratio 1 : 8 to form water, they may also unite in the ratio 2 : 8, 3 : 8, 4 : 8, or 1 : 16, 1 : 24, 1 : 32 (or, generally, in the ratio $n \times 1 : m \times 8$, where n and m are whole numbers) in forming other compounds; but they cannot combine together in intermediate ratios such as 1·107 : 8 or 1 : 7·823, which are wholly independent of the ratio in which they are present in water. Berthollet, who claimed "that a substance may combine in all proportions with another on which it acts by a reciprocal affinity" (*Journ. de Physique*, 1805, **60**, 347), had no place for the law of multiple proportions. Proust, who recognised the existence in many cases of two or more fixed proportions, and especially of a fixed *maximum* and *minimum*, might easily have discovered the law of multiple proportions if his analyses had been more exact. Thus, in the case of iron and sulphur he gave the proportions as

sulphur to iron = 60 : 100, *minimum*
" " " = 90 : 100, *maximum*

These two proportions are in the simple integral ratio 2 : 3; but as the actual proportions are 57 : 100 and 114 : 100, ratio 1 : 2, it is not surprising that his measurements as a whole did not disclose any simple relationship between the maximum and minimum proportions.

The law of multiple proportions was therefore first discovered by Dalton as a direct and obvious deduction from his atomic theory. No formal statement of the law was made, but several cases were quoted to which the law can be applied, *e.g.* the three oxides of nitrogen in which

the three proportions of oxygen to nitrogen[1] were in the ratio 1 : 2 : 4, and the two oxides of carbon in which the two proportions of oxygen to carbon[2] were in the ratio 1 : 2.

The analytical data which Dalton used were no more exact than those of Proust, and were, indeed, much less exact than those on the strength of which he repudiated Gay-Lussac's Law of Volumes (see below, p. 335). But, guided by his theory, he was able to recognise the existence of simple ratios, even in the imperfect data which were at his disposal. The opinions of Berthollet, "that the chemical agency is proportional to the mass, and that in all chemical unions there exist insensible gradations in the proportions of the constituent principles" (A.C.R. II. 27), was quite incompatible with the atomic theory, according to which one or more atoms of an element could combine with 1, 2, 3, etc., atoms of a second element, but not with any intermediate fractional number. Dalton therefore denounced it as inconsistent "both with reason and observation" (A.C.R. II. 28), whilst Proust was able to show that it had no sufficient experimental basis.

The law of multiple proportions supported by Thomson (1808), by Wollaston (1808) and by Gay-Lussac (1809).

As soon as the law of multiple proportions had been discovered, ample evidence in support of it was forthcoming. **Thomas Thomson**, whose *History of Chemistry* is of undiminished value after being in use for nearly a century, directed attention to the existence of two series of OXALATES, and especially of two potassium oxalates and two strontium oxalates. The composition of these oxalates showed the following simple relationship:

"Suppose 100 parts of potash; if the weight of acid

[1] Dalton gives the proportions as 7 : 10, 7 : 5, 14 : 5.
The actual proportions are . . 4 : 7, 8 : 7, 16 : 7.

Dalton gives the proportions as 7 : 5, 14 : 5.
The actual proportions are . . 4 : 3, 8 : 3.

necessary to convert this quantity into oxalate be x, then $2x$ will convert it into superoxalate."

"It appears that there are two oxalates of strontian. . . . It is remarkable that the first contains just double the proportion of base contained in the second" (A.C.R. II. 41).

In a paper (A.C.R. II. 34–40) read before the Royal Society on Jan. 28, 1808, a fortnight after Thomson's, **William Hyde Wollaston,** the Secretary, showed that a third oxalate of potash existed, the relative quantities of acid in the three salts being in the ratio 1 : 2 : 4. He also showed that in the two series of CARBONATES the quantities of gas were in the ratio 1 : 2, since 4 grains of the bicarbonate,[1] when converted into the carbonate by heating it, lost the same amount of gas as 2 grains of the same salt when wholly decomposed by acid; these observations are confirmatory of those made 40 years before by Cavendish (p. 69). Again, in the case of the SULPHATES, Wollaston found that "super-sulphate[1] of potash may be shown to contain exactly twice as much acid as is necessary for the mere saturation of the alkali present."

The gases which supplied Dalton with illustrations of the law of multiple proportions were studied much more carefully by **Gay-Lussac,** who in his paper on the combining volumes of gases (1809) quoted additional cases and provided more exact data, all tending to uphold the validity of the law (see below, pp. 331–335).

The law of multiple proportions stated and proved by Berzelius (1810).—One of the first chemists to feel the fascination of the new problem of chemical proportions was Berzelius, who published in 1810 a "Research, to determine the fixed and simple Proportions, in which the Constituents of inorganic Nature

[1] Wollaston speaks of sub-carbonate (=carbonate) and carbonate (=bicarbonate); sulphate and super-sulphate (=bisulphate); oxalate, binoxalate, and quadroxalate.

are combined with one another;" this was translated into German and published as a series of papers in Gilbert's *Annalen*, 1811–1812, and has been reprinted as No. 35 of Ostwald's *Klassiker*. Admitting at once the truthfulness of Proust's view that substances could only combine together in a series of fixed proportions, he had already found in his own work some evidence that these fixed proportions were related together in a very simple way. Further experiments on the same range of compounds that had been studied by Proust enabled him to assert that

"If two substances, A and B, combine with one another in different ratios, this always takes place in the following definite ratios: 1A with 1B (minimum); 1A with $1\frac{1}{2}$B (or perhaps more correctly 2A with 3B); 1A with 2B; 1A with 4B. In my experiments there is no example of 1A with 3B" (*Fixed Proportions*, 1811–1812; *Klassiker*, XXXV. 5).

The following cases were studied by Berzelius: —

	Lead and Oxygen.	
Brown oxide	100 : 15·6	*Ratio* **2·00** : 1
Yellow oxide	100 : 7·8	
	Sulphur and Oxygen.	
Sulphuric acid [1]	100 : 146·427	*Ratio* **1·497** : 1
Sulphurous acid [1]	100 : 97·83	
	Copper and Oxygen.	
Black oxide	100 : 25	*Ratio* **2·00** : 1
Red oxide	100 : 12·5	
	Iron and Sulphur.	
Maximum	100 : 117	*Ratio* **1·993** : 1
Minimum	100 : 58·73	
	Iron and Oxygen.	
Ferric oxide	100 : 44·25	*Ratio* **1·495** : 1
Ferrous oxide	100 : 29·6	

In each of these cases, the exact analyses of Berzelius enabled him to recognise the validity of the law of multiple proportions, which had remained disguised in the rougher analyses of Proust.

[1] *i.e.* sulphuric anhydride and sulphurous anhydride.

Accuracy of the law of multiple proportions.—The measurements of Stas provide two opportunities of testing the exactness of the law of multiple proportions.

(1) Dumas and Stas, in 1841 (see above, p. 148), showed that 100 parts of carbonic anhydride contain

carbon **27·27** per cent.,
oxygen **72·73** per cent.

Stas, in 1849 (see above, p. 151), showed that 224·683 grams of carbonic oxide combined with 128·367 grams of oxygen to form 353·050 grams of carbonic anhydride. Therefore, 100 parts of carbonic anhydride contain

carbonic oxide **63·64** per cent.
oxygen **36·36** per cent.

Thus 27·27 grams of carbon unite with **72·73** grams of oxygen to form 100 grams of carbonic anhydride, and with 63·64 — 27·27 = **36·37** grams of oxygen to form 63·64 grams of carbonic oxide. The ratio $\frac{72·73}{36·37} = \mathbf{1·9997}$. This ratio differs from the integral ratio 2 : 1 by only one part in 7000 or 0·015 per cent.

(2) Stas's analysis of silver sulphate (*Works*, I. 410) showed that it contained 69·203 per cent. of *silver*, united with 69·203 × 14·852 ÷ 100 = 10·278 per cent. of *sulphur* and 100 − 69·203 — 10·278 = 20·519 per cent. of *oxygen*. In the sulphate, then, 100 parts of silver are united with 20·519 ÷ 69·203 × 100 = **29·650** parts of oxygen.

A second relationship between oxygen and silver is afforded by the fact that 100 parts of silver were precipitated by 69·103 parts of potassium chloride, which could be derived from potassium chlorate containing 60·846 per cent. of the salt and 39·154 per cent. of oxygen; 69·103 parts of chloride would therefore combine with

$$69·103 \times \frac{39·154}{60·846} = \mathbf{44·467}$$

parts of oxygen.

In the sulphate then the ratio of silver to oxygen is 100 : 29·650, the corresponding ratio derived from the study of the chlorates is 100 : 44·467. These two quantities of oxygen are in the ratio $\frac{44{\cdot}467}{29{\cdot}650} = \mathbf{1{\cdot}4997}$. This differs from the integral ratio 3 : 2 by only 1 part in 5000 or 0·02 per cent.

D. Reciprocal Proportions

The law of reciprocal proportions.—The LAW OF RECIPROCAL PROPORTIONS deals with the case in which two elements combine with a third element, and also with one another. It states that :

The relative proportions in which two elements combine with a third element are in a simple ratio to those in which they combine with a fourth element or with one another.

The significance of the law may be illustrated by a simple example. In water, 1 part of hydrogen is combined with 8 *parts of oxygen ;* in marsh gas it is combined with 3 *parts of carbon*, whilst in olefiant gas it is combined with 6 *parts of carbon*, just twice as much as in marsh gas. What will happen if oxygen on the one hand combines with carbon on the other ? The law of reciprocal proportions suggests that these elements will combine with one another in the proportion

$$oxygen : carbon = 8 : 3 \text{ or } 8 : 6$$

or some simple multiple of these numbers. The two proportions suggested by the law are found in fact to be those in which the elements are united in carbonic anhydride and in carbonic oxide respectively ; in a recently-discovered suboxide of carbon the proportions are

$$oxygen : carbon = 8 : 9.$$

Again, suppose that oxygen and carbon unite with a fourth

element such as sulphur, instead of with one another. The law of reciprocal proportions suggests that equal quantities of sulphur will combine with 8 parts of oxygen and with 3 parts of carbon, or with some simple multiple of these numbers. In practice it is found that 16 parts of sulphur unite with 3 parts of carbon and with $2 \times 8 = 16$ or with $3 \times 8 = 24$ parts of oxygen.

Like the two preceding laws, the law of reciprocal proportions may be interpreted most easily with the help of Dalton's atomic theory. But as an experimental law it had been recognised and used twenty years previously. Thus Cavendish had recognised in 1788 (*Phil. Trans.*, **78**, 178) that the quantities of nitric and sulphuric acid which neutralised equal weights of potash would also decompose equal weights of marble. The weights of potash and of marble which saturated the same quantity of acid he had described as long ago as 1766 as EQUIVALENT to one another ("On Rathbone Place Water," *Phil. Trans.*, 1767, **57**, 102).

The law of reciprocal proportions was developed and tested experimentally for a large range of acids and bases by the German chemist **J. B. Richter** (1762–1807) in his *Stöchiometry* (1792–1794) and in a series of eleven volumes on *New Chemical Topics*, published between 1791 and 1802. Richter noticed that:

"When two neutral solutions are mixed, and a decomposition follows, the new resulting products are almost without exception neutral also."

"The elements must, therefore, have amongst themselves a certain fixed proportion of mass" (*Stöchiometry*, I. 124).[1]

Thus muriate of lime and sulphate of ammonia, when mixed together in solution, were changed into sulphate of lime and muriate of ammonia. The sulphate of lime

[1] Quoted from Angus Smith's *Dalton and the Atomic Theory* (1856), p. 190. In this book, twenty pages are given to translations from Richter's works.

separated as a white precipitate of gypsum, but the neutrality of the solution was not affected by the double decomposition and the liquid above the precipitate contained nothing but perfectly-formed common sal-ammoniac (Angus Smith, p. 207). No free acid or alkali was produced because the relative weights of alkali and of earth required to saturate one acid could be shown to be the same as those required to saturate the other; the lime and sulphuric acid combining to form gypsum, therefore, liberated ammonia and muriatic acid in exactly the right proportions to form a neutral solution of sal-ammoniac.[1]

Richter's observations were collected by one of his contemporaries[2] into a table which shows the weight of base which will neutralise 1,000 parts of sulphuric acid or a tabulated quantity of any other acid. A part of this table is reproduced below.

EQUIVALENT WEIGHTS OF

(1) BASES		(2) ACIDS	
Alumina	525	Hydrofluoric	427
Magnesia	615	Carbonic	577
Ammonia	672	Muriatic	712
Lime	793	Oxalic	755
Soda	859	Phosphoric	979
Strontia	1329	Sulphuric	1000
Potash	1605	Nitric	1405
Baryta	2222	Acetic	1480

[1] Wenzel, who studied (*Theory of Affinity*, Dresden, 1777) the mixing of copper sulphate with lead acetate to produce lead sulphate and copper acetate, concluded from his analyses that the acetic acid set free from the acetate of lead was not sufficient to dissolve the copper set free from the sulphate of copper; he calculated that $9\frac{1}{8}$ out of 124 parts of copper would remain undissolved in the precipitate of sulphate of lead. There is therefore no justification for the circumstantial statement of Berzelius, which attributes to Wenzel the discovery of the law enunciated fifteen years later by Richter.

[2] Fischer, in German translation (1802) of Berthollet's *Researches on the Laws of Affinity*; quoted by Berthollet, *Chem. Statics*, tr. 1804, I. 402.

Berzelius's work on equivalents.—The importance of Richter's observations was realised, perhaps for the first time, by Berzelius, who writes:

"It follows from the researches of Richter, that from good analyses of a few salts, one could calculate with precision the composition of all the others.

"I formed [in 1807] the project of analysing a series of salts, with the idea that it would be superfluous to examine the others." Thus

"It is evident that if analyses are made of all the salts formed by one acid, for instance, by sulphuric acid with all the bases, and of those formed by one base, for example baryta with all the acids, one would have the necessary data to calculate the composition of all the salts formed by double decomposition, provided that they retained their neutrality" (*Chemical Proportions*, 1819, 16).

To Berzelius belongs the credit of having done more than any of his contemporaries to provide the data whereby the composition of a large range of compounds might be calculated from the results of a few careful analyses,—not merely in the case of acids, bases and salts, but throughout the whole field of chemical combination.

The proportions by weight in which elements and compounds interact with one another are described as their EQUIVALENTS or COMBINING WEIGHTS. As these weights are all relative, some standard has to be selected to take the place of the 1,000 parts of sulphuric acid used above in summarising Richter's data.

Dalton selected one part of hydrogen, whilst Berzelius preferred one hundred parts of oxygen. The standard used at the present time is eight parts of oxygen, so that "*The equivalent of an element is that weight which combines with eight parts by weight of oxygen.*"

The choice of oxygen instead of hydrogen as the standard has the practical advantage that all the elements

except fluorine combine directly with oxygen, whilst the formation of hydrides, at least in the case of the metals, is the exception rather than the rule. The figure 8 is chosen because it gives for hydrogen a value, 1·008, which approximates very closely to unity.

Table of equivalents of elements.—The following table shows the equivalents or combining weights of some of the common elements.

Hydrogen . . .	1·008	Lithium . . .	6·94
Carbon . . .	3·00	Calcium . . .	20·03
Oxygen . exactly	**8**	Sodium . . .	23·00
Nitrogen (in nitrous oxide) . . .	14·01	Copper . . .	31·78
		Potassium . . .	39·10
Sulphur . . .	16·03	Mercury . .	100·3
Chlorine . . .	35·46	Lead	103·55
Bromine . . .	79·92	Silver	107·88
Iodine	126·92		

The table shows at a glance the composition of lime as containing 20·03 parts of calcium combined with 8 parts of oxygen, whilst litharge contains 103·55 parts of lead combined with 8 parts of oxygen. Muriate of lime or calcium chloride contains 20·03 parts of calcium combined with 35·46 parts of chlorine, whilst common salt contains 23·00 parts of sodium combined with 35·46 parts of chlorine.

In drawing up a table of equivalents it is customary, when multiple proportions are observed, to tabulate the equivalent of the element as deduced from the analysis of one compound, selected as typical, and to represent the composition of the others by multiples of the tabulated equivalents. Thus, in the table, carbon and oxygen are shown as uniting together in the ratio 3·00 to 8 to form carbonic anhydride; but they also unite in the ratio $2 \times 3{\cdot}00$ to 8 to form carbonic oxide. Again carbon and hydrogen unite in the ratio 3·00 to 1·008 in marsh gas, but in the ratio $2 \times 3{\cdot}00$ to 1·008 in olefiant gas. Such multiple

proportions are particularly common in compounds of three or more elements, *e.g.*

LITHARGE . . lead : oxygen = 103·55 : 8

and

SULPHURIC ANHYDRIDE . sulphur : oxygen = 16·03 : 3 × 8

unite in these proportions to form

LEAD SULPHATE . . lead : sulphur : oxygen
= 103·55 : 16·03 : 4 × 8

Equivalents and atomic weights.—The possibility of making use of a series of equivalents to express the proportions in which elements combine together finds an obvious explanation in the atomic theory. But, whilst the equivalents and the atomic weights are closely related to one another, they are not necessarily identical. Thus, in the case of hydrogen and oxygen the weights in which the elements combine together to form water are approximately 1 to 8. These are, therefore, the equivalents, or combining weights, of the two elements. But whilst Dalton preferred to regard water as a compound of 1 atom of hydrogen with 1 atom of oxygen, Berzelius regarded it as a compound of 2 atoms of hydrogen with 1 atom of oxygen. On Dalton's hypothesis the equivalents and the atomic weights are both expressed by the numbers 1 : 8, *i.e.* water is composed of *one* atom of hydrogen of weight 1, and *one* atom of oxygen of weight 8. On Berzelius's hypothesis the equivalents are still in the ratio 1 : 8, but the atomic weights were given as 6·2177 : 100 = 1 : 16, *i.e.* water is composed of *two* atoms of hydrogen of weight 1, and *one* atom of oxygen of weight 16, the combining ratio being 2 × 1 : 16 = 1 : 8 as before. *The numbers expressing the equivalent and the atomic weight of an element must, however, be in a simple integral ratio to one another, e.g.* in the above instance 2 : 1, or, in general, $m : n$.

It may be noted that analytical data, such as those em-

ployed by Dalton, can only give the equivalents of the elements and not their true atomic weights. Dalton's table of atomic weights was thus really only a table of equivalents, selected so as to give the simplest possible formulæ to the different compounds, but bearing little resemblance to the real atomic weights as determined by the methods described in the following chapter. The only check upon his arbitrary selection of formulæ was that a heavy gas was usually represented as containing more atoms than a lighter one; for this reason he regarded carbonic oxide as a binary compound, and carbonic anhydride as ternary, and therefore calculated the atomic weight of carbon from the ratio 6 : 8 of carbon to oxygen in carbonic oxide instead of from the ratio 3 : 8 of the combining weights of the two elements in carbonic anhydride.

Stas's determination of equivalents.—A description has already been given of the methods used by Stas in determining the combining weights of carbon with oxygen (pp. 148—153). During a period of about 25 years, ending in 1882, Stas determined with extreme care and accuracy the combining weights of all the elements quoted in the above table, with the exception of calcium, copper and mercury. The method he adopted was as follows :

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

(a) By ignition
(b) By heating with hydrochloric acid.

It was found that 100 parts of potassium chlorate gave 60·846 parts of potassium chloride, so that 6×8 parts of oxygen were combined with $48 \div (100 - 60{\cdot}846) \times 60{\cdot}846 =$ **74·592** parts of potassium chloride; this number is, therefore, the equivalent of **potassium chloride.**

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

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

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

At the close of his work Stas had determined the equivalents of ten elements, as follows:

Nitrogen . .	14·055	Lithium . .	7·022
Sulphur . .	16·037	Sodium . .	23·0455
Chlorine . .	35·457	Potassium .	39·1425
Bromine . .	79·955	Lead . .	103·456
Iodine . .	126·848	Silver . .	107·930

A comparison with the list of equivalents given in the table above (p. 313) will show that Stas's final values (which differ slightly from those worked out in the four preceding paragraphs) are almost identical with those accepted at the present time.

Accuracy of the law of reciprocal proportions.—Perhaps the best proof of the accuracy of the law of reciprocal proportions is the existence of tables of atomic weights, which chemists everywhere use to calculate the composition of their compounds, rather than trust to even the best of their own analytical data. Further evidence is afforded by the maintenance of neutrality when neutral salts interact, as noticed first by Richter (p. 310). The question was, however, tested

definitely in 1811–1812 by Berzelius, who showed that 10 grams lead sulphide could be oxidised to lead sulphate without leaving any excess of litharge or of sulphuric acid thus proving "that lead sulphide contains its two constituents in the exact ratio required for the formation of lead sulphate" (*Fixed Proportions*, 1811–1812; Ostwald's *Klassiker*, XXXV. 11).

A still more stringent test was carried out by Stas, in 1865 (*Works*, I. 481–536), in response to the criticisms of Marignac. Stas removed the oxygen from silver iodate and examined the silver iodide produced, in order to see if it contained any excess of silver or of iodine. The excess was always less than 1 part in a million, and was often quite imperceptible, showing that *the proportion by weight of silver to iodine, in the iodate and in the iodide, is invariably the same* (*Works*, I. 500). Similar experiments were made with silver bromate, using about 20 grams for each experiment. In the case of silver chlorate, "259·4535 grams of this salt were transformed into chloride without liberating a trace of silver or of chlorine," thus proving that *the proportion by weight of silver and of chlorine is absolutely the same* in the two salts (*Works*, I. 535). Although fifty years have elapsed since this test was carried out by Stas, it would scarcely be possible to devise a more stringent proof of the accuracy of the law of reciprocal proportions.

Summary and Supplement.

John Dalton, about the year 1802, whilst studying the nature of the atmosphere, revived the atomic theory of the Greek philosophers and suggested that the "simple atoms" of an element (1) are all alike in size and weight, and (2) cannot be created or destroyed; but (3) may unite with other atoms in simple ratios to form "compound atoms," or molecules, as they are now called. These atoms were represented by symbols, *e.g.* hydrogen ⊙, oxygen ○, water ⊙○, which Berzelius, in 1819, replaced by letters *e.g.* H, O, H+O.

The atomic theory afforded an obvious explanation of—

(1) *The Law of Fixed Proportions.* "The elements combine together in fixed proportions by weight."

(2) *The Law of Multiple Proportions.* "When two compounds are formed, these proportions are in a simple ratio."

(3) *The Law of Reciprocal Proportions.* "The proportions in which two elements combine with a third are in a simple ratio to those in which they combine with a fourth element or with one another."

The Law of Reciprocal Proportions as applied to acids and alkalis was tacitly assumed by **Cavendish,** when in 1766 he referred to certain quantities of marble and of potash as *equivalent* to one another in their power of neutralising acids. It was formulated more definitely about 1792 by **J. B. Richter** (1762—1807), who showed that neutral salts remain neutral after double decomposition because the acids and alkalis unite reciprocally in equivalent quantities, *e.g.* the quantities of lime and potash which neutralise a fixed weight of sulphuric acid are identical with those required to neutralise a (different) fixed weight of nitric acid. A complete table of equivalents of acids and alkalis was drawn up by Fischer in 1802.

Berzelius in 1807 recognised the practical value of the Law of Reciprocal Proportions as consisting in the fact that, after analysing carefully the compounds of all the bases with (*e.g.*) sulphuric acid and of all the acids with (*e.g.*) baryta, one could calculate the composition of all other neutral salts. He applied the same idea to the elements and set to work to determine their *combining weights* by the exact analysis of a few typical compounds of each. This work was continued by **J. S. Stas** (1813—1891), who determined with extraordinary care the equivalents of carbon, nitrogen, sulphur, chlorine, bromine, iodine, lithium, sodium, potassium, lead and silver. In recent years similar work has been carried on by Prof. Guye at Geneva and by Prof. T. W. Richards at Harvard University.

Lists showing the chief analyses used in determining the equivalents or combining weights of the elements have been given by Ostwald (*Outlines of General Chemistry*, tr. 1912, pp. 126 to 150), and by Freund (*Study of Chemical Composition*, 1904, pp. 220 to 224).

It should be noted that Dalton had no trustworthy method of finding out the numbers of atoms of each element which were present in the molecule (Dalton's "compound atom") of a compound: his tables of atomic weights were therefore similar to a modern list of equivalents or combining weights.

CHAPTER XV

THE MOLECULAR THEORY

A. The Properties of Gases

The atomic and molecular theories.—The chief purpose of Dalton's atomic theory was to explain the laws which determine the composition of chemical compounds. The molecular theory, which we owe to Avogadro, was on the other hand very largely a physical theory, introduced in order to account for the extremely simple properties which characterise all substances when in the gaseous state. This simplicity is specially obvious in the changes of volume which are produced by

(1) changes of pressure (Boyle, 1662) ;
(2) changes of temperature (Charles, 1787) ;
(3) chemical combination (Gay-Lussac, 1809).

Boyle (1660) shows that air is an "elastic fluid."—In his "New Experiments, Physico-Mechanical, touching the Spring of the Air, and its Effects," published in 1660 (*Works*, 1725, II. 407–474), **Boyle** described an air-pump (Fig. 45) which was an improvement upon the pump used by Otto von Guericke in the celebrated experiment of the Magdeburg hemispheres (1654). With the help of this pump Boyle showed that a bladder, strongly tied at the neck, could be dilated and even burst by the "spring" of the air which

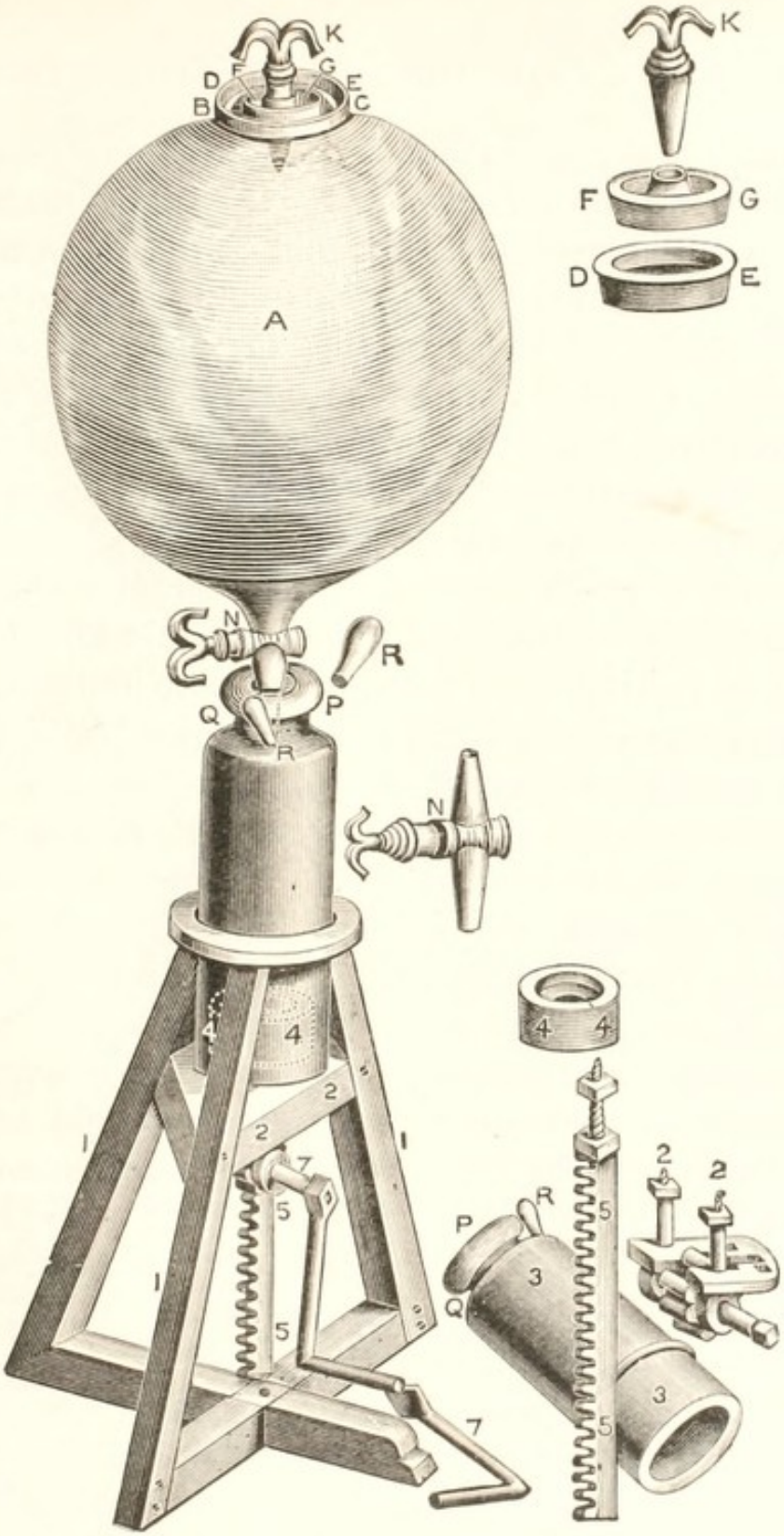


FIG. 45—BOYLE'S PNEUMATIC ENGINE OR AIR PUMP.

The air was exhausted from the glass globe A by means of a sucking-pump supported on a wooden frame 12. The insets show: 1. A brass ring DE cemented to the lip BC of the large glass A: it carries a glass stopper FG, pierced in the middle to receive the brass key K. 2. The stopcock N, cemented above to the glass DA, and below to the top PQ of the sucking-pump. 3. The brass cylinder 3, 3 of the sucking-pump, 14 inches long and 3 inches bore; the sucker 44 was fitted with a ring of tanned leather, and was driven by a handle 7 acting through a rack-and-pinion gear 5, 5. The cylinder was charged with a little oil or water to make the sucker air-tight. During the downward stroke of the sucking-pump, the valve R was closed and the tap N opened to admit air from the globe; during the upward stroke N was closed and R opened.

it contained, if the air outside the bladder was removed by means of the pump (*Works*, 1725, II. 413). Quantitative measurements showed that air could be dilated in this way to 9, 32, or 60 times its original volume; in an extreme case, a "bubble of air possessing the space of but one grain weight of water, . . . by its own spring, was rarefied to one hundred and fifty-two times its former dimensions; though it had been compressed only by the ordinary weight of the contiguous air" (*Works*, 1725, II. 415). Analogous experiments in which water was "freed from the pressure of the atmosphere," revealed numerous little bubbles, produced by air lurking in the water, but gave no indication at all "that water uncompressed, has an elastic power" (*ibid.*, p. 428).

A few years later **Mayow** showed that "air in which an animal or a lamp had expired, possessed elastic force in an equal degree with unimpaired air." He also experimented with gases prepared artificially by the action of acids on iron (Boyle, 1660; *Works*, 1725, II. 432), and "ascertained that air of that kind expands to more than two hundred times its volume; and indeed if it had been relieved from the pressure of the surrounding water, it would have expanded twice as much. Nor will common air, when treated in the same manner, expand more" (A.C.R. XVII. 115).

By the experiments of Boyle and of Mayow, air was shown to be typical of a group of "elastic fluids," which differed from liquids in that they could expand in every direction when the pressure acting upon them was reduced. It was, however, left to Cavendish and to Priestley (p. 70) to show clearly that the different gases or "airs" which possess this remarkable property are distinct substances and not merely different varieties of common air.

Boyle's explanation of the "spring of the air." In order to explain his observations, Boyle suggested:

"That there is a Spring, or Elastical power in the Air we live in. By which Spring of the Air, that which I mean is

this : That our Air either consists of, or at least abounds with, parts of such a nature, that in case they be bent or compress'd by the weight of the incumbent part of the Atmosphere, or by any other Body, they do endeavor, as much as in them lies, to free themselves from that pressure, by bearing against the contiguous Bodies that keep them bent ; and, as soon as those Bodies are remov'd or reduced to give them way, by presently unbending and stretching out themselves, either quite, or so far forth as the contiguous Bodies that resist them will permit, and thereby expanding the whole parcel of Air, these elastical Bodies compose.

"This Notion may perhaps be somewhat further explain'd, by conceiving the Air near the Earth to be such a heap of little Bodies, lying one upon another, as may be resembled to a Fleece of Wool. For this (to omit other likenesses betwixt them) consists of many slender and flexible Hairs ; each of which may, indeed, like a little Spring, be easily bent or rolled up ; but will also, like a Spring, be still endeavouring to stretch itself out again. . . ."

"There is yet another way to explicate the Spring of the Air, namely, by supposing with that most ingenious Gentleman, Monsieur **Des Cartes**, that the Air is nothing but a Congeries or heap of small and (for the most part) of flexible Particles ; of several sizes, and of all kind of Figures which are rais'd by heat (especially that of the Sun) into that fluid and subtle Etherial Body that surrounds the Earth ; and by the restless agitation of that Celestial Matter wherein those Particles swim, are so whirl'd round that each Corpuscle endeavours to beat off all others from coming within the little Sphear requisite to its motion about its own Center ; and (in case any by intruding into that Sphear shall oppose its free Rotation) to expel or drive it away : So that according to this Doctrine, it imports very little, whether the particles of the Air have the structure requisite to Springs, or be of any other form (how irregular soever) since their Elastical power is not made to depend upon their shape or structure, but upon the vehement agitation, and (as it were) brandishing motion, which they receive from the fluid *Ether* that swiftly flows between them, and whirling about each of them (independently from the rest) not only keeps

those slender Aerial Bodies separated and stretcht out (at least, as far as the Neighbouring ones will permit) which otherwise, by reason of their flexibleness and weight, would flag or curl; but also makes them hit against, and knock away each other, and consequently require more room, then that which if they were compress'd, they would take up.

"By these two differing ways, . . . , may the Spring of the Air be explicated. But though the former of them be that, which by reason of its seeming somewhat more easie, I shall for the most part make use of in the following Discourse: yet am I not willing to declare peremptorily for either of them, against the other ("New Experiments touching the Spring of the Air," 1660, pp. 22-26; compare *Works*, 1725, II. 410).

The second explanation, which Boyle borrowed from Descartes, resembled somewhat closely that which is generally adopted at the present day under the name of the KINETIC THEORY OF GASES. According to this theory, gases consist of elastic particles, moving with a high velocity, and by their incessant collisions producing a constant pressure upon each other and upon the walls of the containing vessel. Their velocity is an expression of the heat energy which the gas possesses, and increases with the temperature in such a way that the temperature of a gas may be measured by the pressure which it produces in a vessel of given volume.

Boyle (1662) measures the condensation and rarefaction of the air. Boyle's law.

In a "Defence of the Doctrine touching the Spring and Weight of the Air . . . . against the Objections of Franciscus Linus," published in 1662, Boyle described "two new Experiments touching the measure of the Force of the Spring of Air compressed and dilated" (*Defence*, pp. 57 68; *Works*, 1725, II. 670).

In the first experiment, air was compressed by means of a column of mercury into one limb of a long glass tube, shaped like an inverted syphon (Fig. 46). The column of

air was gradually compressed from 12 to 3 inches, and the pressures (including the atmospheric pressure of $29\frac{2}{16}$ inches) were measured for twenty-five different volumes of the air. These pressures were found to agree very closely with "what that pressure should be according to the *Hypothesis*, that supposes the pressures and expansions to be in reciprocal proportion."

In the second experiment, on the debilitated force of expanded air, a slender glass tube was immersed in mercury and closed at the top with sealing wax, in such a way as to enclose a column of air an inch long. The tube was raised gradually until the air had expanded to 32 inches and the position of the mercury was read for a series of nineteen different volumes. Once again the pressures were found to agree closely with those calculated from the *Hypothesis*.

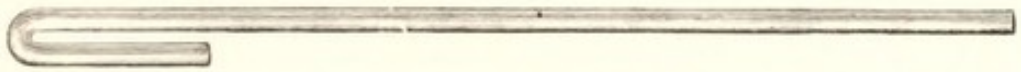


FIG. 46—TUBE USED IN BOYLE'S EXPERIMENTS ON THE CONDENSATION OF THE AIR.

Boyle's two tables are reproduced on p. 326, where all the numbers represent inches.

The *Hypothesis*, now known as BOYLE'S LAW, states that if the temperature is constant *the volume of a gas is inversely proportional to its pressure.* Although applied at first only to air, it was found to be approximately true for all other gases and vapours. But in no case is it accurately true; thus in the case of both hydrogen and nitrogen the volume under a pressure of 300 atmospheres is about 25 per cent. greater than that calculated from Boyle's law.

Gay-Lussac (1802) measures the expansion of gases by heat.—The fact that air is expanded by heat was well known in the time of **Boyle** (see, for instance, Boyle's *Works*, II.

A Table of the Condensation of the Air.

A	B	C	D	E
12	00	Added to $29\frac{3}{4}$ makes	$29\frac{2}{16}$	$29\frac{2}{16}$
$11\frac{1}{2}$	$01\frac{7}{16}$		$30\frac{9}{16}$	$30\frac{6}{16}$
11	$02\frac{13}{16}$		$31\frac{15}{16}$	$31\frac{12}{16}$
$10\frac{1}{2}$	$04\frac{6}{16}$		$33\frac{8}{16}$	$33\frac{1}{7}$
10	$06\frac{3}{16}$		$35\frac{5}{16}$	35
$9\frac{1}{2}$	$07\frac{14}{16}$		37	$36\frac{15}{16}$
9	$10\frac{2}{16}$		$39\frac{4}{16}$	$38\frac{7}{8}$
$8\frac{1}{2}$	$12\frac{8}{16}$		$41\frac{10}{16}$	$41\frac{2}{7}$
8	$15\frac{1}{16}$		$44\frac{3}{16}$	$43\frac{14}{16}$
$7\frac{1}{2}$	$17\frac{15}{16}$		$47\frac{1}{16}$	$46\frac{2}{5}$
7	$21\frac{3}{16}$		$50\frac{5}{16}$	50
$6\frac{1}{2}$	$25\frac{3}{16}$		$54\frac{5}{16}$	$53\frac{10}{16}$
6	$29\frac{11}{16}$		$58\frac{13}{16}$	$58\frac{8}{8}$
$5\frac{3}{4}$	$32\frac{3}{16}$		$61\frac{5}{16}$	$60\frac{8}{13}$
$5\frac{1}{2}$	$34\frac{15}{16}$		$64\frac{1}{16}$	$63\frac{6}{11}$
$5\frac{1}{4}$	$37\frac{15}{16}$		$67\frac{1}{16}$	$66\frac{4}{7}$
5	$41\frac{9}{16}$		$70\frac{11}{16}$	70
$4\frac{3}{4}$	45		$74\frac{2}{16}$	$73\frac{11}{19}$
$4\frac{1}{2}$	$48\frac{12}{16}$		$77\frac{14}{16}$	$77\frac{2}{3}$
$4\frac{1}{4}$	$53\frac{11}{16}$		$82\frac{12}{16}$	$82\frac{4}{17}$
4	$58\frac{2}{16}$		$87\frac{14}{16}$	$87\frac{3}{8}$
$3\frac{3}{4}$	$63\frac{15}{16}$		$93\frac{1}{16}$	$93\frac{1}{5}$
$3\frac{1}{2}$	$71\frac{3}{16}$		$100\frac{7}{16}$	$99\frac{6}{7}$
$3\frac{1}{4}$	$78\frac{11}{16}$		$107\frac{13}{16}$	$107\frac{7}{13}$
3	$88\frac{7}{16}$		$117\frac{9}{16}$	$116\frac{4}{8}$

A. The number of equal spaces in the shorter leg, that contained the same parcel of Air diversely extended.

B. The height of the Mercurial Cylinder in the longer leg, that compressed the Air into those dimensions.

C. The height of a Mercurial Cylinder that counterbalanced the pressure of the Atmosphere.

D. The Aggregate of the two last columns B and C, exhibiting the pressure sustained by the included Air.

E. What that pressure should be according to the *Hypothesis*, that supposes the pressures and expansions to be in reciprocal proportion.

A Table of the Rarefaction of the Air.

A	B	C	D	E
1	$00\frac{9}{16}$	Subtracted from $29\frac{3}{4}$ leaves	$29\frac{3}{4}$	$29\frac{3}{4}$
$1\frac{1}{2}$	$10\frac{5}{16}$		$19\frac{1}{2}$	$19\frac{5}{16}$
2	$15\frac{3}{8}$		$14\frac{3}{8}$	$14\frac{3}{8}$
3	$20\frac{9}{16}$		$9\frac{4}{8}$	$9\frac{15}{16}$
4	$22\frac{5}{8}$		$7\frac{1}{8}$	$7\frac{7}{16}$
5	$24\frac{1}{8}$		$5\frac{5}{8}$	$5\frac{13}{16}$
6	$24\frac{3}{8}$		$4\frac{3}{8}$	$4\frac{3}{4}$
7	$25\frac{4}{8}$		$4\frac{1}{8}$	$4\frac{1}{4}$
8	$26\frac{6}{8}$		$3\frac{2}{8}$	$3\frac{3}{32}$
9	$26\frac{8}{8}$		$3\frac{1}{8}$	$3\frac{11}{16}$
10	$26\frac{6}{8}$		$3\frac{3}{8}$	$2\frac{3}{4}$
12	$27\frac{1}{8}$		$2\frac{5}{8}$	$2\frac{3}{4}$
14	$27\frac{4}{8}$		$2\frac{2}{8}$	$2\frac{1}{8}$
16	$27\frac{5}{8}$		$2\frac{1}{8}$	$1\frac{5}{64}$
18	$27\frac{7}{8}$		$1\frac{7}{8}$	$1\frac{47}{32}$
20	28		$1\frac{6}{8}$	$1\frac{9}{16}$
24	$28\frac{2}{8}$		$1\frac{4}{8}$	$1\frac{3}{8}$
28	$28\frac{3}{8}$		$1\frac{3}{8}$	$1\frac{1}{16}$
32	$28\frac{4}{8}$		$1\frac{2}{8}$	$0\frac{19}{128}$

A. The number of equal spaces at the top of the Tube, that contained the same parcel of Air.

B. The height of the Mercurial Cylinder, that together with the Spring of the included Air counterbalanced the pressure of the Atmosphere.

C. The pressure of the Atmosphere.

D. The complement of B to C, exhibiting the pressure sustained by the included Air.

E. What that pressure should be according to the *Hypothesis*.

671). During the next hundred years many attempts were made to measure this expansion; but the results were very irregular, mainly because the air, and the vessels in which it was contained, were not sufficiently dried.

Still greater irregularities were observed when **Priestley**, in 1777 ("Experiments on Air," III. 345-348), measured the expansion by heat of different gases and found that

"The different kinds of air are expanded by the addition of ten degrees of heat according to Fahrenheit's thermometer, in the following proportion.

Common air	1·32
Inflammable air	2·05
Nitrous air	2·02
Fixed air	2·20
Marine acid air	1·33
Dephlogisticated air	2·21
Phlogisticated air	1·65
Vitriolic acid air	2·37
Fluor acid air	2·83
Alkaline air	4·75

(*Experiments and Observations*, V. 359).

The fact "that oxygen, azote, hydrogen and carbonic acid, and atmospheric air expand equally between 0° and 80°" was discovered by **Charles** about the year 1787, but his results were never published (Gay-Lussac, *Ann. de Chimie*, 1802, **43**. 157). The more detailed experiments "On the dilatation of gases and vapours," which were described by Gay-Lussac in 1802 (*loc. cit.* 137–175), were made with the apparatus shown in Fig. 47, or with a modified apparatus in which the iron tap was replaced by a mercury valve. The expansion between the freezing-point and the boiling-point of water was measured by heating the gas to the temperature of boiling water, opening the tap to allow the excess of gas to escape, then cooling in ice and weighing the water that was drawn in when the tap was again opened under water. Six experiments with common air showed that

"From the temperature of melting ice to that of boiling water, equal volumes of atmospheric air represented by 100 became 137·40, 137·61, 137·44, 137·55, 137·48, 137·57, of which the mean is nearly 137·50" (*loc. cit.* p. 165).

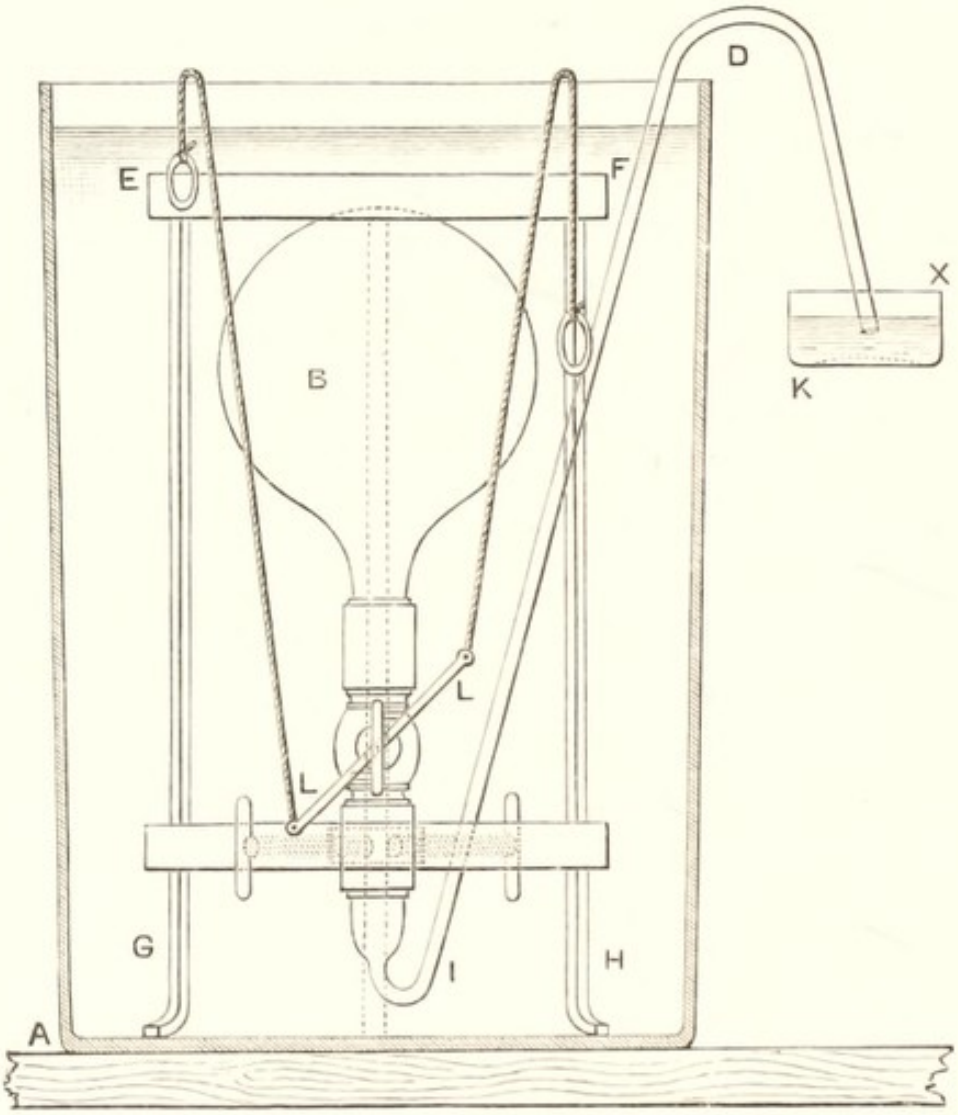


FIG. 47.—GAY-LUSSAC'S APPARATUS FOR MEASURING THE EXPANSION OF GASES AND VAPOURS.

The globe B is provided with a tap worked by a lever LL. After filling it with gas, the globe is fixed in the iron cage EFGH and immersed in a copper vessel AD full of water. The curved tube ID leads to a trap KX filled with mercury.

The increase of volume for four different gases was shown (*loc. cit.* p. 167) in a table as follows :—

	Expansion.	Differences.
Atmospheric air	37·50	—
Hydrogen	37·52	+0·02
Oxygen	37·48	−0·02
Azote	37·49	−0·01

In the case of five gases which were soluble in water comparative experiments were made with tubes of carefully-dried gas inverted over mercury (Fig. 48), the expansion observed being identical in every case with that of atmospheric air. Gay-Lussac summarises his conclusions as follows:

"The experiments which I have just described and which were all made with great care, prove incontestably that atmospheric air and oxygen, hydrogen, azote, nitrous gas, ammonia, muriatic gas, sulphurous acid, and carbonic acid are expanded equally by the same degrees of heat; and that, consequently, their greater or less density . . . , their greater or less solubility in water and their particular nature, have no influence on their expansion."

"From this consideration I conclude that all gases, in general, are expanded equally by the same degrees of heat; provided that they are all placed under the same conditions" (*loc. cit.* p. 172).

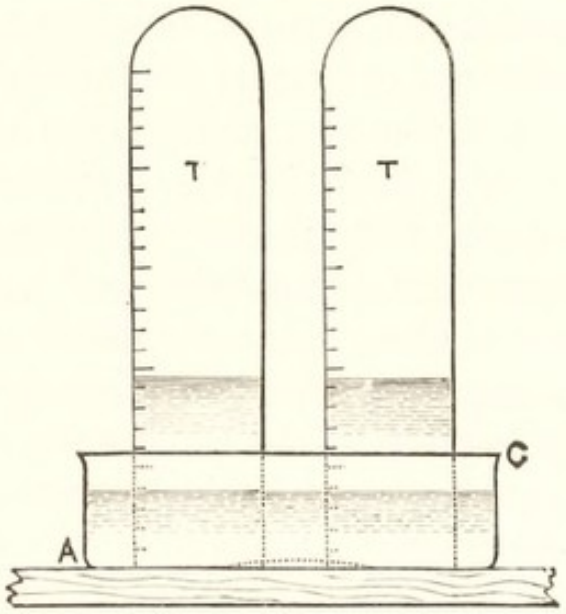


FIG. 48.—GAY-LUSSAC'S APPARATUS FOR COMPARING THE EXPANSION OF AIR WITH THAT OF SOLUBLE GASES AND VAPOURS.

The gases were confined over mercury in two tubes TT standing in a trough of mercury AC.

A further series of experiments on the expansion of the vapour of ether between 60° and 100° C. (*loc. cit.* p. 173) carried out in the presence of Berthollet, showed that the law of equal expansions could be applied to vapours as well as to gases; Gay-Lussac therefore concluded that they would probably be equally compressible, *i.e.* that the simple hypothesis of Boyle could be applied to vapours, so long as they remained uncondensed. All gases and all vapours would then be influenced in the same way by changes of pressure

and of temperature—a remarkable conclusion that has no parallel in the behaviour of liquids or solids.

B. The Combining Volumes of Gases

Cavendish (1781) measures the combining volumes of hydrogen and oxygen.—In his experiments on the composition of water Cavendish found that 423 measures of hydrogen were just sufficient to remove the oxygen from 1000 measures of air. If we assume that 20·9% of the atmosphere consists of oxygen, this would mean that 209 measures of oxygen combine with 423 measures of hydrogen or 100 measures of oxygen with 202 measures of hydrogen. He also found that a mixture of 19500 grain measures of oxygen and 37000 of inflammable air, after a series of explosions, left a residue of 2950 grain measures of gas, of which about 1000 consisted of unburnt oxygen. If it be assumed that the remaining 1950 grain measures consisted of impurities, shared between hydrogen and oxygen in proportion to their original volumes, we find that $19500 - 1000 - 650 = 17850$ measures of oxygen combined with $37000 - 1300 = 35700$ measures of hydrogen; that is, one volume of oxygen combined exactly with two volumes of hydrogen.

Gay-Lussac and Humboldt (1805) measure the combining volumes of hydrogen and oxygen.—In the year 1805, Gay-Lussac and Humboldt (*Jour. de Physique*, 1805, **60**, 129) attempted to determine the "Ratio of the Constituents of the Atmosphere" by exploding air with hydrogen in a Volta's eudiometer and measuring the diminution of volume which resulted. In order to interpret their observations they found it necessary to make a fresh determination of the ratio by volumes in which hydrogen and oxygen unite. The most trustworthy series of experiments was one in which 100 parts of oxygen (of which 99·6 parts could be absorbed by potassium sulphide)

were exploded with 300 parts of hydrogen and produced a diminution of 298·7 parts by volume. In these experiments 99·6 parts of oxygen united with 298·7–99·6 = 199·1 parts of hydrogen, or 100 parts of oxygen united with 199·89 parts of hydrogen, a number that did not differ appreciably from that required for the exact integral ratio 1 : 2 (*loc. cit.* pp. 146—147).

Gay-Lussac (1809) states that gases combine in simple proportions by volume.—(1) *The combination of ammonia with acids.* This simple relationship between the combining volumes of hydrogen and oxygen was in such striking contrast with the complex ratio of the combining weights that Gay-Lussac in 1809 (A.C.R. IV. 8-24) proceeded to examine the ratios of the combining volumes of other gases. As the simplest case he studied first the combination of ammonia with acid gases, including muriatic acid gas and carbonic anhydride. He found that :

" 100 parts of muriatic gas saturate precisely 100 parts of ammonia gas, and the salt which is formed from them is perfectly neutral, whether one or other of the gases is in excess." " If carbonic gas is brought into contact with ammonia gas, by passing it sometimes first, sometimes second into the tube, there is always formed a sub-carbonate composed of 100 parts of carbonic gas, and 200 of ammonia gas " (A.C R. IV. 10).

(2) *Composition by volume of ammonia, sulphuric acid and carbonic anhydride.* Equally simple relationships were found to govern the proportions of nitrogen and hydrogen in ammonia gas, of " sulphurous gas " and oxygen in sulphuric anhydride, and of the carbonic oxide and oxygen in carbonic anhydride.

" According to the experiments of M. Amédée Berthollet, ammonia is composed of :

100 of nitrogen,
300 of hydrogen

by volume.

"I have found (1st vol. of the Société d'Arcueil) that sulphuric acid is composed of :

100 of sulphurous gas,
50 of oxygen gas.

"When a mixture of 50 parts of oxygen and 100 of carbonic oxide (formed by the distillation of oxide of zinc with strongly calcined charcoal) is inflamed, these two gases are destroyed, and their place taken by 100 parts of carbonic acid gas. Consequently carbonic acid may be considered as being composed of :

100 of carbonic oxide gas,
50 of oxygen gas." (A.C.R. IV. 13).

(3) *The oxides of nitrogen.* Gay-Lussac next calculated from Davy's analyses the volumes of nitrogen and oxygen which would be obtained from the oxides of nitrogen, if these could be decomposed into their elements, and showed that the volume ratios were again of the very simplest.

"Davy, from the analysis of various compounds of nitrogen and oxygen, has found the following proportions by weight :—

	Nitrogen.	Oxygen.
Nitrous oxide	63·30	36·70
Nitrous gas	44·05	55·95
[Nitrogen peroxide] . . .	29·50	70·50

Reducing these proportions to volumes, we find :–

	Nitrogen.	Oxygen.
Nitrous oxide	100	49·5
Nitrous gas	100	108·9
[Nitrogen peroxide] . . .	100	204·7

The first and last of these proportions differ only slightly from 100 to 50, and 100 to 200 ; it is only the second which diverges somewhat from 100 to 100. The difference, however, is not very great, and is such as we might expect in experiments of this sort ; and I have assured myself that it is actually nil. On burning the new combustible substance from potash in 100 parts by volume of nitrous gas, there

remained over exactly 50 parts of nitrogen, the weight of which, deducted from that of the nitrous gas (determined with great care by M. Bérard at Arcueil), yields as result that this gas is composed of equal parts by volume of nitrogen and oxygen.

We may then admit the following numbers for the proportions by volume of the compounds of nitrogen with oxygen.

	Nitrogen.	Oxygen.
Nitrous oxide	100	50
Nitrous gas	100	100
[Nitrogen peroxide] . . .	100	200"

(A.C.R. IV. 13-14.)

From the observations recorded above Gay-Lussac concluded that "gases always combine in the simplest proportions when they act on one another" (A.C.R. IV. 15).

Extension of the law of volumes to the products formed by the interaction of gases.—Further experiments convinced Gay-Lussac that :

"Not only, however, do gases combine in very simple proportions, as we have just seen, but the apparent contraction of volume which they experience on combination has also a simple relation to the volume of the gases, or at least to that of one of them."

"I have said, following M. Berthollet, that 100 parts of carbonic oxide gas, prepared by distilling oxide of zinc and strongly calcined charcoal, produce 100 parts of carbonic gas on combining with 50 of oxygen. It follows from this that the apparent contraction of the two gases is precisely equal to the volume of oxygen gas added."

"We know, besides, that a given volume of oxygen produces an equal volume of carbonic acid ; consequently oxygen gas doubles its volume on forming carbonic oxide gas with carbon, and so does carbonic gas on being passed over red-hot charcoal."

"Oxygen gas, in combining with sulphur to form sulphurous gas, only experiences a diminution of a fiftieth of its volume, and this would probably be nil if the data I have employed were more exact."

"Ammonia gas is composed of three parts by volume of hydrogen, and one of nitrogen, and its density compared to the air is 0·596. But if we suppose the apparent contraction to be half of the whole volume, we find 0·594 for the density. Thus it is proved, by this almost perfect concordance, that the apparent contraction of its elements is precisely half the total volume, or rather double the volume of the nitrogen.

"We see, then, from these various examples, that the contraction experienced by two gases on combination is in almost exact relation with their volume, or rather with the volume of one of them" (A.C.R. IV. 15–20).

Gay-Lussac's law of volumes.—Gay-Lussac summarises his conclusions in the following words:

"I have shown in this memoir that the compounds of gaseous substances with each other are always formed in very simple ratios, so that representing one of the terms by unity, the other is 1, or 2, or at most 3. These ratios by volume are not observed with solid or liquid substances, nor when we consider weights, and they form a new proof that it is only in the gaseous state that substances are in the same circumstances and obey regular laws. . . . The apparent contraction of volume suffered by gases on combination is also very simply related to the volume of one of them, and this property likewise is peculiar to gaseous substances" (A.C.R. IV. 24).

In order to include all the cases discussed in the memoir, Gay-Lussac's law of volumes may be stated as follows:

When gases enter or leave chemical combination, the volumes absorbed, or liberated, are in simple ratios to one another.

Modification of Gay-Lussac's law.—Later experiments have shown that Gay-Lussac's law does not hold exactly. Thus, Scott (*Phil. Trans.*, 1893, **184**, 566), by exploding together gases of remarkable purity, found that hydrogen and oxygen combine together at ordinary temperatures in the ratio 2·00245 to 1. This deviation from Gay-Lussac's law is confirmed by the work of Morley (p. 131), who found

the ratio at 0°C to be 2·00269. In the same way it has been shown that the volume of hydrogen contained in two volumes of hydrogen chloride is not 1, but 1·00790 (Gray and Burt, *Trans. Chem. Soc.*, 1909, **95**, 1656), whilst the combining ratio of hydrogen and nitrogen in ammonia is 3·00172 (Guye and Pintza, *Comptes rendus*, 1908, **147**, 928).

These deviations from exact whole numbers probably depend on the fact that gases differ slightly in their compressibility, so that equal volumes under a pressure of 1 atmosphere would become unequal under a pressure of 2 atmospheres or $\frac{1}{2}$ atmosphere. It is, however, believed that Gay-Lussac's law would hold good accurately if the gases could be examined under very low pressures.

Gay-Lussac's law of volumes explained by the atomic theory.—Gay-Lussac's observations provided excellent examples of the laws of chemical combination described in the preceding chapter. Thus, no better illustration could be desired of the law of "Multiple Proportions" than the three oxides of nitrogen, the two oxides of carbon and the two oxides of sulphur, in which the proportions of oxygen to the other element were shown by Gay-Lussac to be in the ratios 1 : 2 : 4, 1 : 2 and 2 : 3 respectively. It is therefore not surprising that Gay-Lussac was ready to interpret his observations by means of the atomic theory which Dalton had suggested a few years previously.

"According to Dalton's ingenious idea, that combinations are formed from atom to atom, the various compounds which two substances can form would be produced by the union of one molecule of the one with one molecule of the other, or with two, or with a greater number, but always without intermediate compounds."

"The numerous results I have brought forward in this Memoir are also very favourable to the theory" (A.C.R. IV. 23).

The law of volumes rejected by Dalton.—It is, however, remarkable that Dalton, instead of welcoming the Law of

Volumes as giving support to his theory, refused to recognise its validity, and even proceeded to question the evidence on which it was based. The argument which influenced him so strongly is summarised in the following paragraphs.

The simplest way of applying the atomic theory to gases was to assume that the space occupied by the atom (or molecule) was the same for all gases. This hypothesis was worked out by Dalton in the first volume of his "New System," published in 1808, where he writes :

"At the time I formed the theory of mixed gases, I had a confused idea, as many have, I suppose, at this time, that the particles of elastic fluids are all of the same size ; that a given volume of oxygenous gas contains just as many particles as the same volume of hydrogenous ; or if not, that we had no data from which the question could be solved" (A.C.R. IV. 6–7).

"By the size or volume of an ultimate particle, I mean in this place, the space it occupies in the state of a pure elastic fluid" (A.C.R. IV. 6).

But the logical consequences of the hypothesis were such that Dalton "became convinced that different gases have *not* their particles of the same size," and concluded :

"*That every species of pure elastic fluid has its particles globular and all of a size; but that no two species agree in the size of their particles*, the pressure and temperature being the same" (A.C.R. IV. 7).

This conclusion was reached as the result of an argument which showed that, if the atoms or molecules of all gases occupied the same volume, there must be a *decrease of volume* and an *increase of density*, whenever the atoms of two simple gases united together to form the molecules of a compound gas. But in the case of nitric oxide (nitrous air), Davy's observations showed :

(1) That the volume of the gas was equal to that of its

constituents, which did not therefore contract in combination, and

(2) That whilst the density of the gas was a little greater than that of nitrogen it was actually less than that of the oxygen which formed one of its constituents. Davy's actual figures (*Works*, III. 9–10) were :

Nitrogen	30·45	grains	per	100	cubic	inches.
Nitric oxide	34·3	,,	,,	,,	,,	,,
Oxygen	35·09	,,	,,	,,	,,	,,

Dalton argues as follows :

"If equal measures of azotic and oxygenous gases were mixed, and could be instantly united chemically, they would form nearly two measures of nitrous gas, having the same weight as the two original measures ; but the number of ultimate particles could at most be one half of that before the union. No two elastic fluids, probably, therefore, have the same number of particles, either in the same volume or the same weight" (A.C.R. IV. 5).

When Gay-Lussac, in 1809, put forward his Law of Volumes, the simple hypothesis to which it seemed to point had therefore already been tested by Dalton, and found to be untenable. It is not surprising then that Dalton should become its foremost opponent, his repudiation extending even to a refusal to accept the experimental facts to which Gay-Lussac had called attention. In the second part of his "New System," published in 1810, he sums up his criticism as follows :

"The truth is, I believe, that gases do not unite in equal or exact measures in any one instance ; when they appear to do so, it is owing to the inaccuracy of our experiments. In no case, perhaps, is there a nearer approach to mathematical exactness, than in that of 1 measure of oxygen to 2 of hydrogen ; but here, the most exact experiments I

have ever made, gave 1·97 hydrogen to 1 oxygen" (A.C.R. IV. 27).

C. AVOGADRO'S HYPOTHESIS

Avogadro (1811) revives Dalton's discarded hypothesis.—The suggestion as to the spacing of gaseous atoms, which Dalton had considered and rejected in 1808, was revived three years later, in 1811, by **Amadeo Avogadro,** (1776–1856) Professor of Physics at Turin, as the most obvious, perhaps even the only possible, method of explaining Gay-Lussac's Law of Volumes. AVOGADRO'S HYPOTHESIS, as it is now generally called, states that:

"When their temperatures and pressures are equal, *equal volumes of different gases contain equal numbers of molecules.*"

Later researches have proved the substantial truth, as well as the usefulness of this hypothesis. But it is now recognised that (like Gay-Lussac's Law of Volumes) it is strictly accurate only when applied to gases under very low pressures; if applied to gases at atmospheric pressures, a correction must be made for their unequal compressibilities.

Avogadro postulates complex molecules in gaseous elements.—The merit of Avogadro's paper on the "Relative Masses of Elementary Molecules," consists in the fact that he was able to find a remedy for the defects which had proved fatal to the hypothesis as discussed and condemned by Dalton. Avogadro suggested that all difficulties would disappear if the molecules of an elementary gas consisted of groups of atoms, similar to those which formed the molecules of a compound gas.

If the molecules of an element were indivisible they could never give rise to more than an equal number of

molecules of a compound; a gaseous element could therefore never give rise to more than its own volume of a gaseous compound. But Gay-Lussac had shown that "the volume of water in the gaseous state is . . . twice as great as the volume of oxygen which enters into it," *i.e.* 1 volume of oxygen produces 2 volumes of steam, or (on the theory of equal spacing) 1 molecule of oxygen produces 2 molecules of steam.

"But a means of explaining facts of this type in conformity with our hypothesis presents itself naturally enough: we suppose namely that the constituent molecules of any simple gas . . . are not formed of a solitary elementary [atom], but are made up of a certain number of these [atoms] united by attraction to form a single [molecule]" (A.C.R. IV. 31).

When the element enters into combination, this molecule may be split into two or more parts, giving rise to two or more molecules of a compound, which would thus occupy a volume two or more times as great as that of the element.

Avogadro pointed out that the molecule of an element does not usually split into more than two parts, although rightly enough he asserts the possibility of further subdivision.

"On reviewing the various compound gases most generally known, I only find examples of duplication of the volume relatively to the volume of that one of the constituents which combines with one or more volumes of the other. We have already seen this for water. In the same way, we know that the volume of ammonia gas is twice that of the nitrogen which enters into it. M. Gay-Lussac has also shown that the volume of nitrous oxide is equal to that of the nitrogen which forms part of it, and consequently twice that of the oxygen. Finally, nitrous gas, which contains equal volumes of nitrogen and oxygen, has a volume equal to the sum of the two constituent gases, that is to say,

double that of each of them. Thus in all these cases there must be a division of the molecule into two; but it is possible that in other cases the division might be into four, eight, etc." (A.C.R. IV. 32).

Molecules which can be divided into four atoms have since been found in the vapours of phosphorus and arsenic, whilst the vapour of boiling sulphur contains molecules which are divisible into eight atoms, exactly as suggested by Avogadro in the preceding paragraph.

Molecular weights determined by means of Avogadro's hypothesis.—Avogadro pointed out that, on the theory of equal spacing, the density of a gas is proportional to the weight of its molecules.

"Setting out from this hypothesis, it is apparent that we have the means of determining very easily the relative masses of the molecules of substances obtainable in the gaseous state . . . for the ratios of the masses of the molecules are then the same as those of the densities of the different gases at equal temperature and pressure" (A.C.R. IV. 30).

This argument may be illustrated by the following example. Suppose that the weights of 1 litre of oxygen and hydrogen are 1·42900 and 0·089873 gram respectively, at 0°C. and 760 mm.; and that there are n molecules in 1 litre of either gas. Then:

$$\frac{1{\cdot}42900 \text{ grams}}{0{\cdot}089873 \text{ gram}} = \frac{\text{Weight of 1 litre of oxygen,}}{\text{Weight of 1 litre of hydrogen.}}$$

$$= \frac{\text{Weight of } n \text{ molecules of oxygen,}}{\text{Weight of } n \text{ molecules of hydrogen.}}$$

$$= \frac{\text{Weight of 1 molecule of oxygen,}}{\text{Weight of 1 molecule of hydrogen}}$$

For the purposes of the argument it is not necessary to know the actual number of molecules in the litre of gas, but recent experiments have shown that the number n has the value 3×10^{22}, the probable error in this number being only about 10 per cent. The "Avogadro constant," N, which represents the number of atoms in the gram-atom or of molecules in the gram-molecule, *e.g.* oxygen atoms in 16 grams of oxygen, or oxygen molecules in 32 grams of oxygen, has been found to be 67×10^{22}, ten different methods of measurement having given values lying between 62 and 72×10^{22}.

Complexity of gaseous molecules determined by means of Avogadro's hypothesis.—The fundamental weakness of Dalton's Atomic Theory arose from the fact that he had no way of finding out how many atoms were present in the molecule of a given compound. He always chose the simplest formulæ that were possible; but this procedure was quite arbitrary, and it was not possible to say whether the conclusions arrived at were correct or not. Avogadro's hypothesis had the merit of supplying a method by which the relative weights of the atoms, and their relative numbers in any given compound, could be determined from the properties of the substances themselves, instead of from the arbitrary whim of the investigator. The following examples were selected as illustrations of the new method:

Water.—Dalton had supposed that water was formed by the union of one atom of hydrogen with one atom of oxygen. Avogadro recognising that:

> 2 volumes of hydrogen + 1 volume of oxygen yield 2 volumes of steam

and that, therefore:

> 2 molecules of hydrogen + 1 molecule of oxygen yield 2 molecules of steam,

regarded the molecule of water as "composed of a half-molecule of oxygen with one molecule, or, what is the same thing, two half-molecules of hydrogen" (A.C.R. IV. footnote, p. 32).

Nitric Oxide and Ammonia —In the same way Avogadro was able to show that since:

> 1 volume of oxygen and 1 volume of nitrogen are present in 2 volumes of nitrous gas

the molecule of nitrous gas is "composed of a half-molecule of oxygen and a half-molecule of nitrogen" (A.C.R. IV. 36). So too in the case of ammonia, Berthollet's observation that:

> 2 volumes of ammonia are decomposed by sparking into 1 volume of nitrogen and 3 volumes of hydrogen

led Avogadro to conclude that the molecule of ammonia is composed of one half-molecule of nitrogen combined with three half-molecules of hydrogen.

Muriatic Acid.—Another case quoted by Avogadro is that of gaseous muriatic acid.

"It follows from the experiments both of Gay-Lussac and Thenard, and of Davy, that muriatic acid gas is formed by the combination of equal volumes of [chlorine] and hydrogen, and that its volume is equal to their sum. This means, according to our hypothesis, that muriatic acid is formed of these two substances united molecule to molecule, with halving of the molecule, of which we have had so many examples." (A.C.R. IV. 44.)

Here since:

> 1 volume of hydrogen and 1 volume of chlorine give 2 volumes of hydrogen chloride,

the molecule of hydrogen chloride is composed of one half-molecule of hydrogen and one half-molecule of chlorine.

In the case of each of the gaseous elements (hydrogen, oxygen, nitrogen and chlorine) discussed by Avogadro in this section of his memoir, the molecule was found to be divisible into two parts, but no further division was observed. *The indivisible atom was therefore probably the half-molecule in the case of each of these gases.* It should be observed, that the facts prove no more than that the molecule can be divided into some *even number* of atoms. In a later section further reasons will be given in support of the belief that in each of these cases not more than two atoms are contained in the molecules; but other cases are known in which the molecules of a gas can be divided into 3, 4, 6 or 8 atoms.

Avogadro's hypothesis neglected for nearly fifty years.—It was unfortunate that Avogadro, having found a trustworthy method of determining the relative weights of gaseous molecules did not limit his deductions to those volatile compounds and elements to which alone his hypothesis could be applied. In attempting to extend his views to non-volatile compounds, such as the oxides and salts of the metals, Avogadro was compelled, like Dalton, to fall back upon mere guess-work. His speculations failed to secure the support of his contemporaries and may well have prejudiced them against the accurate conclusions which he reached in the case of gaseous elements. But, whatever the cause, the fact remains that nearly half a century elapsed before Avogadro's views, re-stated and applied, in 1858, by **Stanislao Cannizzaro** (1826—1910), Professor of Chemistry at Genoa (A.C.R. XVIII.), finally secured the universal recognition that they deserved.

D. Determination of Molecular and Atomic Weights.

Cannizzaro (1858) chooses the half-molecule of hydrogen as a standard of molecular and atomic weights.—In

measuring the density of a gas or vapour it is often convenient to calculate the density relatively to some selected gas as standard, rather than to give the actual density in grams per litre. Thus whilst the actual densities of air, oxygen, hydrogen and nitrogen may be compared at 0°C. and 760 mm. pressure, vapours such as steam cannot be included in the comparison because they would condense to liquids under the conditions selected. But as all gases expand and contract in much the same way (see Section A of this chapter), their relative densities are almost independent of temperature and pressure. A table of relative densities may therefore include vapours as well as gases ; *e.g.* steam may be compared with air at 130°, whilst hydrogen is compared with air at 20° or at 0°. Vapour densities, and gas densities, are often given relatively to air ; but hydrogen, as being the lightest known gas, is usually preferred as a standard, since the relative densities of all other gases can then be represented by numbers greater than unity.

In selecting a standard of molecular weights, the hydrogen molecule would provide a convenient unit, since the relative weights of gaseous molecules could then be represented by the same number as their relative densities. But since the hydrogen molecule is known to contain two atoms, its selection as a standard would necessitate the use of a fraction 0·5 to represent the hydrogen atom ; Cannizzaro therefore selected the half-molecule or atom of hydrogen as a unit both of molecular and of atomic weights. Cannizzaro writes (A.C.R. XVIII 6–7):

"I prefer to take as common unit for the weights of the molecules and for their fractions, the weight of a half and not of a whole molecule of hydrogen, I therefore refer the densities of the various gaseous bodies to that of hydrogen = 2. If the densities are referred to air = 1, it is sufficient to multiply by 14·438 to change them to those referred to that of hydrogen = 1 ; and by 28·87 to refer them to the density of hydrogen = 2.

"I write the two series of numbers, expressing these weights in the following manner:

Names of Substances.	Densities or weights of one volume, the volume of Hydrogen being made = 1, *i.e.* weights of the molecules referred to the weight of a whole molecule of Hydrogen taken as unity.	Densities referred to that of Hydrogen = 2, *i.e.* weights of the molecules referred to the weight of half a molecule of Hydrogen taken as unity.
Hydrogen	1	2
Oxygen, ordinary ...	16	32
Oxygen, electrised ..	64	128
Sulphur below 1000°.	96	192
Sulphur above 1000°	32	64
Chlorine	35·5	71
Bromine	80	160
Arsenic	150	300
Mercury	100	200
Water	9	18
Hydrochloric Acid ...	18·25	36·50
Acetic Acid	30	60"

The table shows amongst other things, "that the same substance in its different allotropic forms can have different molecular weights," but the data for "electrised oxygen" are incorrect, the actual densities of ozone being 24 and 48 instead of 64 and 128.

Oxygen as a standard of molecular and atomic weights.—In Cannizzaro's table, the hydrogen atom = 1 and the hydrogen molecule = 2. The relative density of oxygen is given as 16 and its molecular weight as 32. Later experiments have shown that the exact figures are 15·88 and 31·76.

In recent years, in accordance with a suggestion made by Stas, the half-molecule or atom of oxygen has been adopted as a standard of molecular and atomic weights, its weight

being taken as exactly 16, instead of 15·88. The atomic weight of hydrogen then becomes 1·008 instead of 1 and its molecular weight 2·016 instead of 2; all other molecular and atomic weights are increased in the same proportion.

The choice of oxygen as a standard is justified by the fact that, in practice, molecular and atomic weights are nearly always measured by comparison with oxygen rather than with hydrogen. The actual results of this comparison can now be tabulated, whereas formerly the accuracy of the tables was greatly impaired in reducing the numbers from the oxygen to the hydrogen standard by means of a factor deduced from the composition of water.

Avogadro's hypothesis only approximately true.—Cannizzaro's method of deducing molecular weights has also been modified by the discovery that Avogadro's hypothesis is only approximately true. Like Gay-Lussac's "Law of Volumes," it would probably be exact if applied to gases under very low pressures. Several methods have been used to eliminate the effects of unequal compressibility on the relative densities of gases. The following table shows the nature of the correction, and the large magnitude which it attains in the case of easily-liquefied gases.

Gas.	Ratio of densities.	Corrected Molecular Weights.	Molecular Weight deduced from Equivalents.
Hydrogen	2·0125	2·0150	2·0152
Nitrogen	28·007	28·013	28·02
Carbonic oxide	28·001	28·003	28·00
Oxygen	32	32	32
Carbonic anhydride	44·267	44·003	44·00
Nitrous oxide	44·284	44·000	44·02
Hydrogen chloride	36·741	36·484	36·458
Sulphurous anhydride	65·536	64·565	64·06

Cannizzaro's method of determining atomic weights.—The method used by Cannizzaro in determining the atomic weight of an element depends on setting out in a table all those volatile compounds the vapour density and percentage composition of which are known. From the vapour density the molecular weight is calculated, whilst the percentage composition gives the weights of the different constituents in the molecular weight of the compound.

The substance of Cannizzaro's table[1] is set out in the first three columns of the following series of tables :—

1. HYDROGEN COMPOUNDS. H = 1.

Name of the Substance.	Molecular weight referred to the weight of a half-molecule of Hydrogen = 1.	Weights of the constituents of one molecule, all referred to a half-molecule of Hydrogen = 1.	Formula.
Hydrogen	2	2 Hydrogen	H_2
Hydrogen chloride	36·5	1 Hydrogen, 35·5 Chlorine	HCl
Hydrogen bromide	81	1 Hydrogen, 80 Bromide	HBr
Hydrogen iodide...	128	1 Hydrogen, 127 Iodine	HI
Water-vapour ...	18	2 Hydrogen, 16 Oxygen	H_2O
Sulphuretted hydrogen	34	2 Hydrogen, 32 Sulphur	H_2S
Ammonia	17	3 Hydrogen, 14 Nitrogen	H_3N
Arsine	78	3 Hydrogen, 75 Arsenic	H_3As
Phosphine	34	3 Hydrogen, 31 Phosphorus	H_3P

[1] Cannizzaro gives a general table and a series of special tables for the individual elements. In the following paragraphs the general table has been subdivided, and a few additional substances, quoted in Cannizzaro's special tables, have been added. The values for ozone and for phosphine have been corrected.

It is seen that the quantity of hydrogen in the molecule is always a half-molecule or some integral number of half-molecules ; the half-molecule of hydrogen appears therefore to represent the extreme limit to which the subdivision of the molecule can be carried. Cannizzaro concludes that "The atom of hydrogen is contained twice in the molecule of free hydrogen" (A.C.R. XVIII. 11).

2. Oxygen Compounds. O = 16.

Name.	Molecular Weight.	Composition of Molecule.	Formula
Oxygen	32	32 Oxygen	O_2
Ozone	48	48 Oxygen	O_3
Water vapour ...	18	16 Oxygen, 2 Hydrogen	OH_2
Nitrous oxide ...	44	16 Oxygen, 28 Nitrogen	ON_2
Nitric oxide ...	30	16 Oxygen, 14 Nitrogen	ON
Carbonic oxide ...	28	16 Oxygen, 12 Carbon	OC
Carbonic anhydride	44	32 Oxygen, 12 Carbon	O_2C
Sulphurous anhydride	64	32 Oxygen, 32 Sulphur	O_2S

(See also under Carbon.)

The smallest weight of oxygen in the molecule is 16. This is the weight of the oxygen atom and is now taken as the standard of comparison for all other atomic weights. The molecule of oxygen gas has weight 32 ; it is therefore a "diatomic" molecule containing two atoms, as represented by the formula O_2 ; but ozone, prepared from it by electrification, is seen to be a "triatomic" modification, containing three atoms in the molecule, as represented by the formula O_3.

3. Chlorine Compounds. Cl = 35·5.

Name.	Molecular Weight.	Composition of Molecule.	Formula.
Chlorine gas	71	71 Chlorine	Cl_2
Hydrogen chloride ...	36·5	35·5 Chlorine, 1 Hydrogen	ClH
Mercurous chloride ...	235·5	35·5 Chlorine, 200 Mercury	ClHg [1]
Mercuric chloride ...	271	71 Chlorine, 200 Mercury	Cl_2Hg
Arsenic chloride	181·5	106·5 Chlorine, 75 Arsenic	Cl_3As
Phosphorus chloride ...	138·5	106·5 Chlorine, 32 Phosphorus	Cl_3P
Ferric chloride	325	213 Chlorine, 112 Iron	Cl_6Fe_2

The smallest weight of chlorine in the table is 35·5. This is therefore taken as the atomic weight of chlorine. The weight of the molecule is 71; it therefore contains (like the hydrogen molecule) 2 atoms, and is represented by the formula Cl_2.

4. Nitrogen Compounds. N = 14.

Name.	Molecular Weight.	Composition of Molecule.	Formula.
Nitrogen gas ...	28	28 Nitrogen	N_2
Ammonia	17	14 Nitrogen, 3 Hydrogen	NH_3
Nitrous oxide ...	44	28 Nitrogen, 16 Oxygen	N_2O
Nitric oxide ...	30	14 Nitrogen, 16 Oxygen	NO

The atomic weight of nitrogen is seen to be 14. The gas is again "diatomic," containing two atoms in each molecule, and is represented by the formula N_2.

[1] See later, p. 529.

5. SULPHUR COMPOUNDS. S = 32.

Name.	Molecular Weight.	Composition of Molecule.	Formula.
Sulphur under 1000°	192	192 Sulphur	S_6 [1]
Sulphur above 1000°	64	64 Sulphur	S_2
Sulphuretted hydrogen	34	34 Sulphur, 2 Hydrogen	SH_2
Sulphurous anhydride	64	32 Sulphur, 32 Oxygen	SO_2
Carbon sulphide ...	76	64 Sulphur, 12 Carbon	S_2C

The atomic weight of sulphur is seen to be 32. At temperatures above 1000° the vapour has a molecular weight 64; the molecules of the gas are then diatomic like those of hydrogen, chlorine, nitrogen and oxygen. But at lower

6. CARBON COMPOUNDS. C = 12.

Name.	Molecular Weight.	Composition of Molecule.	Formula.
Carbonic oxide ...	28	12 Carbon, 16 Oxygen	CO
Carbonic anhydride	44	12 Carbon, 32 Oxygen	CO_2
Carbon bisulphide...	76	12 Carbon, 64 Sulphur	CS_2
Marsh gas	16	12 Carbon, 4 Hydrogen	CH_4
Ethylene	28	24 Carbon, 4 Hydrogen	C_2H_4
Propylene	42	36 Carbon, 6 Hydrogen	C_3H_6
Formic acid	46	12 Carbon, 2 Hydrogen, 32 Oxygen	CH_2O_2
Acetic acid	60	24 Carbon, 4 Hydrogen, 32 Oxygen	$C_2H_4O_2$
Acetic anhydride ...	102	48 Carbon, 6 Hydrogen, 48 Oxygen	$C_4H_6O_3$
Alcohol	46	24 Carbon, 6 Hydrogen, 16 Oxygen	C_2H_6O
Ether	74	48 Carbon, 10 Hydrogen, 16 Oxygen	$C_4H_{10}O$

[1] See footnote on p. 351.

temperatures the molecules POLYMERISE, *i.e.* collect together into larger groups of atoms, the average number of atoms in the molecule at the boiling point being about 6.[1]

The smallest weight of carbon in the table is 12 ; this is therefore the atomic weight. In the case of carbon, Cannizzaro points out that "since we cannot determine the vapour-density of free carbon, we have no means of knowing the weight of its molecule, and thus we cannot know how many times the atom is contained in it." But this does not in the least affect our knowledge of the atomic weight of the element, since "the knowledge of the weight of the molecule of this last would merely add a datum more to those which are already sufficient for the solution of the problem" (A.C.R. XVIII. 14).

7. PHOSPHORUS, ARSENIC AND MERCURY. P = 31, As = 75, Hg = 200

Name.	Molecular Weight.	Composition of Molecule.	Formula.
Phosphorus ...	124	124 Phosphorus	P_4
Arsenic	300	300 Arsenic	As_4
Mercury	200	200 Mercury	Hg

(See also under hydrogen and chlorine.)

The smallest quantities of these elements which are found in the molecules of their compounds are 31, 75 and 200 respectively. The vapours of phosphorus and arsenic are therefore composed of "tetratomic" molecules which are subdivided into quarter-molecules by combination with hydrogen or chlorine. The vapour of mercury on the other hand is composed of "monatomic" molecules, which

[1] Recent work has indicated that the vapour is a mixture of S_8 and S_2, the existence of S_6 being very doubtful.

enter as a whole into combination with other elements and are not capable of being further subdivided. "Diatomic" molecules, although abundant amongst the commoner gases, are by no means universal; in a complete table of volatile elements the diatomic molecules are seen to be less abundant than the monatomic:

Monatomic	Na, K, Zn, Cd, Hg, He, Ne, Ar, Xe, Kr, I
Diatomic	H_2, N_2, O_2, F_2, Cl_2, Br_2, I_2, S_2
Triatomic, &c.	O_3, P_4, As_4, S_8.

Formulæ of volatile compounds deduced by Cannizzaro.—Having established a method of determining the atomic weights of their constituents, Cannizzaro was able to assign formulæ to a large number of volatile compounds.

Thus in the case of ether, the molecular weight, 74, deduced from its vapour density, was shown by the analytical data to contain

Carbon 48, *Hydrogen* 10, *Oxygen* 16 parts.

Assuming the weights of the atoms to be

Carbon 12, *Hydrogen* 1, *Oxygen* 16

it was clear that the numbers of atoms in the molecule were

$$\textit{Carbon}\ \frac{48}{12} = 4\quad \textit{Hydrogen}\ \frac{10}{1} = 10\quad \textit{Oxygen}\ \frac{16}{16} = 1$$

and that the formula of the substance was

$$C_4H_{10}O.$$

Formulæ deduced in this way, being based directly upon Avogadro's hypothesis, were entirely independent of the personal bias which had produced so much confusion during the preceding half-century; it is therefore not surprising that they soon met with universal acceptance.

The complexity of gaseous elements confirmed by measurements of their heat capacity.—The conclusions of

Avogadro and Cannizzaro as to the number of atoms present in the molecules of various gases and vapours have been confirmed in a very striking way by independent physical methods. It is well known that the heat required to raise the temperature of a gas is greater when the gas is allowed to expand than when its volume is kept constant; the ratio γ of the two heat-capacities can be calculated to be $5/3 = 1{\cdot}67$ for an ideal or "perfect gas." Experiment has shown that this value is rarely attained in the case of elements, and never in the case of compounds, and further that the value of γ diminishes as the number of atoms in the molecule increases. Typical values are as follows:

Substance.	Ratio γ.
Hg, He	1·67
H_2, N_2, O_2, CO, HCl, HBr, HI	1·41 [1]
Cl_2, Br_2, I_2, ClI	1·29 to 1·32 [1]
CO_2, N_2O, NO_2	1·31

It will be seen from the table that the value 1·4 is characteristic for the lighter diatomic gases and the figure 1·3 for the heavier diatomic and the lighter triatomic gases, whether elementary or compound. This observation supplies a remarkable proof of the correctness of Avogadro's fundamental proposition, that the molecules of the elements nitrogen and oxygen are of the same complexity as those of the compound nitric oxide, that hydrogen and chlorine are as complex as hydrogen chloride, and so forth.

Special interest attaches to the case of mercury, which falls into a special class, giving a value of γ which is much higher than the figure 1·4 characteristic of the diatomic gases. In the case of so heavy a molecule this can only mean that the number of atoms is less than two; the molecule must

[1] The value of γ seems to depend on the moment of inertia of the molecules: the hydride HI has probably a smaller moment of inertia than Cl_2, although its weight is greater.

therefore be monatomic, a conclusion that is in agreement with the rather scanty data for the vapour density of mercury and its compounds (pp. 349 and 351). The same method of investigation has shown that the inert gases HELIUM, NEON, ARGON, XENON, and KRYPTON, discovered by Sir William Ramsay in atmospheric "azote," are monatomic gases; their atomic weights are therefore identical with the molecular weights calculated from their densities.

Accurate determination of atomic weights. Valency.—The *vapour-density* of an element or compound can as a rule be determined only approximately. Moreover, even an accurate measurement must be corrected for compressibility before it can be used to determine the true molecular weight of a volatile substance. It is therefore evident that the method described above does not lend itself readily to the accurate determination of atomic or molecular weights.

On the other hand the *equivalent* of an element or compound can often be determined with extraordinary accuracy by gravimetric analysis: thus, the figures given by Stas for the weight of silver chloride produced from 100 parts of silver show an average deviation from the mean of only 1 part in 40,000.

132·841	132·840	132·846	132·842
132·843	132·849	132·848	132·845 = Mean.

It is therefore important to consider how these accurate analyses may be utilised in drawing up a table of atomic weights based upon Avogadro's hypothesis.

Dalton's Atomic Theory finds expression in tables of combining weights or equivalents, based solely upon the chemical data supplied by analysis, *e.g.*:

H = 1·008, C = 3·00, O = 8 , S = 16·03, Cl = 35·46, etc.

Avogadro's hypothesis, on the other hand, finds its

expression in tables of molecular and atomic weights, based largely upon physical measurements of density, *e.g* :

$$H = 1, \quad C = 12, \quad O = 16, \quad S = 32, \quad Cl = 35\tfrac{1}{2}$$

A glance at the two lists shows that the atomic weights calculated from the vapour densities are either identical with, or are simple multiples of, the equivalents determined by analysis. The ratio of the atomic weight to the equivalent is called the VALENCY of the element. As elements combine together in simple atomic proportions the valency must obviously be a simple number. In practice, therefore, measurements of vapour density are used to determine the valency of an element (*i.e.* the factor by which the equivalent must be multiplied to give the atomic weight) rather than the atomic weight itself. The accurate determination of an atomic weight therefore includes the following operations :

(1) By means of a series of exact analyses, the equivalent or combining weight of the element is determined with the greatest accuracy possible.

(2) Vapour-density measurements are made with as many compounds as possible, but not necessarily attaining a very high order of accuracy. From these the approximate value of the atomic weight is easily deduced by Cannizzaro's method.

(3) The ratio of the (approximate) atomic weight to the (exact) equivalent approximates so nearly to an integer that no doubt can exist as to the correct value of the valency. The equivalent multiplied by the integral number representing the valency gives the exact atomic weight.

These operations may be illustrated in the case of arsenic. Exact analyses show that 24·99 parts of arsenic combine with 8 parts of oxygen or with 35·46 parts of chlorine ; the equivalent of arsenic is therefore 24·99. From the vapour-density of its volatile compounds its atomic weight is seen to be approximately 75. Its valency is therefore 3 and the exact atomic weight is $3 \times 24{\cdot}99 = 74{\cdot}97$.

The exact molecular weight of a compound of known composition may be calculated in a similar way from its approximate vapour-density and the exactly-known atomic weights of its constituents.

Summary and Supplement.

A. The Properties of Gases.

Boyle, in 1660, with the help of a new air-pump, showed that air was an "elastic fluid" which could be expanded to at least 152 times its original volume by merely diminishing the pressure of the atmosphere upon it. To explain the "spring of the air" he suggested that air was composed of elastic fibres, or (following Descartes) of elastic spheres in rapid motion under the influence of heat. In 1662, he showed that the pressure which air could exert was inversely proportional to the volume which it occupied (Boyle's Law).

Mayow, in 1674, showed that air in which a candle or lamp had expired, and "air" prepared by the action of acids on metals, were just as elastic as common air and could be expanded to an equal extent.

Gay-Lussac, in 1802 (following Charles, 1787), showed that air, oxygen, nitrogen and hydrogen all expand to theextent of 37·50 per cent. between 0° and 100° C.: nitric oxide, carbon dioxide, sulphur dioxide, ammonia, hydrogen chloride and the vapour of ether were also shown to expand at the same rate as common air. Gay-Lussac therefore concluded that *the volumes of all gases and vapours are influenced to the same extent by changes of temperature and of pressure.*

B. The Combining Volumes of Gases.

Gay-Lussac and **Humboldt**, in 1805, confirmed the observations of Cavendish (1781) that two volumes of hydrogen unite with one volume of oxygen to form water; their experiments gave the ratio 199·89 : 100.

Gay-Lussac, in 1809, concluded that "gases always combine in the simplest proportions when they act on one another."

The cases which he quotes in support of this view may be represented by the following equations :

$$\underset{2\ vols.}{2H_2} + \underset{1\ vol.}{O_2} = 2H_2O$$

$$\underset{1\ vol.}{NH_3} + \underset{1\ vol.}{HCl} = NH_4Cl$$

$$\underset{2\ vols.}{2NH_3} + \underset{1\ vol.}{CO_2} = (NH_3)_2CO$$

$$\underset{1\ vol.}{N_2} + \underset{3\ vols.}{3H_2} = 2NH_3$$

$$\underset{1\ vol.}{O_2} + \underset{2\ vols.}{2SO_2} = 2SO_3$$

$$\underset{1\ vol.}{O_2} + \underset{2\ vols.}{2\,CO} = 2CO_2$$

$$\underset{2\ vols.}{2N_2} + \underset{1\ vol.}{O_2} = 2N_2O$$

$$\underset{1\ vol.}{N_2} + \underset{1\ vol.}{O_2} = 2NO$$

$$\underset{1\ vol.}{N_2} + \underset{2\ vols.}{2O_2} = 2NO_2 \text{ or } N_2O_4$$

He found further that the change of volume when gases combine has a simple relation to their volume and quotes the following cases :

$$\underset{2\ vols.}{2CO} + \underset{1\ vol.}{O_2} = \underset{2\ vols.\ (\text{contraction } 1\ vol.)}{2CO_2}$$

$$\underset{1\ vol.}{O_2} + 2C = \underset{2\ vols.\ (\text{expansion } 1\ vol.)}{2CO}$$

$$\underset{1\ vol.}{CO_2} + C = \underset{2\ vols.\ (\text{expansion } 1\ vol.)}{2CO}$$

$$\underset{1\ vol.}{O_2} + S = \underset{1\ vol.\ (\text{contraction } nil)}{SO_2}$$

$$\underset{1\ vol.}{N_2} + \underset{3\ vols.}{3H_2} = \underset{2\ vols.\ (\text{contraction } 2\ vols.)}{2NH_3}$$

Gay-Lussac's *Law of Volumes* may be summed up as follows :

"In every chemical change in which gases are concerned, the volumes absorbed and liberated are in simple ratios to one another."

This law is not exact, as the following examples show :

Hydrogen	: oxygen	= 2·00268 : 1
Hydrogen	: hydrogen chloride	= 1·00790 : 2
Hydrogen	: nitrogen	= 3·00172 : 1

It would probably be true at zero pressure, the deviations shown above being due to the lesser compressibility of hydrogen as compared with the other gases.

C. Avogadro's Hypothesis.

Dalton, about 1802, whilst trying to form a mental picture of the atmosphere, concluded that the particles of nitrogen, oxygen, water-vapour, etc., were "all of the same size," in the sense that each occupied an equal space in the gas. Later he was obliged to reject this view, because nitric oxide occupied as much space as the nitrogen and oxygen of which it was composed ; the contraction, which must accompany the production of one "compound atom" from two or more "simple atoms" of equal volume, did not in fact occur.

Avogadro, in 1811, got over this difficulty by suggesting that the molecules of a simple elementary gas might contain two or more atoms. Thus, if the decomposition of nitric oxide were represented by the equation

$$\underset{2\ mols.}{2NO} \rightarrow \underset{1\ mol.}{N_2} + \underset{1\ mol.}{O_2}$$

it would produce no change in the number of molecules and no alteration in the volume of the gas.

The possibility of halving the molecules of oxygen and nitrogen is confirmed by the production of 2 volumes of steam from 1 volume of oxygen and of 1 volume of nitrogen from 2 volumes of ammonia.

The halving of the hydrogen molecule was proved by the presence of $1\frac{1}{2}$ volumes of hydrogen in 1 volume of ammonia,

whilst the presence of $\frac{1}{2}$ volume of hydrogen and $\frac{1}{2}$ volume of chlorine in 1 volume of hydrogen chloride proved the divisibility of both hydrogen and chlorine.

$$\underset{1\ vol.}{2H_2} + \underset{}{O_2} \rightarrow \underset{2\ vols.}{2H_2O}$$

$$\underset{2\ vols.}{2NH_3} \rightarrow \underset{1\ vol.}{N_2} + \underset{3\ vols.}{3H_2}$$

$$\underset{1\ vol.}{H_2} + \underset{1\ vol.}{Cl_2} \rightarrow \underset{2\ vols.}{2HCl}$$

In each of the cases studied by Avogadro, H_2, O_2, N_2, Cl_2, the molecule proved to be divisible into two parts: his suggestion that subdivision into four or eight parts was possible has been realised in the molecules, P_4, As_4, S_8; cases are also known in which the molecule contains only a single atom and cannot be subdivided, *e.g.* Hg, Zn, Cd, Ar; in the case of ozone, O_3, the molecule contains three atoms.

D. Cannizzaro's Exposition.

Avogadro's Hypothesis states that

> "If the temperature and pressure are the same, equal volumes of different gases contain equal numbers of molecules."

From this hypothesis, which is strictly true only at zero pressure, it follows that the molecular weights of different gases are in the same ratios as their densities. **Cannizzaro**, in 1858, selected the half-molecule or atom of hydrogen as the standard for all molecular and atomic weights. The molecular weight of a gas is then equal to its density relative to hydrogen = 2, or, in the modern system, relative to oxygen = 32. The atomic weight of an element is the smallest weight which is found in the molecular weights of its volatile compounds.

The molecular and atomic weights deduced from vapour-densities are not exact. But the ratio of atomic weight to the equivalent (the *valency* of the element) is a whole number, and it is therefore easy to deduce the exact atomic weight from the equation

$$Atomic\ weight = valency \times equivalent.$$

After the atomic weights have been determined, the formula of any volatile compound can be deduced from its vapour density and percentage composition by using the method illustrated on p. 353.

CHAPTER XVI

ATOMIC WEIGHTS OF THE METALS

A. Vapour Densities

The vapour-density of metallic compounds.—Avogadro's hypothesis, which enabled Cannizzaro to establish on a firm basis the atomic weights of the non-metals, failed him in the case of the metals, because of the lack of volatile compounds. Very few of the metals can be vaporised, either as elements or compounds, even under the wide range of conditions now available for vapour-density determinations. The most favourable cases are those of mercury and arsenic, two elements which in some ways serve to bridge the gap between metals and non-metals. The data already given for these two elements, with others derived from their volatile organic compounds, are sufficient to establish the atomic weights, Hg = 200, As = 75.

The following table contains almost all the data that are available for other metals[1]:

[1] The references are :—Dumas, *Ann. Chim. Phys.*, 1826, **33**, 385 ; Dumas quoted by Bineau, *Ann. Chim. Phys.*, 1838, **68**, 427–428 ; Frankland, *Phil. Trans.*, 1855, **145**, 266 ; Deville and Troost, *Ann. Chim. Phys.*, 1860, **58**, 257–299 ; Wanklyn, *Jour. Chem. Soc.*, 1861, **13**, 128 ; Frankland and Duppa, *Jour. Chem. Soc.*, 1864, **17**, 33 ; Buckton and Odling, *Proc. Roy. Soc.*, 1865, **14**, 19–21 ; Ladenburg, *Liebig's Annalen*, 1872, **8**, Suppl. 55–80 ; V. and C. Meyer, *Ber.*, 1879, **12**, 1195–1200 ; Mensching and Meyer, *Ber.*, 1886, **19**, 3295–3298, and *Ber.*, 1887, **20**, 582–583 ; Scott, *Proc. Roy. Soc. Ed.*, 1887, **14**. 410 ; Friedel and Crafts, *Comptes rendus*, 1888, **107**, 306 ; Nilson and Pettersson, *Trans. Chem. Soc.*, 1888, **53**, 814–831 and *Zeit. Phys. Chem.*, 1889, **4**, 206–225 ; Biltz and Meyer, *Ber.*, 1889, **22**, 725 or *Zeit. Phys. Chem.*, 1889, **4**, 249–269 ; Mond, Langer and Quincke, *Trans. Chem. Soc.*, 1890, **57**, 752 ; Dewar and Jones, *Proc. Roy. Soc.*, 1905, **76**, 567.

—		Temperature.	Molecular Weight (V.D. × 2).	Nearest Multiple of Equivalent.	Formula.
Elements—					
Sodium ...	Scott, 1887 ...	1200–1500°	25·5	23·0	Na
Potassium ...	,, ,, ...	1200–1500°	37·7	39·0	K
Zinc	V. Meyer, 1886 ...	1400°	68·9	65·4	Zn
Cadmium ...	Deville, 1860 ...	1040°	113·7	112·4	Cd
Chlorides, etc.—					
Potassium iodide	V. Meyer, 1887 ...	1320°	169	166·0 (K 39·1, I 126·9)	KI
Cuprous chloride	,, 1889 ...	1691°	188	198·0 (Cu 127·1, Cl 70·9)	Cu_2Cl_2
Silver chloride	Scott, 1887 ...	1200–1500°	160·8	143·4 (Ag 107·9, Cl 35·5)	AgCl
Zinc chloride	V. Meyer, 1879 ...	900°	132	136·3 (Zn 65·4, Cl 70·9)	$ZnCl_2$
Lead chloride	Scott, 1887 ...	1200–1500°	262·7	278·0 (Pb 207·1, Cl 70·9)	$PbCl_2$
Cadmium bromide	,, ,, ...	1200–1500°	242·2	272·2 (Cd 112·4, Br 159·8)	$CdBr_2$
Aluminium chloride	Nilson 1889 ...	800–1000°	131·3	133·5 (Al 27·1, Cl 106·4)	$AlCl_3$ [1]
	Deville, 1860 ...	440°	270	267·0 (Al 54·2, Cl 212·8)	Al_2Cl_6
Aluminium bromide	,, ,, ...	440°	537·6	533·7 (Al 54·2, Br 479·5)	Al_2Br_6
Aluminium iodide	,, ,, ...	440°	779	815·7 (Al 54·2, I 761·5)	Al_2I_6
Ferrous chloride	Nilson, 1888 ...	1300–1400°	125·3	126·7 (Fe 55·8, Cl 70·9)	$FeCl_2$ [2]
Ferric chloride	Friedel, 1888 ...	442°	331·4	324·4 (Fe 111·6, Cl 212·8)	Fe_2Cl_6 [3]
Chromyl chloride	Dumas, 1838 ...	137°	159	154·9 (Cr 52·0, O = 32, Cl 70·9)	CrO_2Cl_2
Chromic chloride	Scott, 1887 ...	1200–1500°	154·9	158·4 (Cr 52·0, Cl 106·4)	$CrCl_3$ [4]
Manganese chloride	,, ,, ...	1200–1500°	132·3	125·8 (Mn 54·9, Cl 70·9)	$MnCl_2$
Stannous chloride	V. Meyer, 1879 ...	697°	377·6	379·8 (Sn 238·0, Cl 141·8)	Sn_2Cl_4
Stannic chloride	Dumas, 1826 ...	124°	265·6	260·8 (Sn 119·0, Cl 141·8)	$SnCl_4$
Carbon compounds—					
Zinc methyl ...	Wanklyn, 1861 ...	100°	95·0	95·5 (Zn 65·4, C 24·0, H 6·1)	ZnC_2H_6
Zinc ethyl ...	Frankland, 1855	148°	123·0	123·5 (Zn 65·4, C 48·0, H 10·1)	ZnC_4H_{10}
Zinc amyl ...	Frankland, 1864	235°	200·6	207·6 (Zn 65·4, C 120·0, H 22·2)	$ZnC_{10}H_{22}$
Aluminium methyl	Odling, 1865 ...	220°	81	72·2 (Al 27·1, C 36·0, H 9·1)	AlC_3H_9 [5]
Aluminium ethyl	,, ,, ...	234°	130	114·2 (Al 27·1, C 72·0, H 15·1)	AlC_6H_{15}
Tin triethyl ...	Ladenburg, 1872	255°	423	412·3 (Sn 238·0, C 144·0, H 30·3)	$Sn_2C_{12}H_{30}$
Tin tetramethyl	,, ,,	100°	171·8	179·0 (Sn 119·0, C 48·0, H 12·1)	SnC_4H_{12}
Iron carbonyl	Dewar, 1905 ...	78°	199·0	195·8 (Fe 55·8, C 60·0, O 80·0)	FeC_5O_5
Nickel carbonyl	Mond, 1890 ...	50°	173·5	170·7 (Ni 58·7, C 48·0, O 64·0)	NiC_4O_4

[1] At intermediate temperatures the vapour of aluminium chloride contains both the simpler and the more complex molecules.
[2] The vapour density is greater at lower temperatures on account of the formation of more complex molecules.
[3] At higher temperatures ferric chloride has a much lower vapour density owing to decomposition into ferrous chloride and chlorine.
[4] Nilson and Pettersson (1888) confirmed this observation, but found that chromous chloride gave densities intermediate between those required for the formulae $CrCl_2$ and Cr_2Cl_4.
[5] At the boiling point, 130°, the density increases to 63 (mol. wt. 126·6), owing to the formation of more complex molecules, *e.g.* $Al_2C_6H_{18}$.

Data are also available for antimony, bismuth and tellurium, but no vapour-density determinations appear to have been made in the case of magnesium, calcium, strontium, barium, gold and platinum. It is clear that the data are far too scanty to give trustworthy values for the atomic weights of the metals. Thus the data for iron are :

Compound.	Molecular Weight.	Weight of Iron in Molecular Weight.
Ferrous chloride	125·6	... 56 (about)
Ferric chloride	332·2	... 112 ,,
Iron carbonyl	199·0	... 56 ,,

From so short a table we cannot tell whether 56, or a sub-multiple of 56 (say 28), is the atomic weight of iron ; in other words, we cannot be sure whether the molecule of ferrous chloride or of iron carbonyl contains one, or two or more atoms of iron. The facts show only that 56 is the maximum value for the atomic weight of the metal.

The formulæ given in the last column of the large table are based upon atomic weights deduced by other methods. They show that the smallest weight of metal found in the molecules of its volatile compounds is usually a single atom. But pairs of atoms are frequently found

$$(Al_2Cl_6, Al_2Br_6, Al_2I_6, Fe_2Cl_6, \text{ etc.}).$$

In the case of copper the only compound examined is of this type, the atomic weight of the element being 63·6 and not 127·1.

B. The Law of Atomic Heats.

Dulong and Petit's law of atomic heats (1819).—The difficulty of finding the atomic weights of the metals by means of density determinations renders very important the fact, discovered in 1819 by the French physicists Dulong and Petit (*Ann. Chim. Phys.*, 1819, **10**, 405), that

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

Their table shows:

(1) The elements which they examined.

(2) Their values for the heat-capacity of these elements, compared with that of an equal weight of water.

(3) The values which they selected for the atomic weights of the elements, O = 1.

(4) The product of these numbers.

A fifth column has been added which shows Dulong and Petit's atomic weights reduced to the modern standard, O = 16.

ATOMIC HEATS (DULONG AND PETIT).

Element.	Heat Capacity.	Atomic Weight. O = 1	Product.	Atomic Weight. O = 16
Bismuth	0·0288	13·30	0·3830	212·8
Lead	0·0293	12·95	0·3794	207·2
Gold	0·0298	12·43	0·3704	198·9
Platinum	0·0314	12·16[1]	0·3740	194·6
Tin	0·0514	7·35	0·3779	117·6
Silver	0·0557	6·75	0·3759	108·0
Zinc	0·0927	4·03	0·3736	64·5
Tellurium	0·0912	4·03	0·3675	64·5
Copper	0·0949	3·957	0·3755	63·3
Nickel	0·1035	3·69	0·3819	59·0
Iron	0·1100	3·392	0·3731	54·3
Cobalt	0·1498	2·46	0·3685	39·4
Sulphur	0·1880	2·011	0·3780	32·2

[1] The value 11·16 given in Dulong and Petit's paper appears to be a misprint for 12·16 (Berzelius's number for the atomic weight); but there is some further error in the table, as 12·16 × 0·0314 = 0·3818.

In Dulong and Petit's table the atomic weights of the metals were reduced to one-half of the values given by Berzelius, whilst the value for silver was reduced to one-quarter. The new values were ultimately accepted by Berzelius, and are substantially the same as those employed

at the present time ; tellurium and cobalt (modern values, 127·5 and 58·97) are exceptions to this statement, on account of errors in the values for their specific heats.

Significance of the law of atomic heats.—The SPECIFIC HEAT of a substance is the amount of heat in calories required to raise the temperature of 1 gram through 1° C. The product of the specific heat and the atomic weight of an element is called its ATOMIC HEAT and represents the amount of heat required to raise the temperature of 1 "gram-atom" (*i.e.* the atomic weight expressed in grams) through 1° C. Dulong and Petit's LAW OF ATOMIC HEATS can be expressed algebraically in the form :

$$Specific\ heat \times atomic\ weight = atomic\ heat = constant = 6{\cdot}0.$$

The average value of Dulong and Petit's product was 0·3753 (O = 1). If reduced to the modern standard, O = 16, it becomes 6·00, a number which is practically the same as the average value 6·05 for the atomic heat over the range from 20° to 100° of the 25 solid elements tabulated on page 365.

If the specific heat of an element at ordinary temperatures is known, its atomic weight may be calculated by dividing the specific heat into the figure 6·0. The atomic weights obtained in this way are even less accurate than those deduced from vapour densities ; but they are sufficiently exact to give the valency of the element, *i.e.* the factor which must be used in deducing the atomic weight from the equivalent, as described in the preceding chapter.

The law of atomic heats can be applied most easily in the case of the metals in which the direct application of Avogadro's hypothesis is most difficult. It was much used by Berzelius, and was regarded by him as a more trustworthy guide than Avogadro's hypothesis ; but, as Cannizzaro showed, it is not independent of that hypothesis, and merely provides a method for extending it from hydrogen and

oxygen to silver and gold; this is done with the help of elements such as iodine and mercury, the atomic weights of which can be compared both by means of their vapour densities and by means of their specific heats.

Abnormal atomic heats.—The following table shows the atomic heats, over different ranges of temperature, of 25

ATOMIC HEATS OF SOLID ELEMENTS

Element.	Atomic Weight.	Specific Heat. +20° to +100°.	Atomic Heat. +20° to +100°.	Atomic Heat. −188° to +20°.	Atomic Heat. −253° to −195° C.
C ...	12·00	0·1990	2·4	1·15	0·03
Mg ...	24·32	0·2492	6·1	5·06	1·74
Al ...	27·1	0·2173	5·9	4·73	1·12
Si ...	28·3	0·1833	5·2	3·34	0·77
P ...	31·04	0·1981	6·2	5·24	1·34
S ...	32·07	0·1780	5·7	4·20	1·75
Cr ...	52·0	0·1210	6·3	4·14	0·70
Mn ...	54·93	0·1211	6·7	5·12	1·26
Fe ...	55·84	0·1146	6·4	4·80	0·98
Ni ...	58·68	0·1092	6·4	5·09	1·22
Co ...	58·97	0·1030	6·2	4·88	1·22
Cu ...	63·57	0·0936	6·0	5·01	1·56
Zn ...	65·37	0·0931	6·1	5·53	2·52
As ...	74·96	0·0827	6·2	5·29	1·94
Mo ...	96·0	0·0647	6·2	5·33	1·36
Pd ...	106·7	0·059	6·3	5·51	2·03
Ag ...	107·88	0·0566	6·1	5·51	2·62
Cd ...	112·4	0·0549	6·2	5·79	3·46
Sn ...	119·0	0·0556	6·6	5·97	3·41
Sb ...	120·2	0·0503	6·1	5·63	2·89
Pt ...	195·2	0·0320	6·3	5·45	2·63
Au ...	197·2	0·0316	6·2	5·86	3·16
Tl ...	204·0	0·0326	6·7	6·04	4·80
Pb ...	207·1	0·031	6·4	6·21	4·96
Bi ...	208·0	0·0303	6·3	5·91	4·54
Average	—	—	6·05	5·06	2·12

solid elements. Over the range from +20° to +100° the average atomic heat is 6·05 calories. At lower temperatures,

the atomic heats are much diminished. Between 20° and −180° the average value for the 25 elements is 5·06 (Richards and Jackson, *Annual Reports*, 1910, 16). Between −195° and −253°C. it is 2·12 calories (Dewar, *Proc. Roy. Soc.*, 1913, A. **89**, 168). The values for different elements are then not even approximately equal, elements which have a large atomic volume (at. wt. ÷ density) giving large atomic heats, whilst elements with small atomic volumes have small atomic heats. It is only as the temperature is raised that Dulong and Petit's Law becomes valid.

In the range from 20° to 100° all the solid elements except two give values lying between 5·2 and 6·7. The two exceptions are :

Boron...	At. wt. 11	Sp. ht. 0·2616	At. ht. 2·9
Carbon.	At. wt. 12	Sp. ht. 0·1532 (diamond)	At. ht. 1·84 (diamond)
		0·1990 (graphite)	2·39 (graphite)

In the case of diamond, the atomic heats at different temperatures are as follows (Nernst, *Annual Reports*, 1912, 9) :

Temperature...	896°	85°	−41°	−64°	−181°	−231°	−243°C.
Atomic heat ...	5·45	2·12	0·86	0·66	0·03	0·00	0·00

the values diminishing from a normal figure at about 1000° almost to nothing at temperatures below the boiling point of liquid air. In the case of boron the atomic heats are (Weber, *Phil. Mag.*, 1875, [iv], **49**, 293 ; Dewar, *loc. cit.*) :

Temperature...	233·2°	177·2°	125·8°	76·7°	26·6°	−39·6	−224°
Atomic heat ...	4·03	3·72	3·38	3·01	2·62	2·11	0·24

These exceptions are confined to elements of small atomic weight, to which Avogadro's hypothesis can easily be applied ; they do not, therefore, affect the usefulness of Dulong and Petit's Law as a means for determining the atomic weights of those elements which do not form volatile compounds.

Molecular heat of compounds—Neumann, in 1831 (Pogg, *Ann. der Physik*, 1831, **23**, 1–39), found a constant value for the MOLECULAR HEATS (sp. ht. × mol. wt.) of a series of seven carbonates and another constant value for a series of four sulphates; in each of these cases the atomic heat of the *combined* metals was constant throughout the series.

Cannizzaro, in 1858 (A.C.R. XVIII. 23), showed that mercury and iodine obey Dulong and Petit's Law when combined together, and used this fact as a further proof of his view that the atomic weight of mercury was 200 and not 100, as had been supposed previously. The figures he quotes are as follows:

Atomic heats:

Solid bromine, Br^1	80 × 0·0843 =	6·746
Iodine, I^1	127 × 0·0541 =	6·873
Solid mercury, Hg	200 × 0·0324 =	6·482

Molecular heats:

Mercurous chloride, $HgCl^1$	(200 + 35·5) × 0·0521 = 12·258 = 2 × 6·129	
Mercurous iodide, HgI^1...	(200 + 127) × 0·0395 = 12·913 = 2 × 6·457	
Mercuric chloride, $HgCl_2$.	(200 + 71) × 0·0689 = 18·669 = 3 × 6·223	
Mercuric iodide, HgI_2 ...	(200 + 254) × 0·0420 = 19·054 = 3 × 6·351	

If the atomic weight of mercury were 100, the molecular heats of the mercurous salts should have been 3 × 6, and those of the mercuric salts 4 × 6, for the quantities shown in the table.

A more detailed study of the molecular heats of compounds was made in 1865 by Kopp ("Investigations of the Specific Heat of Solid Bodies," *Phil. Trans.*, 1865, **155**, 71–202), who showed that "Each element has the same specific heat in its solid free state and in its solid compounds" (*loc. cit.* p. 83).

Whilst Cannizzaro assumed that in all cases the

molecular heat of a compound = number of atoms × 6,

[1] The argument is not affected if these formulæ are written Br_2, I_2, Hg_2Cl_2, and Hg_2I_2.

Kopp's rule gives expression to the fact that lower values are found for the molecular heats of compounds containing elements such as boron, carbon and sulphur, of which the atomic heats are abnormally low.

C. The Law of Isomorphism.

Mitscherlich (1819) discovers isomorphism.—In selecting atomic weights, Berzelius adopted the rule that compounds which resemble each other closely should be represented by similar formulæ. A remarkable illustration of this close resemblance between compounds of similar composition was discovered in 1819 by **Mitscherlich**, a pupil of Berzelius. He examined the acid phosphate and arsenate of potassium, which are now represented by the formulæ KH_2PO_4 and KH_2AsO_4, and found that

"these salts are composed of the same number of atoms . . . , and only differ from one another in that the radical in one is phosphorus and in the other arsenic. The crystalline form of these two salts is the same . . . ; for not only the primitive form, but all the varieties, resemble each other so closely in the size, number, and angles of the faces, that it is quite impossible to find any difference, even in the characters which appear to be quite accidental" ("On the Relation between Crystalline Form and Chemical Proportions," *Ann. Chim. Phys.*, 1820, **14**, 172 and 173).

A similar analogy of form was detected in

the sodium salts $\left\{ \begin{array}{l} NaH_2PO_4,H_2O \\ NaH_2AsO_4,H_2O \end{array} \right\}$ and in

the ammonium salts $\left\{ \begin{array}{l} (NH_4)H_2PO_4 \\ (NH_4)H_2AsO_4 \end{array} \right\}$

In each of these cases 75 parts of arsenic could take the place of 31 parts of phosphorus, without producing any alteration of crystalline form.

In the second part of the memoir (*Ann. Chim. Phys.*, 1821, **19**, 350) Mitscherlich described as ISOMORPHOUS

those groups of elements which could take the place of one another in compounds of identical crystalline form. In the case of isomorphous elements, "The same number of atoms combined in the same way produces the same crystalline form; the crystalline form is independent of the chemical nature of the atoms, and is determined only by the number and relative position of the atoms" (*ibid.*, p. 419).

The law of isomorphism.—The LAW OF ISOMORPHISM as now enunciated states that: "*Substances which are similar in crystalline form and in chemical properties should be represented by similar formulæ.*"

This law is limited in two directions: (1) On one hand, mere identity of crystalline form is not sufficient to prove that the formulæ of two compounds should be similar. In the case of crystals of a high degree of symmetry, such as the cube and octahedron, the angles can be calculated as simple fractions or functions of a right angle, and are identical for all the elements and compounds (iron, silver, iron pyrites, salt, sal-ammoniac, etc.) which crystallise in these forms. (2) On the other hand, if the crystalline form is less symmetrical, the angular measurements may differ considerably, even in the most closely-related compounds; thus, the mineral carbonates crystallising in simple rhombohedra show the following angles:

Calcite, $CaCO_3$	74°55′
Magnesite, $MgCO_3$..... ..	72°36′
Chalybite, $FeCO_3$	73°0′
Calamine, $ZnCO_3$	72°20′
Rhodochrosite, $MnCO_3$ ...	72°58′

Isomorphous mixtures or solid solutions.—Some more certain test than mere geometrical form is evidently required before "isomorphism" can be used as trustworthy evidence of analogous chemical composition. Such a test is supplied by the fact (investigated by Mitscherlich) that many

compounds, which are similar both in chemical type and in crystalline form, possess the property of forming crystals in which the two constituents are mixed as intimately as the salt and water in an aqueous salt solution. Crystals of this kind are described as ISOMORPHOUS MIXTURES or SOLID SOLUTIONS. They are formed whenever two or more closely-related substances are allowed to crystallise together from solution or from the fused state. Thus if

potash alum . . . . . $KAl(SO_4)_2,12H_2O$
soda alum . . . . . $NaAl(SO_4)_2,12H_2O$
and chrome alum . . . . $KCr(SO_4)_2,12H_2O$

are dissolved together in water, the crystals which separate will contain all three substances, the colour ranging from a pure white to a deep purple according to the proportion of chrome alum which they contain. So also in the case of minerals, garnets of the type

$$Ca_3Al_2Si_3O_{12} \text{ or } 3CaO,Al_2O_3,3SiO_2,$$

which have crystallised from a magma of complex composition, are all mixtures of isomorphous substances, in which a part of the calcium has been replaced by magnesium, ferrous iron, or manganese, and part of the aluminium by ferric iron, or by chromium. But in all this complex substitution (known to mineralogists as VICARIOUS REPLACEMENT) the type remains constant and the general formula

$$3[Ca,Mg,Fe,Mn]O,[Al,Fe,Cr]_2O_3,3SiO_2$$

may be used to represent every member of the series.

The formation of isomorphous mixtures is a valuable test of chemical similarity, because they cannot be produced from substances of different type, even when absolutely identical in crystalline form; on the other hand, a difference of 5° in the angles of analogous compounds need not prevent the formation of an isomorphous mixture, since composite

crystals may still be formed, the angles of which are a compromise between those of the constituents.

Applications of the law of isomorphism.—In the isomorphous phosphates and arsenates, 75 grams of arsenic replace 31 grams of phosphorus without altering the crystalline form. Since 31 is the atomic weight of phosphorus, the Law of Isomorphism indicates that 75 is the atomic weight of arsenic, thus confirming the value arrived at by other methods. A similar resemblance appears in the crystalline properties of arsenic, antimony and bismuth. In the isomorphous compounds of these elements, 75 grams of arsenic are replaced by 120 grams of antimony, and 120 grams of antimony by 208 grams of bismuth, without producing any large alteration of crystalline form. In this way the Law of Isomorphism leads up from P = 31, through As = 75 to Sb = 120 and Bi = 208.

In 1828 Mitscherlich showed (*Pogg. Ann.*, 1828, **12**, 138) that the selenates and sulphates of sodium and silver formed an isomorphous series in which 23 parts of sodium were replaced by 108 parts of silver, whilst 32 parts of sulphur were replaced by 79 parts of selenium. This isomorphism served to establish the atomic weight of selenium.

Isomorphism of manganese and chromium with chlorine and sulphur.—Two interesting cases of isomorphism were described in detail by Mitscherlich in 1832 (*Pogg. Ann.*, 1832, **25**, 287–302). He showed that the red potassium permanganate was isomorphous with potassium perchlorate. In these compounds 55 parts of manganese replace 35·5 parts of chlorine ; 55 is therefore the atomic weight of manganese. On the other hand, the green potassium manganate was isomorphous with the chromate, selenate and sulphate ; the equivalent quantities, S 32, Se 79, Cr 52, Mn 55, are therefore the atomic weights of these elements.

Mitscherlich had already proved the isomorphism of the

divalent metals Ca, Mg, Mn (manganous), Fe (ferrous), Cu, Zn, Co, Ni in their simple and double sulphates (*Ann. Chem. Phys.*, 1821, **19**, 416), and of the tervalent metals Cr, Mn, Fe, Al in the spinels $MgAl_2O_4$, Fe_3O_4, etc. The way was therefore open to link up the atomic weights of nearly all the metals with those deduced by Avogadro's hypothesis for the non-metals chlorine and sulphur.

Mitscherlich's observations on isomorphism, confirmed as they were by Dulong and Petit's Law of Atomic Heats, led Berzelius in 1827 (*Jahresbericht*, 1828, **7**, 67–78) to write the oxides of iron as FeO and Fe_2O_3 instead of FeO_2 and FeO_3, and to publish a new table of atomic weights in which the values for nearly all the metals were halved. He argued from the isomorphism of the sulphates and chromates that chromic acid must be CrO_3, compare SO_3; chromic oxide was therefore Cr_2O_3. The isomorphism of the salts of chromium, manganese, ferric iron and aluminium gave the formula Mn_2O_3, for manganic oxide, Fe_2O_3 for ferric oxide, and Al_2O_3 for alumina. But if ferric oxide was Fe_2O_3, ferrous oxide must be FeO, and this type of formulæ must also be given to all those oxides the salts of which were isomorphous with the ferrous salts.

Exceptions to the law of isomorphism.—There are many exceptions to the law of isomorphism. On one hand, many substances of similar structure crystallise in totally different forms. Thus Mitscherlich found that the usual form of acid sodium phosphate, NaH_2PO_4, was quite different from that of the acid arsenate, NaH_2AsO_4. This difference is due to the POLYMORPHISM of the phosphate, which forms two types of crystals, only one of which is isomorphous with the arsenate.

On the other hand, perfect isomorphism is often found in substances of dissimilar composition. The most important case is that of the ammonium salts in which the compound radical NH_4 may be displaced by a single atom of sodium

or potassium without producing any change of crystalline form. Again, silver sulphide, Ag_2S, as argentite, is isomorphous with lead sulphide, PbS, as galena, and is nearly always present as an isomorphous impurity in this mineral, in spite of the unequal numbers of atoms in the two molecules. Cases of this sort show that the law of isomorphism, although of great value, cannot be used as a final test in establishing the atomic weights of the elements.

D. Formulæ of Metallic Compounds.

Empirical and molecular formulæ.—In the preceding chapter (p. 352) a method has been described by which the formula of a volatile compound may be deduced from its vapour-density and percentage composition, when the atomic weights of its constituents are known. This method cannot be applied to substances, such as sugar or potassium chlorate, which decompose when heated, or to substances, such as silica, which boil at so high a temperature that their vapour-densities cannot be determined. There is, however, no difficulty in deducing from the analysis of the substance an EMPIRICAL FORMULA, which expresses its composition in the simplest way, but gives only a minimum value for its molecular weight.

The method used in calculating an empirical formula may be illustrated by using Stas's figures for the analysis of cinnamic acid (*Works*, I. 281).

On combustion, 0·900 gram of acid gave 0·444 gram of water and 2·402 grams of carbonic anhydride. The composition of the acid was therefore :

C 72·78 H 5·47 O 21·75%.

Taking the atomic weights as

C 12·00 H 1·008 O 16,

the numbers of atoms are in the proportion

$$C\ \frac{72{\cdot}78}{12{\cdot}00} \qquad H\ \frac{5{\cdot}47}{1{\cdot}008} \qquad O\ \frac{21{\cdot}75}{16} \qquad \text{or}$$

$$C\ 6{\cdot}06 \qquad H\ 5{\cdot}43 \qquad O\ 1{\cdot}36.$$

Dividing by the smallest number, these proportions become

$$C\ 4{\cdot}46 \qquad H\ 3{\cdot}99 \qquad O\ 1,$$

or very nearly

$$C\ 4\tfrac{1}{2} \qquad H\ 4 \qquad O\ 1.$$

Multiplying by two in order to remove fractions, the simplest empirical formula for the compound is seen to be $C_9H_8O_2$. The composition calculated for this formula is

$$C\ 72{\cdot}94 \qquad H\ 5{\cdot}45 \qquad O\ 21{\cdot}61$$

and agrees closely with the composition found by combustion. The MOLECULAR FORMULA, which should express both the composition and the molecular weight of cinnamic acid, is $[C_9H_8O_2]_n$, where n is an integer, the value of which must be determined by other methods, *e.g.* from the chemical properties of the acid or from the boiling-points and freezing-points of its solutions.

Empirical formulæ of metallic salts.—The following examples show how the composition and the empirical formulæ of some typical metallic salts have been determined. The analytical data are taken from Berzelius's[1] papers on *Fixed Proportions*, 1811—1812 (Ostwald's *Klassiker*, No. 35). The atomic weights are substantially those of Stas.

1. *Lead oxide, sulphide and sulphate.*—Berzelius found (*Fixed Proportions*, 1811–1812; *Klassiker*, XXXV, 6–13) that:

[1] In quoting Berzelius's data it has been necessary to distinguish between the actual analyses, and the compositions which he calculated on the assumption that both chlorine and nitrogen were not elements but oxides.

(1) 10 grams of lead, dissolved in nitric acid and ignited, gave 10·78 grams of the oxide (litharge).

(2) 10 grams of lead, when fused with sulphur, gave 11·56 grams of sulphide.

(3) 10 grams of lead sulphide, when digested with aqua regia, gave 12·65 grams of sulphate, no excess of lead or of sulphuric acid being left uncombined.

(4) 10 grams of lead, dissolved in nitric acid and precipitated with sulphuric acid, gave 14·635 grams of lead sulphate, in close agreement with the weight $\frac{11{\cdot}56 \times 12{\cdot}65}{10}$ = 14·623 grams calculated from (2) and (3).

From these experiments Berzelius concluded :

(5) That lead and sulphur in lead sulphide are combined together in exactly the same proportions as when their oxides unite to form lead sulphate.

(6) That 10 grams of lead sulphide in forming lead sulphate unite with 2·65 grams of oxygen ; the 10 grams of sulphide contain $\frac{100}{11{\cdot}56}$ = 8·651 grams of lead, yielding on oxidation $\frac{8{\cdot}651 \times 10{\cdot}78}{10}$ = 9·326 grams of lead oxide, thus accounting for 9·326 − 8·651 = 0·675 gram of oxygen ; the remainder, 2·65 − 0·675 = 1·975 of the oxygen in the sulphate was therefore combined with 10 − 8·651 = 1·349 grams of sulphur to form 3·324 grams of sulphuric anhydride. The composition of sulphuric anhydride was therefore :

Sulphur 1·349 grams = **40·58%**
Oxygen 1·975 grams = **59·42%**

i.e. sulphur : oxygen = 2 : 3 nearly.

(7) In the sulphate, litharge containing 0·675 gram of oxygen was combined with sulphuric anhydride containing 1·975 grams of oxygen. The weights of oxygen in the acid and in the base were therefore in the ratio 3 : 1, a ratio that held good for the sulphates generally (*Chemical Proportions*, 1819, p. 122).

By the analysis of barium sulphite (*Klassiker*, XXXV, 18), the composition of sulphurous anhydride was found to be

Sulphur = 50·55%
Oxygen = 49·45%

i.e. sulphur : oxygen = 1 : 1 nearly. The weights of oxygen in the two oxides were thus in the ratio 3 : 2 as deduced from Gay-Lussac's volumetric analysis (p. 169). Berzelius found that when barium sulphite was oxidised to barium sulphate, no excess of baryta or of sulphuric acid was produced. The ratio of barium to sulphur was therefore the same in the two compounds. The ratio of oxygen in the acid to oxygen in the base was 2 : 1 for the sulphites, as contrasted with 3 : 1 for the sulphates (*Chemical Proportions*, p. 122).

Taking the modern values for the atomic weights, the empirical formulæ of these compounds can be deduced at once.

	Lead		Oxygen
LITHARGE =	10 grams	:	0·78 gram
=	$\frac{10}{207·1}$	:	$\frac{0·78}{16}$ atoms
=	0·0483	:	0·0487 atom
=	1	:	1 atom

Formula PbO.

	Lead		Sulphur
LEAD SULPHIDE =	10	:	1·56 grams
=	$\frac{10}{207·1}$	:	$\frac{1·56}{32·1}$ atoms
=	0·0483	.	0·0486 atom
=	1	:	1 atom

Formula PbS.

	Sulphur		Oxygen
SULPHURIC ANHYDRIDE =	1·349	:	1·975 grams
=	$\frac{1·349}{32·1}$	:	$\frac{1·975}{16}$ atoms
=	0·0420	:	0·1234 atom
=	1	:	3 atoms

Formula SO_3.

	Lead		Sulphur		Oxygen	
LEAD SULPHATE =	8·651	:	1·349	:	2·65	grams
=	$\frac{8·651}{207·1}$	:	$\frac{1·349}{32·1}$	:	$\frac{2·65}{16}$	atoms
=	0·0418	:	0·0420	:	0·1656	atom
=	1	:	1	:	4	atoms

Formula $PbSO_4$.

The corresponding formula for lead sulphite is $PbSO_3$.

2. *Potassium Chlorate.*—In this case Berzelius weighed the oxygen directly (by loss of weight) and the chlorine as silver chloride, and determined the metal by difference.

(1) 3·9850 grams of potassium chlorate, heated in a small retort, lost 1·5475 grams of oxygen and left 2·4375 of potassium chloride (*Klassiker*, XXXV. 122).

(2) 10 grams of potassium chloride, precipitated with silver nitrate, gave 19·21 grams of fused "horn-silver" (silver chloride) (*Klassiker*, XXXV. 93).

(3) 3 grams of pure silver, dissolved in nitric acid, precipitated with muriatic acid, evaporated and fused, gave 3·98 grams of "horn-silver" (*Klassiker*, XXXV. 24).

It follows

(4) From (1), that 3·9850 grams of potassium chlorate contain **1·5475** grams of *oxygen.*

(5) From (2) and (3), that since 3·98 grams of silver chloride contain 3 grams of silver and $3·98 - 3·00 = 0·98$ gram of chlorine, therefore 19·21 grams of horn-silver contain $\frac{19·21}{3·98} \times 0·98 = 4·73$ grams of chlorine, derived from 10 grams of potassium chloride; thus, 3·9850 grams of potassium chlorate or 2·4375 grams of potassium chloride contain $\frac{2·4375}{10} \times 4·73 =$ **1·1529** grams of *chlorine.*

(6) Finally, 3·9850 grams of potassium chlorate must contain $3·9850 - 1·5475 - 1·1529 =$ **1·2846** grams of *potassium.*

The formula of the salt is deduced as follows:

	Potassium		Chlorine		Oxygen	
POTASSIUM CHLORATE =	1·2846	:	1·1529	:	1·5475	grams
	$\frac{1·2846}{39·10}$	:	$\frac{1·1529}{35·46}$	:	$\frac{1·5475}{16}$	atoms
=	0·0329	:	0·0325	:	0·0967	atom
=	1	:	1	:	3	atoms

Formula $KClO_3$.

3. *Chalk.* As Berzelius was not able to obtain pure metallic calcium, he could not determine the composition of lime by direct oxidation; an indirect method of analysis was therefore adopted:

(1) 10 grams of chalk when ignited gave 5·64 grams of lime and 4·36 grams of carbonic anhydride containing 28·4% of carbon.

(2) 10 grams of chalk dissolved in muriatic acid gave 10·96 grams of fused muriate of lime (calcium chloride).

(3) 3·01 grams of this fused muriate, when dissolved and precipitated with silver nitrate, gave 7·75 grams of "horn-silver" (fused silver chloride), containing 75·3% of silver and therefore 24·7% chlorine (*Klassiker*, XXXV. 77).

From these experiments it followed

(4) That 10 grams of chalk contained 0·284 × 4·36 = **1·238** grams of *carbon*, united with 4·36 − 1·238 = **3·122** grams of *oxygen* to form carbonic anhydride.

(5) That 3·01 grams of muriate of lime contained 0·247 × 7·75 = 1·914 grams of chlorine united with 3·01 − 1·914 = 1·096 grams of calcium; therefore the 10·96 grams of muriate of lime derived from 10 grams of chalk contained $\frac{10·96}{3·01} \times 1·096 =$ **3·99** grams of *calcium*.

(6) That the 5·64 grams of lime obtained by igniting 10 grams of chalk contained this 3·99 grams of metal united with 5·64 − 3·99 = **1·65** grams of *oxygen*.

The composition of chalk is therefore:

$$\text{Chalk, 10 grams} = \begin{cases} \text{Lime, 5·64 grams} = \begin{cases} \text{Calcium} \dots & 3·99 \text{ grams} \\ \text{Oxygen} \dots & 1·65 \text{ ,,} \end{cases} \\ \text{Carbonic anhydride} \\ \text{4·36 grams} = \begin{cases} \text{Oxygen} \dots & 3·12 \text{ ,,} \\ \text{Carbon} \dots & 1·24 \text{ ,,} \end{cases} \end{cases}$$

The oxygen in the acid is seen to be double the amount in the base, as in the case of the sulphites.

The proportions of the three elements are:

	Calcium		Carbon		Oxygen	
	3·99	:	1·24	:	4·77	grams
=	$\frac{3·99}{40·1}$	:	$\frac{1·24}{12·0}$	:	$\frac{4·77}{16}$	atoms
=	0·099	:	0·103	:	0·298	atom
=	1	:	1	:	3	atoms

Formula $CaCO_3$.

4. *Lead Nitrate.*—Berzelius found that

(1) 20 grams of dry, powdered lead nitrate, ignited in a weighed platinum crucible, left 13·445 grams of oxide; therefore 100 grams of the salt contain 67·22 grams of lead oxide, composed of **4·85** grams of *oxygen* and **62·37** grams of *lead* (*Klassiker*, XXXV. 129).

(2) Gay-Lussac had proved (p. 203) that nitric anhydride was composed of 2 volumes of nitrogen of density 0·969 and 5 volumes of oxygen of density 1·104 (air = 1); the composition by weight was therefore 0·969 × 2 : 1·104 × 5 = 1·938 : 5·520. The weights of the two gases in 100 − 67·22 = 32·78 grams of nitric anhydride are therefore

$$\frac{1·938}{1·938 + 5·520} \times 32·78 = \mathbf{8·52} \text{ grams of } \textit{nitrogen}$$

$$\text{and } 32·78 - 8·52 = \mathbf{24·26} \text{ grams of } \textit{oxygen}.$$

From these analyses it is clear that the composition of the salt is:

$$\text{Lead nitrate, 100 grams} = \begin{cases} \text{Litharge, 67·22 grams} = \begin{cases} \text{Lead} \dots & 62·37 \text{ grams} \\ \text{Oxygen} \dots & 4·85 \text{ ,,} \end{cases} \\ \text{Nitric anhydride,} \\ \text{32·78 grams} = \begin{cases} \text{Oxygen} \dots & 24·26 \text{ ,,} \\ \text{Nitrogen} & 8·52 \text{ ,,} \end{cases} \end{cases}$$

and that the oxygen in the acid is *five times*[1] that in the base (Berzelius, *Chemical Proportions*, 1819, p. 124).

The proportions of the three elements are:

	Lead		Nitrogen		Oxygen	
LEAD NITRATE =	62·37	:	8·52	:	29·11	grams
=	$\frac{62·37}{207·1}$	:	$\frac{8·52}{14·01}$	:	$\frac{29·11}{16}$	atoms
=	0·301	:	0·608	:	1·819	atoms
=	1	:	2	:	6	atoms

Formula PbN_2O_6.

SUMMARY AND SUPPLEMENT

A. VAPOUR-DENSITIES

Vapour-densities have been determined for the following metals and metallic compounds:

Elements: Na, K, Zn, Cd, Hg.

Haloid Salts: KI, Cu_2Cl_2, AgCl, $ZnCl_2$, $PbCl_2$, $2AlCl_3 \rightleftharpoons Al_2Cl_6$, Al_2Br_6, Al_2I_6, $2FeCl_2 \rightleftharpoons Fe_2Cl_4$, $Fe_2Cl_6 \rightleftharpoons 2FeCl_3 \rightleftharpoons 2FeCl_2 + Cl_2$, CrO_2Cl_2, $CrCl_3$, $MnCl_2$, $SnCl_2 \rightleftharpoons Sn_2Cl_4$, $SnCl_4$, $HgCl_2$, $Hg_2Cl_2 \rightleftharpoons Hg + HgCl_2$, etc., in addition to compounds of As, Sb, Bi.

Carbon Compounds: $Zn(CH_3)_2$, $Zn(C_2H_5)_2$, $Zn(C_5H_{11})_2$, $Al(CH_3)_3$, $Al(C_2H_5)_3$, $Sn(CH_3)_4$, $Sn_2(C_2H_5)_6$, $Fe(CO)_5$, $Ni(CO)_5$.

The data are too scanty to give trustworthy values for the atomic weights of the metals.

B. ATOMIC HEATS

The chief method for determining the atomic weights of the metals is by means of the Law of **Dulong and Petit** (1819),

specific heat × *atomic weight* = *atomic heat* = *constant.*

The value of the "constant" is about 6 for the range from 100°

[1] In 1812 Berzelius regarded nitrogen as an oxide, and concluded that this ratio was *six times*; in 1819 he gave the ratio as six times or five times, according as nitrogen was regarded as a compound or as an element.

to 20°, but falls to 5 in the range from 20° to −188° and to 2 between −188° and −253°. In the lowest range the atomic heat varies very widely and is roughly proportional to the atomic volume ; but at ordinary temperatures the atomic heats of all the elements except boron and carbon fall between 5·2 and 6·7 ; even these two elements give "normal" values at higher temperatures.

In the case of solid compounds, **Kopp** (1865) found that "each element has essentially the same specific or atomic heat in compounds as it has in the free state."

The Law of Atomic Heats only leads to very rough values for the atomic weight, but is sufficiently exact to give the valency, *i.e.* the integral ratio by which the equivalent of an element must be multiplied in order to give its atomic weight.

C. Isomorphism

Mitscherlich, in 1819, discovered that identical crystalline forms were shown by the following pairs of *isomorphous* salts :

$$\left\{\begin{matrix}KH_2PO_4\\KH_2AsO_4\end{matrix}\right\}\quad\left\{\begin{matrix}NaH_2PO_4,H_2O\\NaH_2AsO_4,H_2O\end{matrix}\right\}\quad\left\{\begin{matrix}(NH_4)H_2PO_4\\(NH_4)H_2AsO_4\end{matrix}\right\}.$$

The sodium phosphate also crystallised in a second form and was therefore *dimorphous.*

In series of isomorphous compounds the isomorphous elements replace one another atom by atom ; the analysis of isomorphous salts can therefore be used to determine atomic weights. Thus in the phosphates and arsenates 75 parts of arsenic take the place of 31 parts of phosphorus ; therefore if P = 31, then As = 75.

Isomorphous salts of similar composition possess the property of forming *isomorphous mixtures* or *solid solutions*, *i.e.* composite crystals in which the different constituents are mixed as intimately as in a liquid solution. If these mixtures can be formed in any proportions the isomorphism is *complete* (compare water and alcohol): if one substance will only tolerate a limited amount of the other (compare water and ether) the isomorphism in *incomplete.* An example of incomplete isomorphism is found in the potassium and ammonium phosphates formulated above, which will only mix with one another to the extent of about 20%.

In the cubic system isomorphism is *perfect*, *i.e.* the angles for the different substances are exactly equal. Examples are

(1) the alums $M^{I}M^{III}(SO_4)_2,12H_2O$.
where M^{I} = K, Na, NH_4, &c.
M^{III} = Al, Fe(ferric), Cr, &c.

(2)			
Spinel	$MgAl_2O_4$	Also	$MgFe_2O_4$
Gahnite	$ZnAl_2O_4$		$MnFe_2O_4$
Magnetite	$FeFe_2O_4$		$FeAl_2O_4$
Chromite	$FeCr_2O_4$		&c.

In less symmetrical crystals the isomorphism is *imperfect*, but mixed crystals may be formed if the angles do not differ more than 5°. The rhombohedral angles of a series of isomorphous carbonates are given on page 369.

Isomorphism often occurs in compounds of dissimilar structure, *e.g.* $CaCO_3$ and $NaNO_3$, Mg_2SiO_4 and Al_2BeO_4, and even in compounds which contain unequal numbers of atoms in the molecule, *e.g.* PbS and Ag_2S or $(NH_4)Al(SO_4)_2,12H_2O$ and $KAl(SO_4)_2,12H_2O$. A remarkable collection of cases of isomorphism (in which fluorine replaces oxygen, water replaces chlorine, &c., without producing any change of crystalline form) has been made by T. V. Barker (*Trans. Chem. Soc.*, 1912, **101**, 2484).

D. Formulæ of Salts

In the case of salts it is usually possible to give only an *empirical formula*, which expresses its composition, but not its molecular weight. Such a formula can be deduced readily from the analytical data by methods indicated on pp. 373 to 380.

CHAPTER XVII

MOLECULAR ARCHITECTURE

A. The Rise of Organic Chemistry

The development of inorganic chemistry, 1766–1816.— It can scarcely fail to be noticed that almost the whole of the work described in the sixteen preceding chapters falls within a very narrow period of time. Occasionally it has been necessary to go back to study the origins of things, or forward to study their more mature developments ; but by far the greater part of the experiments that are described were carried out during the latter part of the eighteenth and the early years of the nineteenth century.

This narrow period, undoubtedly the most fertile in the history of chemistry, begins with Black's work on "Magnesia Alba," published in 1755. If this investigation be set aside as merely a herald of the dawn, it will be found that almost every chapter is filled with accounts of experiments made in the fifty years from 1766 to 1816. The former date saw the publication of Cavendish's papers "On Factitious Air," and was followed almost immediately by the wonderful development of Pneumatic Chemistry which we owe to the successful labours of Priestley. The latter date saw the completion of Gay-Lussac's work on the

oxides of nitrogen and his final solution of the problem of the composition of nitric and nitrous acids. On the practical side, it may be noticed that by the year 1816 all the commoner gases had been prepared and analysed, some fifty different elements had been recognised clearly, water had been decomposed and recomposed, the alkalis and most of the earths had yielded up their metals, and the composition of all the important mineral acids had at last been established. On the theoretical side, it will be sufficient to notice that, by the year 1816, the atomic and molecular theories had been enunciated by Dalton and by Avogadro, and that the Laws of Chemical Combination to which they lead had been tested by Berzelius and proved to be correct. The brief period of fifty years had thus sufficed, not merely to lay the foundations of Inorganic Chemistry, but also to reveal all the main outlines of the edifice.

The rise and development of organic chemistry, 1815–1865.—It now remains to condense into a single chapter the work of the succeeding fifty years, which witnessed a corresponding development in the daughter science of Organic Chemistry. For the sake of convenience the two fifty-year periods may be made to overlap by a single year. The second of the periods will then extend from 1815, when Gay-Lussac discovered the cyanogen radical and isolated cyanogen gas, up to 1865, when Kekulé first put forward his structural formula for benzene.

The period begins with some of the earliest accurate analyses of organic compounds, leading at once to correct formulæ, based upon the theories of Dalton and of Avogadro, for compounds such as alcohol and ether. Unfortunately, a few obstinate exceptions threw discredit upon Avogadro's hypothesis, with the result that, in the matter of formulæ, darkness and confusion reigned almost all through the fifty years that we are now considering. The marvellous energy of the many workers, coupled with the complex and unfamiliar formulæ which they used, render this period

only less difficult to study than the alchemistic period itself.

The supreme feature of the period was the gradual development of structural chemistry, leading at last to a clear knowledge of the way in which the atoms are linked together, even in the more complex products of vegetable and animal life. But apart altogether from all progress in the region of theory, there was a marvellous growth in the experimental knowledge of organic compounds. In this period we find recorded the discovery, or the first analysis, of methyl alcohol and its higher homologues, of a series of fats and fatty acids, of acetone and the ethers, of chloral and chloroform, glycerol and glycol, aniline and the amines, camphor and camphoric acid, benzene and naphthalene, and the many products obtained by chlorinating, brominating, nitrating and sulphonating these different materials. The organic chemist of to-day will recognise in this imperfect list evidences of advance along most of the principal routes by which the growth of knowledge is proceeding in his science at the present time ; and the structural formulæ assigned by Kekulé to ethyl acetate and to benzene are but typical of those which are now being assigned, fifty years later, to the more complex terpenes and alkaloids.

Lavoisier (1784) shows that organic substances are compounds of carbon and hydrogen.—The formation of fixed air and of water as products of the combustion of organic materials had been recognised vaguely from the time of Van Helmont (p. 64). In the case of fixed air the information first became definite in the hands of Black,[1]

[1] In his *Lectures on the Elements of Chemistry*, published in 1803, after his death, Black says that in the year 1757 he had discovered or proved :—

(1) That fixed air "is deadly to all animals that breathe it by the mouth and nostrils together."

(2) That "the change produced on wholesome air by breathing it consisted chiefly, if not solely, in the conversion of part of it into fixed air," for "by blowing through a pipe into lime-water, or a solution

of Cavendish (p. 95), and of Priestley (p. 95). The production of water during the burning of spirit of wine was frequently recorded, right up to the time of Lavoisier, who in 1784 obtained 18 ounces of water by burning 16 ounces of spirit (*Works*, II. 358). But these observations could not be used to explain the composition of organic compounds until the experiments of Lavoisier (p. 97) and Cavendish (p. 113) had disclosed the composite character both of fixed air and of water. When these substances had been proved to be "oxide of carbon" and "oxide of hydrogen" respectively, Lavoisier was in a position to describe correctly the nature of combustible organic substances as compounds of carbon and hydrogen; indeed, some years before these names were introduced, he had already (pp. 145–148) made analyses to determine the proportions of carbon and hydrogen in spirit of wine, in wax, and in olive oil. In his *Elementary Treatise*, published in 1789, Lavoisier was able to enumerate the chief elements present in organic compounds, usually in combination with oxygen:

"I have already observed that, in the mineral kingdom, almost all the oxidisable and acidifiable radicals were simple; that, in the vegetable kingdom on the contrary, and above all in the animal kingdom, there were scarcely any which were composed of less than two substances, hydrogen and carbon; that often nitrogen and phosphorus were united with them, and that there were produced radicals with four bases" (*Works*, I. 147).

Thus, "the acetic radical is formed by the union of

of caustic alkali, the lime was precipitated, and the alkali was rendered mild."

(3) That "fixed air is the chief part of the elastic matter which is formed in liquids in the vinous fermentation."

(4) That the "deadly vapour of burning charcoal . . . must be fixed air," since a piece of red-hot charcoal, inserted in the nozzle of a pair of chamber-bellows, imparted to the air which passed over it the power to render lime-water milky (*Lectures*, 1803, II. 87–88).

These observations were not published for nearly fifty years, though manuscript copies of the lectures (which can still be purchased) appear to have been sold to the students by the lecture-assistant.

carbon and of hydrogen brought to the state of acid by the addition of oxygen. This acid is, consequently, composed of the same principles as tartaric acid, malic acid, etc. but the proportion of the principles is different for each of these acids, and it would seem that acetic acid is the most oxygenated of all" (*Works*, I. 218).

Alcohol and ether.—It would be difficult to exaggerate the importance to organic chemistry of the process of vinous fermentation. Fermented liquors have been known from time immemorial. The spirit or "aqua vitæ" prepared from them by distillation was known in the time of Geber. A minute description of the methods of purifying it is given by **Raymond Lully** (1235–1315). The spirit, prepared from dark wine, was subjected to repeated fractional distillation; in the first distillation only one-tenth of the distillate was collected, then one-fourth, one-third, one-half, and finally (in 14 further distillations) almost the whole of the volatile distillate. The spirit was also dried by distilling from calcined tartar (dry potassium carbonate). There can be little doubt that by such methods Lully would obtain almost pure ALCOHOL. Lully also tried the action of oil of vitriol on alcohol, and was one of the first to convert it into the still more volatile ETHER. The further action of oil of vitriol on alcohol, whereby it is converted into a gas, OLEFIANT GAS or ETHYLENE, was referred to by Becher in 1669 and has already been described in detail (pp. 154–156).

In view of its unique importance, it is not surprising that alcohol was selected by Lavoisier as the subject of his first organic analysis (pp. 146–148). Both alcohol and ether were analysed by de Saussure in 1807 (*Ann. de Chimie*, 1807, **62**, 225–241), by a variety of methods, but with no great measure of success; in 1814, however (*Ann. de Chimie*, 1814, **89**, 273–305), he obtained a very good analysis of alcohol, by first decomposing it in a red-hot tube, and a less accurate analysis of ether, by exploding

it directly with oxygen in a eudiometer. The results are shown below :

	Alcohol.			Ether.	
	Lavoisier.	de Saussure.	Calculated.	de Saussure.	Calculated.
Carbon .	28·5	52·0	52·2	68·0	64·9
Hydrogen	17·4	13·7	13·0	14·4	13·5
Oxygen .	54·1	34·3	34·8	17·6	21·6

The vapour densities of alcohol and ether were determined by Gay-Lussac in 1815 (*Ann. de Chimie*, 1815, **95**, 311–318).

Lavoisier's work on vinous fermentation (1789).— More important than the isolated analysis of spirit of wine is Lavoisier's complete investigation of the process of vinous fermentation, as described in his *Treatise*, in 1789 (*Works*, I. 100–108) Lavoisier was able to show that

"The effects of fermentation reduce themselves to a separation of the sugar, which is an oxide, into two portions, oxygenating one portion at the expense of the other to form carbonic acid ; deoxygenating the other in favour of the first to form a combustible substance, which is alcohol ; so that, if it were possible to recombine these substances, alcohol and carbonic acid, sugar would be reproduced" (*Works*, I. 107).

Lavoisier took 100 lb. of sugar, 400 lb. of water and 10 lb. of yeast-paste containing about 7 lb. of water. At the end of some days 35 lb. of carbonic acid had escaped, carrying with it 14 lb. of water. There remained 460 lb. of liquor, containing 409 lb. of water, 58 lb. of alcohol, 2 lb. of acetic acid, 4 lb. of sugar and 1 lb. of (dry) yeast. Lavoisier worked out a balance-sheet as follows :

Before Fermentation :—

	Hydrogen.	Oxygen.	Carbon.	Nitrogen.		Total.
Water .	61.1.3[1]	346. 2.4	—	—	=	407. 3·7
Sugar .	8.0.0	64. 0 0	28. 0.0	—	=	100. 0.0
Yeast .	0.4.5	1.10.2	0.12.5	0.0.5	=	2.12.1
	69.6.0	411.12.6	28.12.5	0.0.5	=	**510. 0.0**

[1] 8 gros = 1 ounce, 16 ounces = 1 pound ; the grains have been omitted from the table.

After Fermentation :—

	Hydrogen.	Oxygen.	Carbon.	Nitrogen.	Total.
Carbonic acid	—	25. 7.1	9.14.3	—	= 35. 5.4
Water . .	61.5.4	347.10.1	—	—	=408.15.5
Alcohol . .	9.9.2	31. 6.2	16.11.6	—	= 57.11.2
Acetic acid .	0.2.4	1.11.4	0.10.0	—	= 2. 8.0
Sugar . .	0.5.2	2. 9.7	1. 2.3	—	= 4. 1.4
Dry yeast .	0.2.3	0.13.1	0. 6.2	0.0.3	= 1. 6.1
	71.8.7	409.10.0	28.12.6	0.0.3	=**510. 0.0**

Lavoisier's chapter on "Vinous Fermentation" will always be remarkable for the fact that it contains one of the first clear statements of the law of CONSERVATION OF MASS during chemical change, sometimes described also as the INDESTRUCTIBILITY OF MATTER, and one of the first descriptions and illustrations of a CHEMICAL EQUATION. The indestructibility of the atom had already been postulated by Newton (p. 292). The proof that the total mass is unaltered by chemical changes is closely bound up with the proof that heat is imponderable; this proof had been given by Cavendish for the explosion of hydrogen and oxygen (p. 113) and by Lavoisier himself for the calcination of tin in closed vessels (pp. 35–38). Lavoisier was therefore able to enunciate, as a guiding principle for his work on fermentation the law that :

"Nothing is created, either in the operations of art, or in those of nature, and it may be set out as a principle that, in every operation, there is an equal quantity of matter before and after the operation; that the quality and the quantity of the principles is the same, and there are only changes, only modifications."

"On this principle is based the whole art of making experiments in chemistry : in all of them one must suppose a true equality or equation between the principles of the body which one examines and those which one obtains from them by analysis. Thus, since grape-juice gives carbonic acid gas and alcohol, I can say that *grape-juice = carbonic acid + alcohol*" (*Works*, I. 101).

Organic analyses of Gay-Lussac and Thenard (1810).—The foundations of organic analysis were laid by Lavoisier in the two papers that have already been quoted (pp. 145–147); but it was not until many years later that simple and accurate methods became generally available. Some of the earlier workers, including Berthollet, relied upon decomposing the organic compounds by heat into charcoal, which could be weighed, and gaseous products which could be analysed in the eudiometer.

In 1810 a general method of analysis was worked out by Gay-Lussac and Thenard (*Physico-Chemical Researches*, 1811, II. 265–350) and applied to four substances containing nitrogen and fifteen substances free from nitrogen. The substance was mixed with a known weight of potassium chlorate, made into pellets and burnt by dropping into a hot tube (Fig. 49). The gases produced by burning the pellets (oxygen, carbonic anhydride, and nitrogen, if present) were collected and analysed. From the volume of carbonic anhydride the weight of *carbon* in the substance could be calculated; a similar calculation gave the weight of *nitrogen*. Blank experiments showed what volume of oxygen was set free by igniting the chlorate alone. In several cases the deficiency of oxygen was exactly equal to that due to the formation of carbonic anhydride; any part of the weight of the substance not accounted for after adding together the carbon and nitrogen, together with other easily recognised elements, such as chlorine, phosphorus and the metals, was then regarded as *water*. A greater or less deficiency of oxygen indicated the presence of an excess of *hydrogen* or of *oxygen*, above the proportions required to produce water.

The analyses of Gay-Lussac and Thenard revealed the remarkable fact that six of the substances analysed (sugar, gum, starch, milk-sugar, oak-wood, and beech-wood) contained carbon united with hydrogen and oxygen in just the proportions in which they are required to form water. Such compounds are now known as CARBOHYDRATES. These six

substances were all *neutral.* Five *acids* (mucic, oxalic, tartaric, citric, acetic) contained an excess of oxygen. Four *resinous* and *oily* substances (resin, copal, wax, olive-oil) contained an excess of hydrogen.

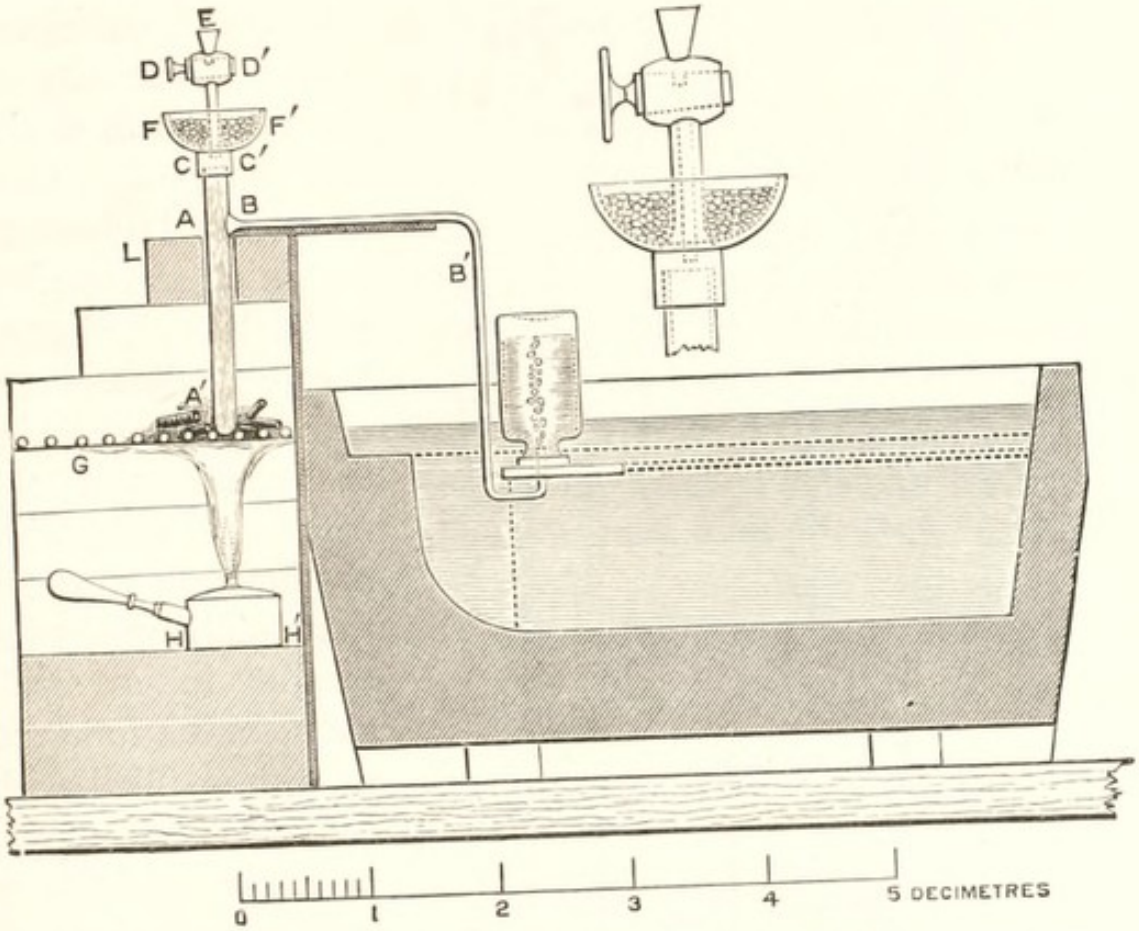


FIG. 49.—GAY-LUSSAC AND THENARD'S APPARATUS FOR THE COMBUSTION OF ORGANIC COMPOUNDS.

The tube AA', of hard glass, 20 cm. long and 8 mm. wide, carried a side-tube BB', leading into a trough of mercury. A copper cap CC', cemented to the top of the tube AA', carried a glass tap DD' (shown on a larger scale as an inset) and a cup of broken ice FF', to prevent the grease on the tap from melting down into the hot tube. The tap DD' was not pierced in the usual way, but had a small cavity, in which a pellet could be inserted, and dropped into the hot tube without opening it to the air. Several pellets were burnt to displace the air from the apparatus, and the gases set free by burning a known weight of the dry pellets were then collected, measured and analysed.

Berzelius (1815) assigns formulæ to organic compounds.—In 1815 Berzelius described a new series of organic analyses which he carried out "in order to determine how far the laws which I had established in inorganic nature could be

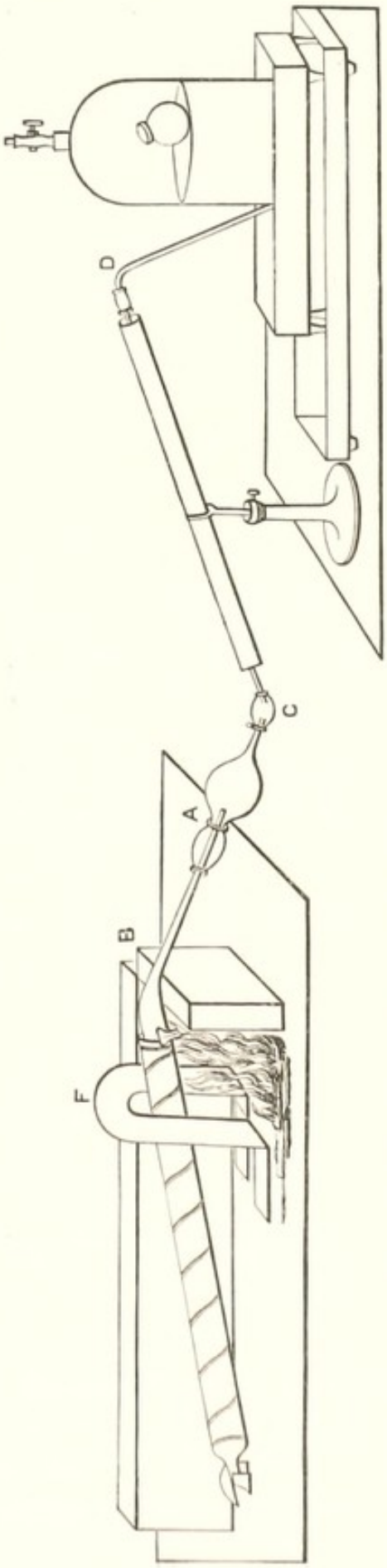


FIG. 50.—BERZELIUS'S APPARATUS FOR THE COMBUSTION OF ORGANIC COMPOUNDS.

The combustion-tube, wrapped in tin-foil, rested upon a brick at *B*, and was heated progressively by moving the iron screen *F* from right to left. The receiver, in which the water was condensed, was connected to the combustion-tube at *A* and to the drying tube at *C*, by means of home-made rubber tubes tied with silk. The gases from the drying tube were led, through another flexible joint at *D*, into a trough where they were collected over mercury. The bulb, in which the carbonic anhydride was absorbed slowly by solid potash, is seen floating on the mercury.

applied to organic bodies" (*Ann. de Chimie*, 1815, **94**, 1–28, 170–190, 296–323, **95**, 51–90).

These analyses were made by a modified form of the method of Gay-Lussac and Thenard, in which the carbon and the hydrogen were determined directly, by *weighing* the water and the carbonic anhydride produced by combustion. The water was caught in a small glass bulb, followed by a tube filled with calcium chloride; the carbonic anhydride was driven forward into a bell-jar filled with mercury, where it was absorbed in a small bulb containing solid potash (Fig. 50). The substance was burnt by mixing it with potassium chlorate, copiously diluted with common salt to restrain the violence of the combus-

tion; potassium chlorate, not mixed with the substance, was placed at both ends of the combustion-tube, in order to provide an ample supply of oxygen (1) to complete the burning, (2) to drive the products of combustion forward into the absorption-apparatus. Extreme care was needed to dry perfectly all the materials with which the combustion-tube was charged.

Berzelius analysed nine organic acids in the form of their lead salts, and four carbohydrates, thus covering much the same ground as Gay-Lussac and Thenard. But, unlike them, he was able to check his analyses by the requirements of the newly-established atomic theory and to express the composition of his compounds by means of formulæ. Berzelius's formulæ for the acids are usually those of the lead salt minus lead oxide, or of the acid minus water; apart from this, they agree very well with those adopted to-day, the few differences that occur being due to an over-estimation of the hydrogen. This is shown by the following comparison :

	Berzelius's formulæ.	Modern formulæ.
Citric acid	CHO	$C_6H_8O_7 - H_2O = C_6H_6O_6 = [CHO]_6$
Tartaric acid	$C_4H_5O_5$	$C_4H_6O_6 - H_2O = C_4H_4O_5$
Oxalic acid	$C_{12}HO_{18}$	$C_2H_2O_4 - H_2O = C_2O_3$
Succinic acid	$C_4H_4O_3$	$C_4H_6O_4 - H_2O = C_4H_4O_3$
Acetic acid	$C_4H_6O_3$	$2C_2H_4O_2 - H_2O = C_4H_6O_3$
Gallic acid	$C_6H_6O_3$	$C_6H_6O_3$ (pyrogallol)
Mucic acid	$C_6H_{10}O_8$	$C_6H_{10}O_8$
Benzoic acid	C_5H_3O	$C_7H_6O_2$
Tannin	$C_6H_6O_4$	
Sugar	$C_{12}H_{21}O_{10}$	$C_{12}H_{22}O_{11} - H_2O = C_{12}H_{20}O_{10}$
Milk-sugar	CH_2O	$C_{12}H_{22}O_{11}$, $H_2O = [CH_2O]_{12}$
Gum	$C_{13}H_{24}O_{12}$	
Starch	$C_7H_{13}O_6$	$C_6H_{10}O_5$

Combustion by means of metallic oxides.—It should be noticed that metallic oxides were used for the quantitative combustion of organic substances by Lavoisier, who used red lead (p. 146), as well as by Berzelius, who used the brown peroxide in his earlier analyses. The oxides of leads were discarded in favour of potassium chlorate, because they

could not easily be freed from moisture and from carbonic anhydride. The black oxide of copper was first used by Gay-Lussac, in 1815, for the combustion of mercuric cyanide (*Ann. de Chimie*, 1815, **95**, 184), and in the hands of Liebig (*Pogg. Ann. der Physik*, 1831, **21**, 1–43) soon became the standard oxidising agent in organic analysis (see Fig. 51).

B. The Structure of Salts.

Lavoisier's oxygen-theory of the structure of salts.—The idea that compounds possess a definite structure originated from observations on the interactions of acids and bases to form salts. Mayow, in considering this action, concluded (A.C.R. XVII. 160) that "although [acids] and alkalis pass into a neutral substance when they meet, yet they do not, as is generally supposed, entirely destroy each other." Each grain of salt must then contain, intimately united within it, a certain portion of acid and a certain portion of alkali. Lavoisier elaborated this idea by regarding the acid and base as themselves compounded of a non-metal or a metal united with oxygen, so that the structure of the salt might be represented as:

$$\text{SALT} = \text{ACID} + \text{BASE}$$
$$= \{\text{NON-METAL} + \text{OXYGEN}\} + \{\text{METAL} + \text{OXYGEN}\}$$

"The acidifiable substances, when combined with oxygen and converted into acids, acquire a great tendency to combination; they become capable of uniting with earthy and metallic substances, and it is by this union that neutral salts are produced" (*Treatise*, 1789; *Works*, I. 115).

Berzelius's dualistic theory (1819).—Lavoisier's theory broke down when it was discovered that acids (such as muriatic acid) and bases (such as ammonia) existed, in which no oxygen was present, but its essential features were revived by Berzelius in his "Theory of Chemical Propor-

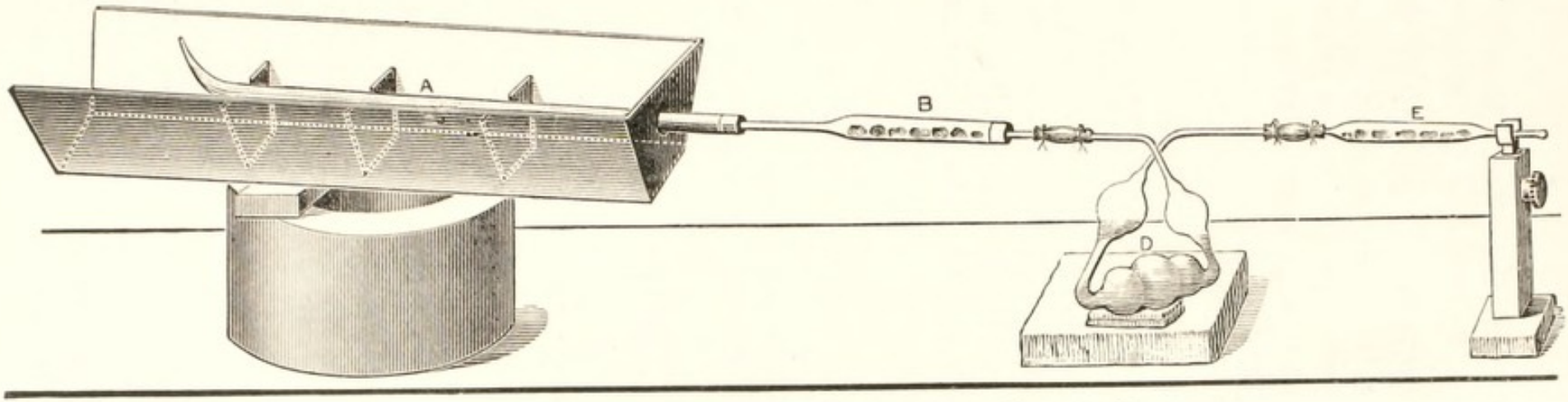


FIG. 51.—LIEBIG'S APPARATUS FOR THE COMBUSTION OF ORGANIC COMPOUNDS.

The substance was mixed with copper oxide and burnt in the combustion-tube *A*. Moisture was collected with the help of fused calcium chloride in the drying-tube *B*. Carbonic anhydride was absorbed in the "potash bulbs" *D*, protected when necessary by a drying-tube *E*, to prevent loss of moisture. At the end of the experiment, the tip of the combustion-tube was broken and a little air drawn through, in order to carry forward the last traces of moisture and carbonic anhydride.

In modern practice Liebig's method has been modified in the following points:

(1) the substance is contained in a platinum boat inserted between two columns of copper oxide, and is burnt in a slow current of purified air or oxygen.

(2) the combustion-tube is heated by a series of gas-burners arranged to allow of very easy regulation of temperature.

(3) the moisture is collected in a U-tube of calcium chloride, provided with a small bulb in which most of the water is condensed.

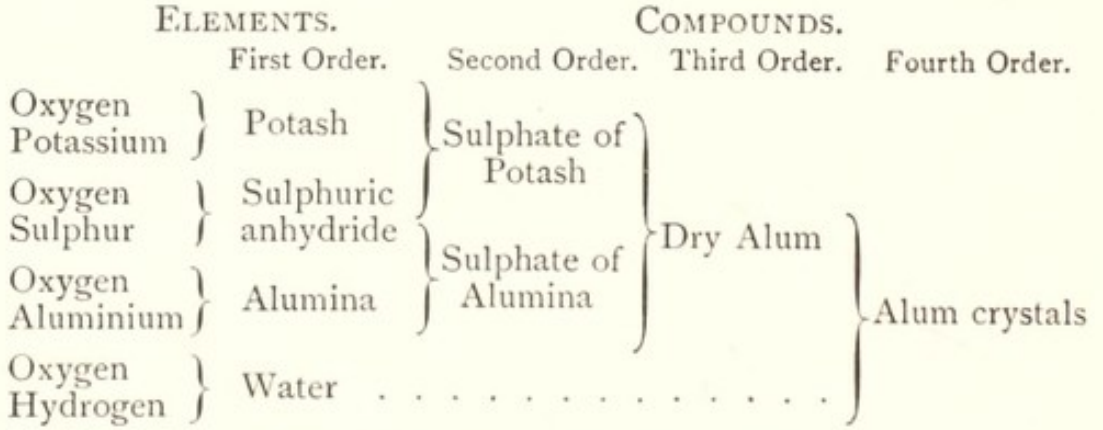
(4) the two parts of the "potash bulbs" are made into one appartus; improved forms of absorption apparatus have also been devised.

Most of these improvements may be seen in a description given by C. Glaser in 1869 (Liebig's *Ann. Chem. Pharm.*, 1870, **7**, Suppl., 213–217) of the apparatus used in Kekulé's laboratory shortly after the introduction in 1866 of Bunsen's well-known burner (*Ann. Chem. Pharm.*, 1866, **138**, 257).

tions" 1819. Speaking in terms of Dalton's Atomic Theory he suggests that

"When atoms of two different substances combine, a compound atom is produced, in which we suppose the force producing combination to be infinitely stronger than all the conditions which might tend to separate the united atoms. This compound atom must be considered to be as indivisible by mechanical means as an elementary atom."

"These compound atoms combine with other compound atoms, giving rise to atoms still more compound in their nature. When these in their turn combine with others, they produce atoms of still more complex composition. These different atoms must be distinguished. We will divide them into atoms of the first, second, third order, etc." (*Chemical Proportions*, 1819, p. 26). As an example he quotes the case of alum :



The chief feature of Berzelius's theory of the structure of salts is the combination of elements and compounds in pairs; it is therefore frequently described as the DUALISTIC THEORY. Although it was applied in the first place only to the combination of elements with oxygen, and of basic with acidic oxides, it was easily extended to include the combination of metals with chlorine, even when the chlorides were proved to be binary compounds, analogous with the oxides, instead of ternary compounds analogous with the sulphates. Further, in his "Memoir on the Sulpho-salts," (*Ann. Chim. Phys.* 1826, **32**, 60) Berzelius had no difficulty in showing that these salts, formed by the combination of

two sulphides, were strictly analogous with the oxy-salts formed by the combination of two oxides.

Berzelius's electro-chemical theory (1819).—Berzelius's theory included one other unifying feature to which attention must be directed. Berzelius and Hisinger (p. 273) had been the first to show that the electric battery could produce, not only a decomposition of water, but also a resolution of the dissolved salts into acid and base. This observation was soon followed by Davy's discovery of the decomposition of the alkalis and earths into metal and oxygen when the same agency was applied to these substances in the absence of water. As the electric current was thus proved to be the most powerful agency for resolving chemical compounds, Berzelius concluded that chemical affinity was electrical in character.

"We are now confident that substances on the point of combining, exhibit opposite electric charges, increasing in strength as they approach the temperature at which combination takes place, until, at the moment of union, the charges disappear with a rise of temperature which is often so great that fire blazes out. On the other hand, we are equally confident that compound substances, exposed in a suitable form to the action of the electric fluid produced by the discharge of the pile, are separated and recover their original chemical and electrical properties, whilst the charges acting on them disappear."

"In the actual state of our knowledge, the most probable explanation of combustion and of the ignition resulting therefrom, is then: *that in all chemical combination there is a neutralisation of opposite electric charges, and that this neutralisation produces fire in the same way as in the discharge of a Leyden jar, an electric pile or lightning, although not accompanied, in these last phenomena, by a chemical combination*" (*Chemical Proportions*, 1819, 72–73).

Berzelius's ELECTRO-CHEMICAL THEORY, as thus enunciated, accounted not only for chemical combination, but also for the liberation of light and heat, thus destroying the necessity

which Lavoisier had felt for postulating the existence of "matter of fire" and "matter of heat" as imponderable constituents of substances, set free from them when they combined together. In this attempt at unification Berzelius anticipated, not only the science of Thermo-chemistry, which attempts to measure the energy of chemical combination in units of heat, but also the later and more accurate method of expressing energy of combination in terms of electro-motive forces.

C. The Theory of Compound Radicals.

Structure of organic compounds. Presence of compound radicals.—Berzelius's dualistic electro-chemical theory was based upon his observations of the decomposition of mineral substances by the electric current, and was applied primarily to salts, acids and bases, which yielded readily to this treatment. But it threw very little light upon the structure of organic substances, such as sugar, alcohol, or olive-oil, which would not conduct the current and were not decomposed by it. Lavoisier, who regarded the mineral acids as binary compounds of oxygen with a simple elementary radical such as carbon, sulphur or phosphorus, had been obliged to recognise that the organic acids contained oxygen in combination with both carbon and hydrogen, and sometimes also with nitrogen and phosphorus (*Works*, I. 147). These compound radicals could not be resolved by the dualistic theory and were frankly recognised by Berzelius as demanding exceptional treatment.

"[Compounds] of the first order are composed of simple elementary atoms; they are of two kinds, *organic* and *inorganic*. The latter never contain more than two atoms; the latter always contains at least three" (*Chemical Proportions*, 1819, p. 26).

"In inorganic nature all oxidised bodies contain a *simple radical*, while all organic substances are *oxides of compound*

radicals. The radicals of vegetable substances consist generally of carbon and hydrogen, and those of animal substances of carbon, hydrogen and nitrogen" (*Textbook*, 1817, I, 544).

Gay-Lussac on the cyanogen radical (1815).—An excellent example of a compound radical of organic origin was available in the case of prussic acid, which Gay-Lussac had described in 1815 as a compound of hydrogen with the compound radical CYANOGEN (p. 245). The analogy between the compound organic radical cyanogen and the simple inorganic radical chlorine was remarkable. It could combine, not only with hydrogen, but with chlorine and with metals such as potassium, silver and mercury; it could also exist alone in the form of a gas, which was evidently the analogue of chlorine gas. The similarity of the two series of compounds may be shown by writing their formulæ, as is often done with the symbol Cy (Berzelius, *Jahresbericht*, 1839, **18**, 120), to represent the compound-radical CN. Thus we have

Cyanogen, CN or Cy.		Chlorine, Cl.	
Cyanogen gas	C_2N_2 or Cy_2	Chlorine gas . .	Cl_2
Cyanogen chloride	ClCN or ClCy		
Prussic acid . .	HCN or HCy	Muriatic acid . .	HCl
Potassium cyanide	KCN or KCy	Potassium chloride	KCl
Silver cyanide .	AgCN or AgCy	Silver chloride .	AgCl
Mercuric cyanide .	HgC_2N_2 or $HgCy_2$	Mercuric chloride .	$HgCl_2$

Wöhler and Liebig (1832) on the benzoyl radical.—The importance of the theory of radicals became evident when **Wöhler**[1] and **Liebig**, in 1832, published their "Researches on the Radical of Benzoic Acid" (Liebig's *Ann. der Pharm.*, 1832, **3**, 249–282). In these researches they showed that oil of bitter almonds could be converted into a

[1] Wöhler was already well-known for his preparation of aluminium (*Pogg. Ann. der Physik*, 1827, **11**, 146–161) and for his synthesis of urea, a typical animal product, from inorganic materials (*Pogg. Ann. der Physik*, 1828, **12**, 253–256); the urea was obtained in attempting to prepare ammonium cyanate, and is formed as a product of "isomeric change," $(NH_4)CNO \longrightarrow CO(NH_2)_2$.

series of compounds, all of which might be regarded as derived from a compound radical, which they proposed to call BENZOYL (*loc. cit.* p. 279). This radical combined with hydrogen to form oil of bitter almonds, with oxygen and hydrogen to form benzoic acid, with chlorine, bromine, iodine, sulphur and cyanogen to form benzoyl chloride, bromide, iodide, sulphide and cyanide. These compounds may by represented by the following formulæ :[1]

BENZOYL = C_7H_5O.

Oil of bitter almonds = benzoyl hydride . .	= $C_7H_5O{\cdot}H$
Benzoic acid = benzoyl hydroxide . .	= $C_7H_5O{\cdot}OH$
Benzoyl chloride	= $C_7H_5O{\cdot}Cl$
Benzoyl cyanide	= $C_7H_5O{\cdot}CN$

Wöhler and Liebig also prepared :—

Benzamide	= $C_7H_5O{\cdot}NH_2$
Ethyl benzoate	= $C_7H_5O{\cdot}OC_2H_5$
Benzoin, a solid having the same composition as oil of bitter almonds, but now regarded as a polymer $(C_7H_5OH)_2$	= $C_{14}H_{12}O_2$

Berzelius was delighted with the discovery made by Wöhler and Liebig. The compound radicles which had been studied hitherto had been binary compounds of two elements, *e.g.*, cyanogen, CN, ammonium, NH_4; the benzoyl group was the first example of a compound radical containing three elements, which nevertheless showed very many of the properties of a simple substance. In a well-known letter to Wöhler and Liebig, dated from Stockholm, Sept. 2, 1832, and published at the conclusion of their paper (Liebig's *Ann. der Pharm.*, 1832, **3**, 282–287), Berzelius writes :

"The facts that you have ascertained suggest so many considerations, that they may well be regarded as the beginning of a new day in vegetable chemistry. I would therefore propose, to call the first example of a compound radical containing more than two substances *Proin* (from πρωί, the

[1] Wöhler and Liebig doubled these formulæ and wrote benzoyl = $C_{14}H_{10}O_2$; chlorobenzoyl (benzoyl chloride) = $C_{14}H_{10}O_2Cl_2$, etc.

beginning of the day. . .) or *Orthrin* (from ὀρθρὸς, dawn of the morning)" (*loc. cit.* p. 285).

As in the case of the ammonium radical, which he had represented by the symbol **Am**, Berzelius proposed to represent the benzoyl radical by a single symbol, Bz, thus

Oil of bitter almonds = BzH
Benzoyl chloride = BzCl, etc.

He also proposed to describe by the name AMIDE the compound radical NH_2, which is formed by removing an atom of hydrogen from ammonia as in

$C_7H_5O{\cdot}NH_2$ = Benzamide,
$K{\cdot}NH_2$ = Potassamide,
$Na{\cdot}NH_2$ = Sodamide.

The structure of alcohol and ether. Dumas and Boullay (1827) on the aetherin radical.—The action of sulphuric acid on alcohol had long been known to give rise on one hand to olefiant gas (Chap. VIII, p. 155), and on the other hand to a volatile, inflammable liquid, which was generally described as "sulphuric ether," but is now known simply as "ether." Gay-Lussac in 1815 (*Ann. de Chimie*, 1815, **95**, 311–318), by measuring the vapour-densities of alcohol and of ether, showed that their composition might be represented as follows:

Alcohol 1 *vol.*	=	Olefiant Gas 1 *vol.*	+	Water-vapour 1 *vol.*
Ether 1 *vol.*	=	Olefiant Gas 2 *vols.*	+	Water-vapour 1 *vol.*

In an important memoir "On the Compound Ethers"[1] (*Ann. Chim. Phys.*, 1828, **37**, 15–53), **Dumas** and **Boullay** showed further that the ethereal substances formed by the action of acids on alcohol could all be represented as com-

[1] Read at the Paris Academy of Sciences on Dec. 24, 1827, and published in the *Mémoires de l'Institut*, 1838 (!), **15**, 457–494.

pounds of the acids with olefiant gas formed by the removal of water from the alcohol. They concluded:

"That olefiant gas plays the part of a very powerful alkali, endowed with a capacity of saturation equal to that of ammonia, of which it would probably show most of the reactions, if it were, like ammonia, soluble in water.

2. That alcohol and ether are hydrates of olefiant gas.

3. That the compound ethers are salts of olefiant gas, etc." (*loc. cit.* p. 52).

The analogy of composition between the compound ethers and the salts of ammonia was shown in a table, a part of which (using modern atomic weights and formulæ) would read as follows:

Compound Ethers.[1]		*Ammonium Salts.*	
Alcohol,	C_2H_4,H_2O	[3] Ammonium hydroxide,	NH_3,H_2O
Sulphuric ether,	$2C_2H_4,H_2O$	[3] Ammonium oxide,	$2NH_3,H_2O$
Hydrochloric ether,	C_2H_4,HCl	Ammonium chloride,	NH_3,HCl
Hydriodic ether,	C_2H_4,HI	Ammonium iodide,	NH_3,HI
Nitric ether,	C_2H_4,HNO_2	Ammonium nitrite,	NH_3,HNO_2
Acetic ether,	$C_2H_4,C_2H_4O_2$	Ammonium acetate,	$NH_3,C_2H_4O_2$
Sulphovinic acid [2]	C_2H_4,H_2SO_4	Ammonium bisulphate,	NH_3,H_2SO_4

Liebig (1834) on the ethyl radical.—Berzelius in discussing Wöhler and Liebig's paper "On the Radical of Benzoic Acid," adopted the view of Dumas and Boullay in reference to the composition of alcohol and the ethers. He suggested (*Ann. der Pharm.*, 1832, **3**, 286) that the group of atoms present in olefiant gas should be described as AETHERIN and represented by the symbol Ae. Liebig himself ("On the Constitution of Ether and its Compounds," *Ann. der Pharm.*, 1834, **9**, 1–39) adopted a different view.

[1] The compound ethers were named after the acids used in preparing them but "sulphuric, phosphoric, arsenic ethers . . . are identical amongst themselves" (*loc. cit.* p. 15), being merely alcohol deprived of water.

[2] Examined just before by Dumas and Boullay ("Memoir on the Formation of Sulphuric Ether," *Ann. Chim. Phys.*, 1827, **36**, 294–310) as the first product of the action of sulphuric acid on alcohol.

[3] Isolated in 1909, see p. 287.

Just as Ampère in 1816 had regarded the salts of ammonia as formed by the union of "ammonium" (ammonia and hydrogen) with chlorine, iodine, sulphur, etc., so Liebig regarded the compound ethers as formed by the union of ETHYL (aetherin and hydrogen) with chlorine, bromine, iodine, etc. If aetherin be represented by the modern formula, C_2H_4, of olefiant gas, then ethyl must be represented as C_2H_5, thus :

$$\begin{aligned} \text{ammonium} &= NH_3 + H = NH_4 = Am \\ \text{ethyl} &= C_2H_4 + H = C_2H_5 = Et \end{aligned}$$

On this view

alcohol = ethyl hydroxide = $(C_2H_5)OH$ or EtOH
ether = ethyl oxide = $(C_2H_5)_2O$ or Et_2O
muriatic ether = ethyl chloride = $(C_2H_5)Cl$ or EtCl

just as, according to Ampère's view,
sal-ammoniac = ammonium chloride = $(NH_4)Cl$ or AmCl
Actually, Berzelius and Liebig doubled the formulæ of these radicals and wrote

aetherin = C_4H_8 = Ae
ethyl = C_4H_{10} = E
ether = $C_4H_{10}O$ = Ae + H_2O, or EO
alcohol = $C_4H_{12}O_2$ = Ae + $2H_2O$ or EO + H_2O
ethyl chloride = $C_4H_{10}Cl_2$ = Ae + H_2Cl_2 or E + Cl_2.

It will be seen that in doing this they broke away finally from the idea that the relative sizes of the molecules could be deduced from measurements of vapour density; thus, alcohol, with a lighter vapour than ether, was now represented as a compound of ether and water, and all their derivatives were regarded as containing at least four atoms of carbon.

Dumas and Péligot (1834) discover a new alcohol in spirit of wood. Methylene and methyl as radicals.— In 1834 Dumas and Péligot read to the Academy a paper "On a New Alcohol and on the different Ethereal Compounds derived from it" (*Mem. Inst.*, 1838, **15**, 557–632).

They showed that spirit of wood [1] contained a compound in which they "recognised all the characters of a true alcohol." In order to describe the new alcohol and its derivatives they proposed to give the name METHYLENE (from "μέθυ, wine, and ὕλη, wood; that is to say, wine or spirituous liquor of wood") to the radical which it contained (*loc. cit.* p. 561).

They showed that

"1. Spirit of wood corresponds with alcohol.

2. By losing half its water, it forms a gaseous ether.

3. Its radical unites volume by volume with the hydracids to form neutral anhydrous ethers, etc." (*loc. cit.* p. 620).

They regarded the radical methylene, which they were not able to isolate, as a hydrocarbon having the same composition as ethylene, but containing only half as many atoms; in just the same way, ethylene in its turn had the same composition as the hydrocarbon (butylene) which Faraday had isolated from oil-gas, but contained only half as many atoms. Using modern formulæ [2] the three compounds are

Methylene (not known)	CH_2
Ethylene (olefiant gas)	C_2H_4
Butylene (Faraday's hydrocarbon)	C_4H_8

All the ethers derived from spirit of wood could be considered as formed by the addition of water or of acids to methylene, but it was pointed out (*loc. cit.* p. 625) that they might also be regarded as oxides, chlorides, etc., of a hypothetical radical, analogous with ethyl, to which the name METHYL is now given. Thus, again using modern formulæ,[2]

[1] Discovered by Philip Taylor in 1812, and described by him ten years later in a letter to the editors of the *Philosophical Magazine*, 1822, 60, 315–317.

[2] Dumas formulated the three hydrocarbons as CH, C_2H_2, C_4H_4. But these were multiplied by four in their compounds; methylene hydrate (methyl ether, C_2H_6O) was C_4H_4,H_2O or C_4H_6O (C=6); spirit of wood (methyl alcohol, CH_4O) was methylene bihydrate, $C_4H_4,2H_2O$ or $C_4H_8O_2$; ordinary alcohol (C_2H_6O) had now grown to $C_8H_{12}O_2$, Dumas having followed Berzelius and Liebig in regarding it as a hydrate of ether.

spirit of wood, CH_4O
= methylene hydrate, CH_2,H_2O,
or methyl hydroxide, $CH_3{\cdot}OH$;
its gaseous ether, C_2H_6O
= methylene hydrate, $2CH_2,H_2O$,
or methyl oxide, $(CH_3)_2O$;
its gaseous chloride, CH_3Cl
= methylene hydrochloride, CH_2,HCl,
or methyl chloride, CH_3Cl.

Dumas and Liebig united.—The discovery of METHYL ALCOHOL, CH_4O, and its derivatives greatly strengthened the theory of radicals, since it showed that when applied to a new group of ethers "in a series of very complicated phenomena, one could predict everything, explain everything and submit everything to calculation" (*loc. cit.* p. 621). It had further become evident that the difference between Dumas and Boullay's "ethylene" or "aetherin" and Liebig's "ethyl" theory of the ethers was only of secondary importance; both radicals might, in fact, be regarded as hydrides of the still simpler radical, C_2H_3, which Liebig called "acetyl."[1] In just the same way ammonia and ammonium could be regarded as two hydrides of Berzelius's "amide" radical, NH_2. Thus, in modern formulæ

Amide	$=NH_2=Ad$	"Acetyl"[1]	$=C_2H_3=Ac$
Ammonia	$=NH_3=AdH$	Aetherin (ethylene)	$=C_2H_4=AcH$
Ammonium	$=NH_4=AdH_2$	Ethyl	$=C_2H_5=AcH_2$

(Liebig, *Ann. der Pharm.*, 1839, **30**, 139).

Having thus settled their main points of difference Dumas and Liebig decided in 1837 to combine their forces in a great campaign to establish a "natural classification of organic compounds" by a detailed study of their component radicals. A joint manifesto in reference to their programme was issued in the form of a "Note on the present position of organic chemistry" (*Comptes rendus*, 1837, **5**, 567–572),

[1] The word "acetyl" is now used to describe the radical C_2H_3O (see page 431).

a joint report on the subject was to be prepared in response to a request from the Liverpool meeting of the British Association, and from 1838 to 1841 Dumas and Graham appeared as collaborators with Liebig in the publication of his *Annalen*. This happy collaboration was to be made effective by training a new generation of chemists; it was therefore no mere coincidence that resulted, ten years later, in the association together of Auguste **Laurent** (1807–1853, pupil of Dumas) and Charles **Gerhardt** (1816–1856, pupil of Liebig) in another campaign to establish a rational system of atomic weights and formulæ in chemistry; only the early death of these two workers prevented them from seeing the triumph of their ideas through the masterly exposition of Cannizzaro.

D. The Theory of Substitution.

Dumas (1834) on substitution or metalepsy.—In the second part of his Researches in Organic Chemistry, "On the Action of Chlorine on Alcohol. The Law of Substitutions or Metalepsy," read before the Academy of Sciences at Paris, on Jan. 13, 1834, Dumas directed attention to the fact that

"Chlorine possesses the remarkable power of seizing hold of the hydrogen of certain substances, and replacing it atom by atom. This law of nature, this law or theory of substitutions, has seemed to me to be worthy of a special name. I propose to call it *metalepsy*, from μετάληψις, which expresses well enough that the body on which one acts, has taken one element in the place of another, chlorine in place of hydrogen, for example" (*Mem. Inst.*, 1838,[1] **15**, 548).

The laws of substitution were set out in the following year in his Treatise on Chemistry as follows:

"1. When a hydrogenated compound is submitted to the dehydrogenating action of chlorine, of bromine, of

[1] This passage does not appear in the paper as published four years earlier in the *Ann. Chim. Phys.*, 1834, **56**, 113–154.

iodine, of oxygen, etc., for each atom of hydrogen which it loses, it gains an atom of chlorine, of bromine or of iodine, or half an atom of oxygen;

2. When the hydrogenated compound contains oxygen, the same rule applies without modification;

3. When the hydrogenated compound contains water, this loses its hydrogen without replacement, and hereafter, if a further quantity of hydrogen is removed, it is replaced as in the preceding cases" (*Treatise on Chemistry*, 1835, V. 99).

The following examples of simple substitution of chlorine for hydrogen are given in his Memoir (*loc. cit.* pp. 549–556) and quoted again in his Treatise (*loc. cit.* pp. 99–102).

(*a*) Gay-Lussac, in 1815, (*Ann. de Chimie*, 1815, **95**, 210) had shown that hydrogen cyanide, in passing into cyanogen chloride "loses one volume of hydrogen and gains exactly one volume of chlorine."

$$HCN + Cl_2 = ClCN + HCl.$$

(*b*) Wöhler and Liebig, in 1832 (see above p. 400), had shown that oil of bitter almonds "treated with chlorine, loses two volumes of hydrogen and gains precisely two volumes of chlorine."

$$C_7H_6O + Cl_2 = C_7H_5OCl + HCl.^1$$

(*c*) Faraday, in his experiments on the chlorination of Dutch liquid (ethylene chloride) (*Phil. Trans.*, 1821, 47–74), had found that "chlorine, acting on it in sunlight, produces a chloride of carbon, absolutely free from hydrogen." The composition of this solid perchloride of carbon can be predicted by the law of substitution and agrees exactly with Faraday's analysis.

$$C_2H_4Cl_2 + 4Cl_2 = C_2Cl_6 + 4HCl.$$

Removal of hydrogen without replacement.—The reservation in the third law of substitution was introduced to

[1] These formulæ were doubled: hence the "two volumes" of hydrogen and chlorine.

account for the fact that hydrogen was sometimes removed (wholly or in part) without replacement. Thus, in the conversion of alcohol into chloral by the action of bleaching powder it was seen that "the ten volumes of hydrogen, removed from the alcohol, have been replaced by only six volumes of chlorine," or, in terms of modern formulæ, five atoms of hydrogen have been replaced by only three atoms of chlorine.

$$C_2H_6O + 4Cl_2 = C_2HCl_3O + 5HCl.$$

Dumas explained this on the view that alcohol was composed of ethylene and water; the ethylene obeyed the ordinary law of substitution, whilst the water (as Berthollet had observed in 1785) gave oxygen and hydrogen chloride, thus:

$$\begin{array}{rcl} C_2H_4 + 3Cl_2 & = & C_2HCl_3 + 3HCl \\ H_2O + Cl_2 & = & O \quad\quad + 2HCl \\ \hline C_2H_6O + 4Cl_2 & = & C_2HCl_3O + 5HCl \end{array}$$

This removal of hydrogen without replacement was regarded as a test for the presence of water, as distinct from other forms of hydrogen, in the molecule. Thus, oxalic acid, which loses hydrogen on oxidation to carbonic acid,

$$H_2C_2O_4 - H_2 = 2CO_2,$$

was regarded as containing the whole of its hydrogen in the form of water, and was written as a hydrate, C_2O_3,H_2O.[1]

Berzelius (1838-1843) objects to the presence of oxygen and chlorine in organic radicals and to the whole theory of the substitution of oxygen and chlorine for hydrogen. — Berzelius, who had welcomed Wöhler and Liebig's discovery of the benzoyl radical as the dawn of a new day in organic chemistry, soon repented of his rashness in admitting oxygen as a constituent of an electro-positive organic radical. In the particular case of oil of bitter

[1] C_4O_3,H_2O in the original (C=6).

almonds (benzaldehyde) he proposed to remedy this error by regarding the compound, not as benzoyl hydride,

$$(C_7H_5O)H,$$

but as an oxide, $(C_7H_6)O$, of a radical PICRAMYL = Pk = C_7H_6,[1] from πικρός, bitter, ἀμυγδάλη, almond (*Jahresbericht*, 1843, **22**, 328). This policy of robbing the radicals of their oxygen had already been adopted in 1830 by Hermann, who had suggested that

"The vegetable acids all share the characteristic that they are compounds of oxygen with hydrocarbons. They are thus all to be regarded as different stages of oxidation of hydrocarbons. Thus vegetable acids = $CH + xO$" (Poggendorf's *Annalen der Physik*, 1830, **18**, 396).

This view had been favourably received by Berzelius (*Jahresbericht*, 1832, **11**, 210) and was afterwards adopted by Liebig (p. 405) when he gave to the radical C_2H_3 the name "acetyl," thus implying that the radical of acetic acid was a simple hydrocarbon.

But, if Berzelius thus objected to the presence of oxygen and chlorine in the organic radicals, he had a still greater objection to the idea that these elements could creep in by a process of substitution for hydrogen.

"An element so eminently electro-negative as chlorine, can never enter an organic radical: this idea is contrary to the first principles of chemistry; its electro-negative nature and its powerful affinities would prevent it from entering except as an element in a combination peculiar to itself" (*Comptes rendus*, 1838, **6**, 633; *Ann. Chim. Phys.*, 1838, **67**, 309).

In order to maintain this opinion, Berzelius was obliged, in every actual case of substitution, to extradite the chlorine from the electro-positive to the electro-negative part of the molecule and to invent some new method of constructing the radical. One example will suffice to illustrate his

[1] $C_{14}H_{12}$, in the original.

method. Malaguti (*Comptes rendus*, 1837, **5**, 334) had succeeded in introducing four atoms of chlorine into ordinary ether.

$$C_4H_{10}O + 4Cl_2 = C_4H_6Cl_4O + 4HCl.$$

The simplest explanation was to suppose that chlorine had entered the ethylene or ethyl radicals; but this would imply the co-existence in the electro-positive radical of hydrogen and chlorine. Berzelius preferred, therefore, to reconstruct the whole molecule and to write it thus:

$$C_4H_6Cl_4O = C_2H_6O + C_2Cl_4;$$

the molecule then no longer contained any trace either of ethyl or of ethylene, but was now composed of methyl oxide and carbon chloride (*Comptes rendus*, 1838, **6**, 634; *Ann. Chim. Phys.*, 1838, **67**, 310).

Chlorine, in organic compounds, "takes the place" and "plays the part" of hydrogen.—Dumas at first accepted Berzelius's view that the chlorination of an organic compound might involve a reconstruction of the radicals which it contained and in replying to Berzelius' letter emphasised the fact that the theory of substitution "is an empirical rule" (*Comptes rendus*, 1838, **6**, 702).

"The theory of substitutions expresses then a simple relation between the hydrogen that goes out and the chlorine that enters. In the majority of cases this relation is one of volume for volume. In announcing it, I believe that I rendered a real service to science. Indeed, before it had been signalised, there existed hardly a single exact analysis of a compound formed by the action of chlorine on an organic substance. Since it has fixed the attention of chemists on this kind of reactions, the facts have multiplied, the analyses have received a precision of which the importance has been recognised" (*Comptes rendus*, 1838, **6**, 699).

It was not long, however, before the amazing complexities of Berzelius's formulæ, and the extreme simplicity of the theory of direct replacement, compelled him to adopt the

view of his colleague Laurent that (as he expressed it some years later)

"In the phenomena of substitution the type is conserved, that is to say that not only does the chlorine *take the place* of the hydrogen, but that it *plays the same part*" (Dumas, "Note on Substitutions," *Ann. Chim. Phys.*, 1857, **49**, 487–496, p. 496).

At the same time he repudiated, definitely and finally, Berzelius's electrochemical theories, as being neither "based on evident facts," nor even valuable as a hypothesis in "explaining and predicting facts" (*Comptes rendus*, 1839, **8**, 621).

Liebig also was soon compelled to break away from the complexities into which Berzelius's electrochemical theories had led him and, in footnotes to two of Berzelius's papers, added that:

"I do not share the views of Berzelius, since they rest upon a mass of hypothetical assumptions, for the correctness of which proof of every kind is lacking."

"I do not share the views, by which he explains the composition of the compounds discovered by Malaguti,[1] I believe on the contrary, that these materials are produced by simple substitutions" (*Ann. Chem. Pharm.*, 1839, **31**, 119, **32**, 72).

E. Organic Types, Nuclei and Residues

Dumas (1839) adopts the theory of types.—Dumas was led to believe in the direct replacement of hydrogen by chlorine mainly through his own experiments on TRICHLOROACETIC ACID. He added small quantities of acetic acid to a series of fifteen to twenty five-litre flasks filled with chlorine, exposed them to sunlight, and on the next day found the interiors frosted over with a crystalline acid, readily soluble in water and deliquescent on exposure to air. The acid

[1] Chlorinated ethers, *e.g.* $C_4H_6Cl_4O$ from $C_4H_{10}O$ (p. 410).

was very caustic to the skin and its vapour was irritating and suffocating even in small doses; it was a strong acid, but had none of the bleaching properties of chlorine. Its chemical properties were almost identical with those of acetic acid, from which it differed only in the replacement of hydrogen by chlorine; using modern formulæ,

$$C_2H_4O_2 + 3Cl_2 = C_2HCl_3O_2 + 3HCl.$$

Dumas prepared and analysed its silver, ammonium and potassium salts, and its methyl and ethyl ethers, and showed that these were similar in type to the corresponding derivatives of acetic acid, and that the composition of each could be predicted from the simple theory of substitution. A similar fixity of type was observed in the conversion of aldehyde[1] into chloral

$$C_2H_4O + 3Cl_2 = C_2HCl_3O + 3HCl,$$

in Malaguti's chlorination of ether

$$C_4H_{10}O + 4Cl_2 = C_4H_6Cl_4O + 4HCl,$$

and in Regnault's conversion of ethylene into chloroethylene or vinyl chloride (*Ann. de Chimie*, 1835, **58**, 301–320)

$$C_2H_4 + Cl_2 = C_2H_3Cl + HCl.$$

Dumas sums up these observations as follows:

"Acetic acid, aldehyde, ether, olefiant gas, losing hydrogen and taking an equal volume of chlorine, produce substances belonging to the same type as themselves, chloracetic acid, chloraldehyde, chlorether and chlorolefiant gas."

"In all these substances, chlorine, taking the place of hydrogen, did not change the properties of the compound at all, whether it was acid, base or neutral substance, for it remained acid, neutral substance or base, and even retained exactly its power of saturation". . . .

"From the conversion of acetic acid into chloracetic acid, from that of aldehyde into chloraldehyde, from the fact that

[1] Prepared by Liebig as an oxidation-product of alcohol, $C_2H_6O + O = C_2H_4O + H_2O$, and described by him as *aldehyde*, abbreviated from *alcohol dehydrogenatus* (*Ann. Chim. Phys.*, 1835, **59**, 290).

all the hydrogen of these substances is replaced by chlorine in equal volume, without changing their fundamental character, we must conclude :

"*That in organic chemistry there exist certain* TYPES *which persist even when in place of the hydrogen which they contain one introduces equal volumes of chlorine, of bromine or of iodine.*"

"That is to say that the theory of substitutions rests upon facts, and on the most striking facts of organic chemistry" (*Comptes rendus*, 1839, **8**, 620–622; also *Ann. Chem. Pharm.*, 1839, **32**, 117–119).

Dumas (1840) on chemical and mechanical types.—In a fuller memoir "On the Law of Substitutions and the Theory of Types" (*Comptes rendus*, 1840, **10**, 149–178; *Ann. Chem. Pharm.*, 1840, **33**, 259–300), Dumas distinguished as belonging to the same CHEMICAL TYPE "*substances which contain the same number of equivalents, united in the same way and showing the same fundamental chemical properties*," whilst, following Regnault, he included under the heading of MECHANICAL TYPES "*substances having the same formula, produced by substitution, but essentially different in their most salient chemical properties*" (*Comptes rendus*, 1840, **10**, 158, 162). In the latter class he included a large number of cases of oxidation, in which a neutral substance was converted into an acid by substituting oxygen for hydrogen, etc. In the same paper the system of naming substitution-products by means of the prefix CHLORO-, etc., was formally set out (*Comptes rendus*, **10**, 169). In both memoirs (*Comptes rendus*, **8**, 621; **10**, 169) Dumas referred to the analogy between substitution without change of type in organic chemistry and isomorphism in inorganic chemistry. The two phenomena were equally fatal to Berzelius's theories, since, as Liebig pointed out (*Ann. Chem. Pharm.*, 1839, **31**, 119), the replacement of the hydrogen of acetic acid by chlorine without change of type was no more remarkable than the replacement of the manganese of the permanganates by chlorine in the isomorphous perchlorates. Liebig, however, regarded both cases as exceptions, rather than as examples of a general

rule (*ibid.* **33**, 301), and had an obvious motive in appending to Dumas's paper a still more remarkable illustration of the possibilities of substitution without change of type.

Wöhler (1840) on substitution without change of type.—The substance selected was manganous acetate, and the action of chlorine upon it was described as follows :

"I passed a current of chlorine through a solution of manganous acetate, under the direct influence of sunlight. After 24 hours I found in the liquid a superb crystallisation of a violet-yellow salt." This was manganous chloroacetate, the whole of the hydrogen of the acetic acid having been displaced by chlorine.

"This salt, heated at 110° in a current of chlorine, was converted with liberation of oxygen gas into a new golden-yellow compound." In this compound, the oxygen of the base, as well as the hydrogen of the acid, had been displaced by chlorine.

"The new substance was dissolved with the aid of heat in pure chloral, and this liquid, which is not attacked by chlorine, was used to continue the treatment by this agent. I passed dry chlorine into it, during 4 days, keeping the liquid always very near its boiling-point. During this time a white substance was constantly deposited, which on careful examination was recognised as manganous chloride. I cooled the liquid some time after, when there was no longer any more precipitate and I obtained a third substance in small, greenish-yellow, silky needles." It contained no manganese, as this in its turn had now been displaced by chlorine.

"On acting again with chlorine on an aqueous solution of this substance, carbonic acid was set free and on cooling the liquid to +2° it deposited a yellow mass formed of small plates, closely resembling chlorine hydrate. The carbon had, in fact, been replaced by chlorine, which was now the only element present in the compound. The manganous acetate had been converted by substitution into pure chlorine, which, however, had a vapour-density which indicated the presence in the molecule of not fewer than twenty-four atoms of chlorine, $MnO,C_4H_6O_3$, having been converted into $Cl_2Cl_2,Cl_8Cl_6Cl_6$."

Such was the graphic description of one of the most surprising discoveries ever made in organic chemistry as set out in a letter to Liebig ("On Substitution and the Theory of Types," Liebig's *Ann. Chem. Pharm.*, 1840, **33**, 308–310) signed by S. C. H. Windler. The "s(ch)windler" who, wrote this skit on Dumas's theories was Wöhler. Liebig was perhaps responsible for a footnote, appended to the statement, that "in the decolorising action of chlorine there is a replacement of hydrogen by chlorine, and that the fabrics which are now bleached in England according to the laws of substitutions preserve their types." The footnote runs:

"I have just learnt that there are already in the shops in London fabrics of spun chlorine, much sought after in the hospitals and preferred to all others for night-caps, caleçons, etc." (*loc. cit.* p. 310).

Laurent (1837) on nuclei.—Laurent, working in Dumas's laboratory on lines suggested by Dumas, assimilated most of Dumas's ideas; but, with the enterprise of youth, he developed them more quickly than Dumas, and was able therefore to claim priority on certain important points. These claims were, however, put forward in language which did not err on the side of moderation. "I could scarcely restrain my indignation on seeing certain chemists tax my theory at first with being absurd, then later, when they saw that the facts agreed better with my theory than with all the others, pretend that I had taken possession of the ideas of Dumas" (*Ann. Chim. Phys.*, 1837, **66**, 326). If so, Dumas borrowed from Liebig, Liebig from the chemist who first showed that oxide of potassium could exchange its oxygen for an equivalent of chlorine, this latter from Richter and Wenzel, and so to Hermes and Tubal Cain. His dominant idea of simplicity in the combination of atoms would probably be attributed to Berzelius, and consequently to Moses! (*ibid.* p. 330).

Dumas acknowledged that Laurent had been the first to suggest that chlorine not merely *took the place* but *played the part* of hydrogen (*Ann. Chim. Phys.*, 1857, **49**, 496). Laurent claimed further (*Comptes rendus*, 1840, **10**, 412) that he had anticipated in all but the name Dumas's discovery of the permanence of types. He had recognised from the first that the law of substitutions was often incorrect; when it happened to be true this was simply because of the strong tendency of the radical attacked by the chlorine to conserve its type, and not to any inherent accuracy of the law. These stable groupings of atoms he had described in his Thesis (1837) as "fundamental radicals" before substitution, and as "derived radicals" after substitution (*ibid.* 412 and 416); in a book published after his death they are described as FUNDAMENTAL NUCLEI and as DERIVED NUCLEI (*Chemical Methods*, tr. Odling, 1854, p. 195). To render his theory more intelligible, he translated his idea into a geometrical figure:

"Let us imagine a four-sided prism, of which the eight angles are occupied by eight atoms of carbon, and the centres of the twelve edges by twelve atoms of hydrogen. Let us call this prism the *form* or *fundamental nucleus*, and let us represent it by C_8H_{12}.

"Let us suppose that chlorine, put in presence of this simple prism, removes one of the edges or hydrogen atoms; the prism deprived of this edge would be destroyed, unless it were supplied with some other edge, whether of chlorine, bromine, zinc, etc.; no matter what the nature of the edge, provided it succeeds in maintaining the equilibrium of the other edges and angles. Thus will be formed a new or *derived nucleus* similar to the preceding, and of which the form may be represented by $C_8(H_{11}Cl)$" (*Chemical Method*, 1854, 195: compare *Comptes rendus*, 1840, **10**, 416, where a similar but more complex figure is described in an extract from his *Thesis*, 1837).

Addition-products could be derived from the fundamental nucleus by adding pyramids to the ends of the prisms, to

represent the added atoms of hydrogen, hydrogen and chlorine, hydrogen and oxygen, etc.

Gerhardt (1839) on residues.—A third aspect of the theory of substitutions, differing both from Dumas's empirical conceptions and from Laurent's ideas of conservation of type, was developed in 1839 by **Charles Gerhardt** (1816–1856), a pupil of Liebig, who left Germany to become Professor of Chemistry at Montpellier and afterwards at Strassburg.

Berzelius had laid stress on the formation of compounds by direct addition, *e.g.*

$$BaO + SO_3 = BaSO_4.$$

Dumas had been impressed by the action of chlorine in displacing hydrogen from organic compounds, *e.g.*

$$HCN + Cl_2 = ClCN + HCl.$$

Gerhardt directed attention to the formation of new compounds by COPULATION, *i.e.* by the combination of two substances with the simultaneous "production of a very simple compound, such as water, hydrochloric acid, hydrobromic acid, etc." (*Ann. Chim. Phys.*, 1839, **72**, 196). From a series of over twenty examples of copulation, the following may be selected for representation by modern equations:

Original compound.	Reagent.		Simple inorganic product.		Copulated product = residue of compound + residue of reagent.
$2C_6H_6$ Benzene.	$+SO_3$	=	**H_2O**	+	$(C_6H_5)_2SO_2$ Sulphobenzene.
C_6H_6 Benzene.	$+HNO_3$	=	**H_2O**	+	$(C_6H_5)NO_2$ Nitrobenzene.
C_2H_6O Alcohol.	$+C_2H_4O_2$ Acetic acid.	=	**H_2O**	+	$(C_2H_5)C_2H_3O_2$ Ethyl acetate.
C_2H_6O Alcohol.	$+C_7H_6O_2$ Benzoic acid.	=	**H_2O**	+	$(C_2H_5)C_7H_5O_2$ Ethyl benzoate.
C_7H_5OCl Benzoyl chloride.	$+NH_3$	=	**HCl**	+	$(C_7H_5O)NH_2$ Benzamide.
or NH_3	$+C_7H_5OCl$ Benzoyl chloride.	=	**HCl**	+	$(NH_2)C_7H_5O$ Benzamide.

It will be seen at once that this conception is much broader than Dumas's Law of Substitutions, which was restricted to those special cases of copulation in which the reagent was an element, the original compound a hydride, and the product a chloride, etc., derived from it by substitution, *e.g.*

$$\underset{\substack{\text{Oil of bitter almonds.}\\ \text{Benzoyl hydride.}}}{(C_7H_5O)H} + Cl_2 = \mathbf{HCl} + \underset{\substack{\text{Benzoyl}\\ \text{chloride.}}}{(C_7H_5O)Cl}$$

Gerhardt (*loc. cit.*) expressed the contrast as follows:

"If the reagent is an element in the free state, the material removed is replaced, as Dumas has said, equivalent by equivalent; if, on the other hand, it is a compound, *the element removed is replaced by the residual elements of the reagent*," *e.g.*

SO_2 from SO_3 minus O ; NH_2 from NH_3 minus H;
NO_2 from HNO_3 minus OH ; C_7H_5O from C_7H_5OCl minus Cl.

Gerhardt's conception of copulated compounds led him very far in the direction in which a solution of the complex problem of structural chemistry was ultimately found. It showed him that the products of copulation (or CONDENSATION, as it is now called) must be regarded as formed from the mutilated RESIDUES of two molecules—residues which might well be incapable of separate existence. His residues (or radicals) thus differed essentially from the radicals of Dumas and Boullay and of Wöhler and Liebig, which were always regarded as real substances, capable of separate existence, as in the case of ammonia and ammonium amalgam. Again, the older radicals were considered to have a real existence in their compounds; but Gerhardt was content to regard his residues or radicals as expressing merely the possible methods of formation and decomposition of a compound; he was therefore prepared to write barium sulphate indifferently as $BaSO_4$ *or* $BaO + SO_3$, *or* $BaO_2 + SO_2$ *or* $BaS + O_4$, according as he wished to interpret one of its chemical changes or another (*Treatise on Chemistry*, 1856, IV. 561).

Gerhardt (1843) halves the formulæ of organic compounds.—Further important developments were made in Gerhardt's "Investigations on the Chemical Classification of Organic Compounds" (*Journ. prakt. Chem.*, 1842, **27**, 439–464; 1843, **28**, 34–53, 65–100, **30**, 1–10). His theory of copulation had compelled him to bring together into one equation both complex organic products and simple inorganic substances. He therefore soon discovered "*that the formulæ of most organic substances are too great by half in comparison with the formulæ of inorganic chemistry*" (*Journ. prakt. Chem.*, 1843, **30**, 8). In inorganic chemistry. (following Berzelius), water, ammonia and hydrogen chloride were written as H_2O, NH_3, and HCl; but as products of the copulation of organic compounds they always appeared as H_4O_2, N_2H_6, and H_2Cl_2. Gerhardt was therefore led to fall back again upon Avogadro's hypothesis as a valid guide to the molecular formulæ of organic compounds, and rewrote them as follows:

	New formula.	Old formulæ.
Acetic acid . .	$C_2H_4O_2$	$C_8H_8O_4 = C_8H_4O_2, H_4O_2$,
Silver acetate . .	$C_2(H_3Ag)O_2$	etc.
Chloracetic acid .	$C_2(HCl_3)O_2$	
Silver chloracetate	$C_2(AgCl_3)O_2$	

These formulæ were only rendered possible by the fact that Gerhardt had abandoned the older form of the theory of radicals, according to which silver acetate was a binary compound of silver oxide and "anhydrous acetic acid" (acetic anhydride), whilst "hydrated acetic acid" (acetic acid) was a binary compound of water with the anhydrous acid, thus (in modern formulæ)

$$\begin{aligned} \text{Silver acetate} &= C_4H_6O_3, Ag_2O = Ag_2C_4H_6O_4. \\ \text{Acetic acid} &= C_4H_6O_3, H_2O = C_4H_8O_4. \end{aligned}$$

To the student of this bewildering period of chemical history nothing is more refreshing than to find once more in Gerhardt's papers the simple formulæ, based upon

Avogadro's hypothesis, which had been abandoned even by Dumas and were only established finally when Deville's experiments on dissociation (Chapter XX) had cleared the ground for Cannizzaro's epoch-making exposition.

Gerhardt (1856) distinguishes the hydrogen and chlorine radicals from hydrogen and chlorine gas.—It is typical of the difficulties that had been introduced into chemistry by Berzelius's dualistic theories that Gerhardt appeared to be breaking new ground when he wrote the formula of hydrogen gas as H_2 and the formula of chlorine as Cl_2. Berzelius would not recognise that hydrogen could combine with hydrogen or chlorine with chlorine, since there could be no electrical polarity to produce an attraction between similar atoms. He therefore discarded Avogadro's hypothesis as applied to elements, even when he was prepared to apply it to compounds. Dumas, on the other hand, fell into error when he attempted to apply Avogadro's hypothesis to the elements on the assumption that all elementary molecules were diatomic, whence $Hg = 100$, $P = 62$ instead of $Hg = 200$, $P = 31$. Gerhardt, however, saw that a distinction must be drawn between the hydrogen radical and hydrogen gas, between the chlorine radical and chlorine gas. Thus he writes:

"In opposition to most chemists, *I regard the expression radical in the sense of a relationship, and not in that of a body that may be or has been isolated.* I distinguish, therefore, the hydrogen radical from hydrogen gas, the chlorine radical from free chlorine; or better, if free hydrogen or chlorine is to be represented by rational formulæ, a study of their reactions shows that hydrogen gas must be represented by the two radicals HH, and chlorine gas by the two radicals ClCl. In the usual nomenclature, hydrogen gas would then be the hydride of hydrogen, and chlorine gas would be the chloride of chlorine; that is to say that chlorine gas and hydrogen gas may be formed by, or may give rise to, double decompositions precisely similar to those which have caused oil of bitter almonds to be described as

benzoyl hydride, and the chlorinated oil as benzoyl chloride" (*Treatise*, 1856, IV. 568).

The formation of hydrogen chloride from its elements was, therefore, not a mere combination of an electro-positive with an electro-negative element to form a compound of the first order,

$$H + Cl = HCl$$

but rather a double decomposition, similar to those which had been studied by Dumas in developing the theory of substitution

$$H_2 + Cl_2 = 2HCl$$

compare $HCN + Cl_2 = HCl + ClCN$

As Laurent expressed it in 1846 (*Ann. Chim. Phys.*, 1846, **18**, 295) :—

"The molecule of hydrogen, of chlorine . . . . is formed of two atoms which constitute a *homogeneous compound*, (HH), (ClCl), (MM), etc. These homogeneous compounds, placed in presence of one another, may give rise to a double decomposition or to a substitution, and thus form a *heterogeneous compound* :

$$(HH) + (ClCl) = (HCl) + (ClH)$$
$$(MM) + (ClCl) = (MCl) + (ClM).$$"

F. Simple Inorganic Types.

Inorganic types.—One of the most far-reaching consequences of Gerhardt's theory of copulation was his recognition of the essential equality of the two residues which are united together in a copulated compound. This is shown by the fact that he classified benzamide as a product of the action, on one hand, of the reagent ammonia on the substance benzoyl chloride, and on the other of the reagent benzoyl chloride on the substance ammonia

$$C_7H_5O{\cdot}Cl + H{\cdot}NH_2 = \mathbf{ClH} + C_7H_5O{\cdot}NH_2.$$

benzoyl chloride. ammonia. benzamide.

The way was thus opened up for a development of the theory of types, which soon culminated in the modern theory of valency.

Dumas's "types," like Laurent's "nuclei," were complex organic structures, in which hydrogen could be displaced by chlorine, or by a small group of atoms (such as the nitro-group, NO_2), without causing the structure to collapse. To Gerhardt mainly belongs the credit of introducing a series of simple INORGANIC TYPES, from which complex organic compounds could be derived by substituting organic radicals (ethyl, benzoyl, etc.) for the hydrogen atoms of the simple type substance.

The ammonia-type (Hofmann, 1850).—Of these simple types, the AMMONIA TYPE was the first to be recognised clearly. **Wurtz** in 1849 (*Ann. Chem. Pharm.*, 1849, **71**, 331) discovered the simple bases, *methylamine*, $CH_3{\cdot}NH_2$, and *ethylamine*, $C_2H_5{\cdot}NH_2$. These two volatile organic bases showed a remarkable resemblance to ammonia, from which they could be derived by replacing a hydrogen atom by methyl or ethyl. **Hofmann**, in the following year, showed that *all* the hydrogen atoms of ammonia could be displaced by alkyl radicals:—

"I have indeed found, that aniline and the bases which are analogous to it, under the influence of methyl, ethyl, or amyl bromide, lose *one* or *two* equivalents of hydrogen, which is replaced by the corresponding alcohol-radical. Under the same conditions ammonia loses *one*, *two*, or *three* equivalents of hydrogen, which are likewise replaced by a corresponding number of equivalents of the radical" (Preliminary note in *Ann. Chem. Pharm.*, 1850, **73**, 91. Published in full *Phil. Trans.*, 1850, 93–131; 1851, 357–398).

Using modern formulæ and writing

C_2H_5 = Et = Ethyl
C_5H_{11} = Ay = Amyl
C_6H_5 = Ph = Phenyl

the substances tabulated by Hofmann are

1. *Amide-bases* (primary amines)

H, H, Ph } N Aniline or phenylamine

H, H, Et } N Ethylamine

2. *Imide-bases* (secondary amines)

H, Et, Ph } N Ethylphenylamine (ethylaniline)

H, Ay, Ph } N Amyl-phenylamine (amylaniline)

H, Et, Et } N Diethylamine

3. *Nitrile-bases* (tertiary amines)

Et, Et, Ph } N Diethylphenylamine (diethylaniline)

Et, Ay, Ph } N Ethylamyl-phenylamine (ethylamylaniline)

Et, Et, Et } N Triethylamine

The classification into PRIMARY, SECONDARY, and TERTIARY AMINES was introduced in 1856 by Gerhardt, who suggested that

"One might call the nitrogen-compounds *primary*, *secondary*, and *tertiary*, according as they represent the ammonia-type with substitution of one, of two, or of three atoms of hydrogen" (*Treatise*, 1856, IV. 592).

Williamson (1852) on etherification.—As recently as 1852 it was still uncertain whether or not alcohol "*contains* ether and water," *i.e.* whether the formation of ether from alcohol should be represented by the equation

$$C_4H_{10}O,H_2O = C_4H_{10}O + H_2O,$$

or, as Dumas had represented it twenty-four years before, by the equation

$$2C_2H_6O = C_4H_{10}O + H_2O.$$

Williamson ("Theory of Etherification," *Journ. Chem. Soc.*, 1852, **4**, 106–112, 229–239) tested this point by acting on alcohol with potassium, forming potassium ethoxide and hydrogen,

$$C_2H_6O + K = C_2H_5OK + \tfrac{1}{2}H_2$$

Potassium ethoxide.

and then with ethyl iodide, when ordinary ether (boiling at 37° C.) was formed

$$C_2H_5OK + IC_2H_5 = KI + (C_2H_5)_2O.$$

Ether was thus proved to be a copulated compound containing two ethyl groups, C_2H_5, and not merely the oxide of a single radical, C_4H_{10}. This view was confirmed by acting on potassium ethoxide with methyl iodide, CH_3I, when *ethyl methyl ether*, $\left.\begin{matrix}C_2H_5\\CH_3\end{matrix}\right\}O$, was produced and with amyl iodide, $C_5H_{11}I$, when *ethyl amyl ether*, $\left.\begin{matrix}C_2H_5\\C_5H_{11}\end{matrix}\right\}O$, was produced; *methyl amyl ether*, $\left.\begin{matrix}CH_3\\C_5H_{11}\end{matrix}\right\}O$, was also prepared by the action of amyl iodide, $C_5H_{11}I$, on potassium methoxide, CH_3OK.

Williamson concluded that:

"Alcohol is therefore water in which half the hydrogen is replaced by carburetted hydrogen,[1] and ether is water in which both atoms of hydrogen are replaced by carburetted hydrogen, thus:

$$\begin{matrix}H\\H\end{matrix}O \qquad \begin{matrix}C_2H_5\\H\end{matrix}O \qquad \begin{matrix}C_2H_5\\C_2H_5\end{matrix}O.$$

"From the perfect analogy of properties between the known terms of the alcoholic series, it was to be expected that similar substitutions might be expected in the others; and this expectation has been verified by experiment . . . . Methylic alcohol is, therefore, expressed by the formula $\begin{matrix}CH_3\\H\end{matrix}O$, as common alcohol is $\begin{matrix}C_2H_5\\H\end{matrix}O$; and in the same manner amylic alcohol is $\begin{matrix}C_5H_{11}\\H\end{matrix}O$, and the same of the higher ones." (*loc. cit.* pp. 107 and 108).

Williamson (1852) on the water-type.—In a paper "On the Constitution of Salts" (*Journ. Chem. Soc.*, 1852, **4**,

[1] *i.e.* by the hydrocarbon-radical, C_2H_5.

350–355) published later in the same year, Williamson suggested that :

"Formulæ may be used . . . as an actual image of what we rationally suppose the arrangement of constituent atoms in a compound, as an orrery is an image of what we conclude to be the arrangement of our planetary system ; and decompositions may be actually effected between them by the exchange of a molecule of one group for a molecule in another."

"The adoption of such a method will of course necessitate the adoption of types, from which, by the replacement of certain elements or molecules, we can deduce the constitution of more and more complex groups. I believe that throughout inorganic chemistry, and for the best known organic compounds, one single type will be found sufficient ; it is that of water, represented as containing 2 atoms of hydrogen to 1 of oxygen, thus $\frac{H}{H}O$. In many cases a multiple of this formula must be used, and we shall presently see how we get thereby an explanation of the difference between monobasic and bibasic acids, etc." (*loc. cit.*, pp. 351–352).

Gerhardt (1856) suggests four inorganic types.—In the fourth volume of his *Treatise*, published in 1856, Gerhardt accepted Williamson's "water-type" as of dominant importance in chemistry, but suggested that the number of types should be increased to four, namely, WATER, HYDROCHLORIC ACID, AMMONIA, and HYDROGEN. Unlike Williamson, however, he preferred to regard these types as expressing the double decompositions which a compound might undergo, rather than the actual arrangement of the atoms in the molecule.

Gerhardt expressed his views as follows :—

"My types are *types of double decomposition.* Water, in a large number of double decompositions, may exchange its oxygen and its hydrogen for other elements (simple radicals) or for groups of elements (compound radicals). But I refer

substances to the type water, when one can effect similar changes in them, and when the products are related in the same way as those which result from the substitution of other radicals for one of the radicals of water. For example, I derive ether from the type water, because one can, by double decomposition, replace the oxygen of ether by its equivalent of chlorine, of bromine, of sulphur or of nitrogen, to produce ethyl chloride, ethyl bromide, ethyl sulphide or ethyl nitride (ethylamine) and because the products are related in the same way as the hydrogen chloride, hydrogen bromide, hydrogen sulphide and hydrogen nitride (ammonia), which result from the substitution of the radicals chlorine, bromine, sulphur and nitrogen, for the radical oxygen of water" (*Treatise*, 1856, IV. 586).

"To facilitate the classification of substances according to their functions, one may, instead of taking water alone as a formula-type, join to it, as derived types, compounds which result from the displacement of the radical oxygen from water, such as hydrogen chloride, hydrogen nitride, etc. . . . The study of organic compounds, as will be seen later, proves that the four types water, hydrochloric acid, ammonia, hydrogen, suffice for a methodical classification. These *four formula-types* may be noted as follows :

Water	OH_2	equal volumes.
Hydrochloric acid	ClH	
Ammonia	NH_3	
Hydrogen	HH	

"The water type includes the oxides (bases, acids, salts, alcohols, etc.), the sulphides, the selenides and the tellurides.

"The hydrochloric acid type includes the chlorides, the bromides, the iodides and the cyanides.

"The ammonia type includes the nitrides and the phosphides.

"The hydrogen type includes the metallic hydrides and the metals" (*ibid.* pp. 588–589).

The following examples (with others) are given by Gerhardt as illustrations of his theory of types :—

Type.		Benzoyl derivatives.		Ethyl derivatives.			
Water	$O\{^{H}_{H}$	Benzoic acid	$O\{^{C_7H_5O}_{H}$	Ethyl alcohol	$O\{^{C_2H_5}_{H}$	Ether	$O\{^{C_2H_5}_{C_2H_5}$
Hydrogen chloride	$\{^{H}_{Cl}$	Benzoyl chloride	$\{^{C_7H_5O}_{Cl}$	Ethyl chloride	$\{^{C_2H_5}_{Cl}$		
Ammonia	$N\{^{H}_{H}_{H}$	Benz-amide	$N\{^{C_7H_5O}_{H}_{H}$	Ethyl-amine	$N\{^{C_2H_5}_{H}_{H}$	Triethyl-amine,	$N\{^{C_2H_5}_{C_2H_5}_{C_2H_5}$
				Diethyl-amine	$N\{^{C_2H_5}_{C_2H_5}_{H}$		
Hydrogen	$\{^{H}_{H}$	Benzoyl hydride (oil of bitter almonds)	$\{^{C_7H_5O}_{H}$	Ethyl hydride (ethane)	$\{^{C_2H_5}_{H}$	Diethyl (butane)	$\{^{C_2H_5}_{C_2H_5}$

Williamson (1852 to 1855) and Odling (1855) on multiple types.—Gerhardt's types indicated one stage, but only one stage, in the construction of the molecule of a compound. Ether, for instance, when written as $\left.\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right\}O$, was shown to be composed of two ethyl-groups, C_2H_5, held together by an oxygen atom; but no indication was given as to how the atoms of carbon and hydrogen were held together in the ethyl radical. Until the position of every atom in the scheme of combination could be shown, the structure of the compound was still only partly known.

The first stage in the subdivision of the compound into smaller units came through the introduction of "multiple types" and of "mixed types," *i.e.* of structural formulæ showing not one bracket only, as in Gerhardt's simple types, but two or three brackets, linking together different portions of the molecule.

MULTIPLE TYPES (as Kekulé called them, *Ann. Chem. Pharm.*, 1857, **104**, 133) arose primarily from the study of dibasic and of tribasic acids (Williamson, *Journ. Chem. Soc.*, 1852, **4**, 352; already quoted on p. 425). Nitric acid, HNO_3, and potassium nitrate, KNO_3, could be derived very easily from the simple water type, by writing them as

$$\left.\begin{matrix}NO_2\\H\end{matrix}\right\}O \quad \text{and} \quad \left.\begin{matrix}NO_2\\K\end{matrix}\right\}O$$

But sulphuric acid, H_2SO_4, potassium hydrogen sulphate (potassium bisulphate, $KHSO_4$), and potassium sulphate, K_2SO_4, could not be represented adequately in this way. Williamson, therefore, who had begun by writing sulphuric acid and ethyl hydrogen sulphate (in his two papers "On Etherification," 1852) as:

$$\left.\begin{matrix}H\\H\end{matrix}\right\}SO_4 \quad \text{and} \quad \left.\begin{matrix}H\\C_2H_5\end{matrix}\right\}SO_4,$$

was soon led to regard all the sulphates as derived from two molecules of water and to write their formulæ (in his paper "On the Constitution of Salts," *Journ. Chem. Soc.*, 1852, **4**, 353) as:

$$\left.\begin{matrix}SO_2\\H_2\end{matrix}\right\}O_2 \quad \left.\begin{matrix}SO_2\\HK\end{matrix}\right\}O_2 \quad \left.\begin{matrix}SO_2\\K_2\end{matrix}\right\}O_2, \quad \text{compare} \quad \left.\begin{matrix}H_2\\H_2\end{matrix}\right\}O_2.^{1}$$

The significance of these formulæ is shown clearly in a reply to certain criticisms of Kolbe (*Journ. Chem. Soc.*, 1855, **7**, 111), in which Williamson derives the formula of sulphuric acid from that of water by allowing a molecule of sulphur dioxide to "replace two atoms of hydrogen in two of water," thus

$$\left.\begin{matrix}H\\H\end{matrix}\right\}O \quad \left.\begin{matrix}H\\SO_2\end{matrix}\right\}O$$
$$\left.\begin{matrix}H\\H\end{matrix}\right\}O \quad \left.\begin{matrix}\\H\end{matrix}\right\}O$$

(*Journ. Chem. Soc.*, 1855, **7**, 137). In the last formula, the molecule of sulphuric acid is subdivided into five portions, namely, four single atoms and one small radical, SO_2, the exact structure of which is still doubtful even at the present day.

Williamson's multiple types were developed by **Odling** ("On the Constitution of Acids and Salts," *Journ. Chem. Soc.*,

[1] In the original papers Williamson writes all his formulæ without brackets, whilst Odling writes 2O instead of O_2 in the formulæ of multiple types; for the sake of convenience, one method of representation only is used in this paragraph.

1855, **7**, 1–22), who showed that complex products might result from the displacement of several atoms of hydrogen by an acid or basic radical. Thus *three* molecules of water are required to produce phosphoric acid and bismuth hydroxide,

$$\left.\begin{matrix}H_3\\H_3\end{matrix}\right\}O_3 \qquad \left.\begin{matrix}PO\\H_3\end{matrix}\right\}O_3 \qquad \left.\begin{matrix}H_3\\Bi\end{matrix}\right\}O_3$$

or the salts, such as potassium hydrogen phosphate, and bismuth nitrate, which are derived from them,

$$\left.\begin{matrix}H_3\\H_3\end{matrix}\right\}O_3 \qquad \left.\begin{matrix}PO\\K_2H\end{matrix}\right\}O_3 \qquad \left.\begin{matrix}3NO_2\\Bi\end{matrix}\right\}O_3$$

Kekulé (1857) on mixed types.—Very similar to the multiple types of Williamson and Odling are the MIXED TYPES of Odling and Kekulé.

Odling (like Williamson) had derived sodium sulphate, Na_2SO_4, from two molecules of water, but found it necessary to derive sodium hyposulphite, $Na_2S_2O_3$ (ordinary "hypo," now called sodium thiosulphate), from a molecule of water and a molecule of sulphuretted hydrogen (*Journ. Chem. Soc.*, 1855, **7**, 8), thus

$$\left.\begin{matrix}H_2\\H_2\end{matrix}\right\}O_2 \quad \text{gives} \quad \left.\begin{matrix}SO_2\\Na_2\end{matrix}\right\}O_2 \quad \text{(sodium sulphate)}$$

$$\text{but} \quad \left.\begin{matrix}H_2\\H_2\end{matrix}\right\}O+S \quad \text{gives} \quad \left.\begin{matrix}SO_2\\Na_2\end{matrix}\right\}O+S \quad \text{(sodium thiosulphate).}$$

If written out in full (compare Williamson, p. 428) these formulæ would appear thus:

$$\left.\begin{matrix}H\\H\end{matrix}\right\}O \qquad \left.\begin{matrix}Na\\SO_2\end{matrix}\right\}O \qquad \left.\begin{matrix}H\\H\end{matrix}\right\}O \qquad \left.\begin{matrix}Na\\SO_2\end{matrix}\right\}O$$

$$\left.\begin{matrix}H\\H\end{matrix}\right\}O \quad \text{gives} \quad \left.\begin{matrix}\\Na\end{matrix}\right\}O \qquad \left.\begin{matrix}H\\H\end{matrix}\right\}S \quad \text{gives} \quad \left.\begin{matrix}\\Na\end{matrix}\right\}S$$

These MIXED TYPES differ from the MULTIPLE TYPES only in that the types which are linked together are different instead of being identical. **Kekulé**, who gave them their name (*Ann. Chem. Pharm.*, 1857, **104**, 133), made use very

largely of mixed types to represent the structure of compounds, *e.g.* (*loc. cit.* 135, 136, 137)

$$\left.\begin{matrix} H \\ H \\ H \\ H \end{matrix}\right\}O \quad \text{gave} \quad \left.\begin{matrix} H \\ SO_2 \\ H \end{matrix}\right\}O \qquad (\textit{sulphurous acid}, H_2SO_3)$$

$$\left.\begin{matrix} Cl \\ H \\ H \\ H \end{matrix}\right\}O \quad \text{gave} \quad \left.\begin{matrix} Cl \\ SO_2 \\ H \end{matrix}\right\}O \qquad (\textit{chlorosulphonic acid}, ClSO_3H, \text{ prepared by combining } SO_3 + HCl)$$

$$\left.\begin{matrix} H \\ H \\ H \end{matrix}\right\}N \quad \left.\begin{matrix} H \\ H \\ CO \\ H \end{matrix}\right\}\begin{matrix} N \\ O \end{matrix} \qquad (\textit{carbamic acid}, \text{ the parent substance of } \textit{ammonium carbamate}, 2NH_3 + CO_2 = NH_2 \cdot CO \cdot O \cdot NH_4)$$

Gerhardt (1855) on conjugated radicals.—A parallel method of subdividing the molecules of organic compounds was devised by Gerhardt, who found that the process of "copulation" could be applied, not only to complete molecules, but also to the radicals of which those molecules are composed. In his *Treatise* (1852, IV. 604–610) he makes use of CONJUGATED RADICALS to represent simultaneously "two or several systems of double decomposition of the same body." This method of representation was applied with great success to the fatty acids. Most of their double decompositions (formation of salts, chlorides, amides, esters, etc.) could be expressed by formulæ of the water-type, thus:

Formic acid, $O\left\{\begin{matrix} CHO \\ H \end{matrix}\right.$ Propionic acid, $O\left\{\begin{matrix} C_3H_5O \\ H \end{matrix}\right.$

Acetic acid, $O\left\{\begin{matrix} C_2H_3O \\ H \end{matrix}\right.$ Butyric acid, $O\left\{\begin{matrix} C_4H_7O \\ H \end{matrix}\right.$

But "the acid radicals of the formula $C_nH_{2n-1}O$ may be viewed as composed of the carbonyl radical CO and an alcohol radical C_nH_{2n+1}:

$CO(H)$ formyl $CO(C_2H_5)$ propionyl

$CO(CH_3)$ acetyl $CO(C_3H_7)$ butyryl."

"These formulæ are justified by the reactions. We know, for example, that acetyl-compounds are resolved, in many cases, into carbonic compounds and methyl compounds: acetic acid can be transformed by heat into carbonic acid and hydride of methyl (marsh gas); potassium acetate gives, by the action of an electric battery, methyl[1] and carbonate of potash etc." (*Treatise*, 1852, IV. 606).

Thus in order to express the decompositions represented by the equations

$C_2H_4O_2 = CH_4 + CO_2$ (decomposition by heat)
$2C_2H_4O_2 = (CH_3)_2 + 2CO_2 + H_2$ (decomposition by electrolysis).

it was necessary to write acetic acid, not merely as

$$O\begin{cases} C_2H_3O \\ H \end{cases}, \quad \text{but also as} \quad O\begin{cases} CO(CH_3) \\ H \end{cases},$$

where the ACETYL group, C_2H_3O, is shown as a conjugated radical, composed of CARBONYL, CO and METHYL, CH_3.

Other decompositions suggested that the acetyl group should be represented as $C_2H_3(O)$, *i.e.* as a compound of a hydrocarbon radical C_2H_3 with oxygen. In the same way, "even the alcohol-radicals may be considered as conjugated radicals, of which the constituent radicals are the aldehyde radical[2] and hydrogen." Thus whilst *acetyl* $= C_2H_3(O)$, *ethyl* $= C_2H_3(H_2)$.

The theory of conjugated radicals was also applied effectively to represent nitration-products, obtained by the action of nitric acid on organic compounds such as benzoic acid (*ibid.* p. 664); thus

$$\text{Benzoic acid} = O\begin{cases} C_7H_5O \\ H \end{cases}$$

$$\text{Nitrobenzoic acid} = \begin{cases} C_7H_4(NO_2)O. \\ H \end{cases}$$

[1] The decomposition of the potassium salt is shown by the equation $2C_2H_3O_2K + 2H_2O = (CH_3)_2 + 2KHCO_3 + H_2$. The product, which Gerhardt called *methyl*, CH_3, is really *dimethyl* or *ethane*, $(CH_3)_2$ or C_2H_6.

[2] *i.e.* C_2H_3, aldehyde being $(C_2H_3)HO$. This radical (acetyl *minus* oxygen) was described by Liebig (see p. 405) as "acetyl."

The round brackets which Gerhardt used in formulating his copulated compounds have been retained to the present day as an integral part of the symbolism of structural chemistry. The curly brackets of the theory of types, on the other hand, have long since disappeared.

G. Valency.

Unequal combining-power of the elements indicated in Gerhardt's simple inorganic types.—The theory of types as developed by Gerhardt carried with it the idea that :

(1) In compounds of the hydrogen type, a hydrogen-atom could be linked to *one* radical, but only to one radical, giving compounds such as

$\left.\begin{matrix}CH_3\\H\end{matrix}\right\}$	$\left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}$	$\left.\begin{matrix}C_2H_3O\\H\end{matrix}\right\}$	$\left.\begin{matrix}C_7H_5O\\H\end{matrix}\right\}$
Methyl hydride (marsh gas or methane).	Ethyl hydride (ethane).	Acetyl hydride (aldehyde).	Benzoyl hydride (oil of bitter almonds or benzaldehyde).

(2) In compounds of the hydrochloric acid type, a chlorine-atom could be linked to *one* radical, but only to one radical, giving compounds such as

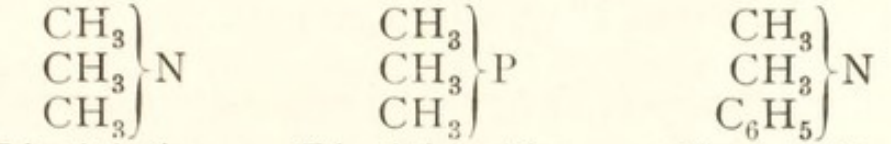
$\left.\begin{matrix}CH_3\\Cl\end{matrix}\right\}$	$\left.\begin{matrix}C_2H_5\\Cl\end{matrix}\right\}$	$\left.\begin{matrix}C_2H_3O\\Cl\end{matrix}\right\}$	$\left.\begin{matrix}C_7H_5O\\Cl\end{matrix}\right\}$
Methyl chloride.	Ethyl chloride.	Acetyl chloride.	Benzoyl chloride.

(3). In compounds of the water type, however, *two* radicals could be linked simultaneously to an oxygen-atom as in

$\left.\begin{matrix}CH_3\\CH_3\end{matrix}\right\}O$	$\left.\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right\}O$	$\left.\begin{matrix}C_2H_3O\\C_2H_3O\end{matrix}\right\}O$	$\left.\begin{matrix}C_7H_5O\\C_7H_5O\end{matrix}\right\}O$
Methyl oxide (Methyl ether).	Ethyl oxide (Ethyl ether).	Acetyl oxide[1] (Acetic anhydride).	Benzoyl oxide[1] (Benzoic anhydride).

[1] As a consequence of Berzelius's dualistic conceptions of molecular structure these acid-anhydrides had been regarded for many years as the real acids, of which ordinary acetic acid, benzoic acid, etc., were hydrates. They were, however, purely hypothetical compounds, until Gerhardt in 1853 (*Ann. Chem. Pharm.*, 1853, **87**, 57–84, 149–179)

(4) In compounds of the ammonia type, *three* radicals could be linked together, as in



Trimethylamine. Trimethylphosphine. Dimethylaniline

Hofmann had also represented the compounds of the amines and phosphines with HI and with CH_3I by formulæ which showed *five* radicals associated with an atom of nitrogen or of phosphorus (*Phil. Trans.*, 1850, 357–398).

Tetramethylammonium iodide from $N(CH_3)_3+CH_3I$. Phosphonium iodide from PH_3+HI.

Kekulé (1857) on substitution-value or atomicity.—These considerations, arising from the study of Gerhardt's simple types, were expressed very clearly by **Kekulé**, who proposed in 1857 to describe the elements according to their "substitution-value" or combining power as MONATOMIC, DIATOMIC, and TRIATOMIC. In the first of his two papers, "On Copulated Compounds and the Theories of Polyatomic Radicals," he writes:

"The molecules of chemical compounds consist of aggregations of atoms."

"The number of the atoms of other elements (or radicals) combined with one atom (of an element. . . . or of a radical) is dependent on the basicity or substitution-value of the constituents."

"From this point of view the elements fall into three principal groups:

prepared them by the same method that Williamson had used for the synthesis of the ethers, *e.g.*

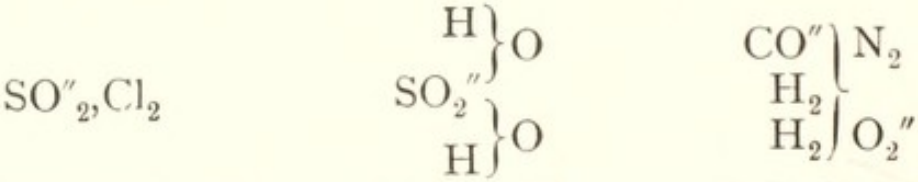
$$C_7H_5O\cdot Cl + C_7H_5O\cdot OK = KCl + (C_7H_5O)_2O$$
$$C_2H_3O\cdot Cl + C_2H_3O\cdot OK = KCl + (C_2H_3O)_2O$$

"(1) Monobasic or monatomic, I, *e.g.* H, Cl, Br, K;
"(2) Dibasic or diatomic, II, *e.g.* O, S;
"(3) Tribasic or triatomic, III, *e.g.* N, P, As."
(*Ann. Chem. Pharm.* 1857, **104**, 132–133).

A study of the *multiple types* and *mixed types* showed that similar considerations could be applied to the radicals, thus:

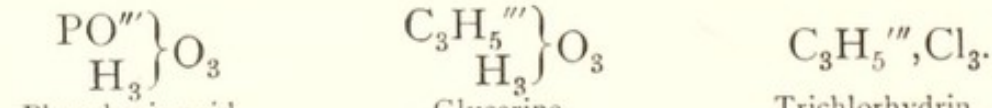
"A *monatomic* radical can never hold together two molecules of the types.

"A *diatomic* radical can unite *two* molecules of the types *e.g.*



Sulphuryl chloride. Sulphuric acid. Carbamide (urea).

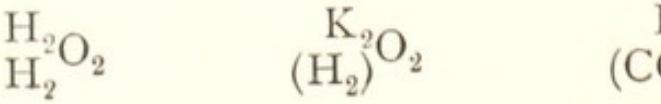
"A *triatomic* radical similarly unites *three* molecules of the types, *e.g.*



Phosphoric acid. Glycerine. Trichlorhydrin.

This "substitution-value" or combining power of elements and radicals is now described as VALENCY, elements and radicals being described as UNIVALENT, BIVALENT, TERVALENT, and QUADRIVALENT (Lothar Meyer, *Moderne Théorien*, 1864, 76), according as they combine with one, two, three or four other univalent elements or radicals.

Williamson (1851), Frankland (1852), and Odling (1855) on combining power or valency.—The conceptions thus clearly set out by Kekulé were by no means wholly new. **Williamson** in 1851 had represented the conversion of "hydrate of potash" (potassium hydroxide) into potassium carbonate by a scheme



which represented carbonic oxide as displacing two atoms of hydrogen in a double-water-type; in doing this he suggested that

"One atom[1] of carbonic oxide is here equivalent to two atoms of hydrogen, and by replacing them, holds together the two atoms[1] of hydrate in which they are contained, thus necessarily forming a bibasic compound, $\overset{(CO)}{K_2}O_2$, carbonate of potash" (*Journ. Chem. Soc.*, 1852, **4**, 353; reprinted from the *Chemical Gazette*, 1851).

Carbonic oxide was therefore, in Kekulé's phraseology, a dibasic or diatomic radical.

Frankland, in the following year, in the memorable paper in which he described a "New Series of Organic Bodies containing Metals" (*Phil. Trans.*, 1852, 417–444), had put forward the conception of a definite COMBINING POWER for each element:

"When the formulæ of inorganic chemical compounds are considered, even a superficial observer is struck with the general symmetry of their construction; the compounds of nitrogen, phosphorus, antimony and arsenic especially exhibit the tendency of these elements to form compounds containing 3 or 5 equivalents. of other elements, and it is in these proportions that their affinities are best satisfied; thus in the ternal group we have NO_3,[2] NH_3, NI_3, NS_3,[2] PO_3,[2] PH_3, PCl_3, SbO_3,[2] SbH_3, $SbCl_3$, AsO_3,[2] AsH_3, $AsCl_3$, etc.; and in the five-atom group NO_5,[2] NH_4O,[2] NH_4I, PO_5,[2] PH_4I, etc. Without offering any hypothesis regarding the cause of this symmetrical grouping of atoms, it is sufficiently evident, from the examples just given, that such a tendency or law prevails, and that, no matter what the character of the uniting atoms may be, the combining power of the attracting element, if I may be allowed the term, is always satisfied by the same number of these atoms (*loc. cit.* p. 440).

[1] *i.e.* molecule, molecules.

[2] *i.e.* N_2O_3, N_2S_3, P_2O_3, Sb_2O_3, As_2O_3, N_2O_5, $(NH_4)_2O$, P_2O_5, etc., using modern atomic weights in place of Gmelin's equivalents.

Odling in 1855 (*Journ. Chem. Soc.*, 1855, **7**, 3) had presented the same idea in a graphical form:

"For the clear elucidation of the succeeding formulæ, I adopt in them, a simple plan of marking these different substitution values, viz., by one or more dashes to the right or left of the symbol, something after the fashion frequently made use of in algebraical formulæ: thus,

H′, an atom of hydrogen, ...
Bi‴, an atom of bismuth, ...

having a value represented by three atoms of hydrogen, etc."

Water was thus represented as $\left.\begin{matrix}H'\\H'\end{matrix}\right\}O''$, and alum as

$$\left.\begin{matrix}2SO_2''\\K'Al_2'''\end{matrix}\right\}4O'', \qquad i.e., \quad Al''' \left\{\begin{matrix}\left.\begin{matrix}K'O''\\O''\end{matrix}\right\}SO_2''\\\left.\begin{matrix}O''\\O''\end{matrix}\right\}SO_2''\end{matrix}\right. ,$$

if the atomic weight of aluminium be doubled, to conform with modern usage.

Frankland and Odling were, however, greatly hampered by their adherence to an old system of equivalents, from which even Kekulé himself did not wholly escape until 1867. The result was that Odling wrote tin and iron as

Sn′ (stannous) Sn″ (stannic) *instead of* Sn″ and Sn‴′
Fe′ (ferrous) Fe_2''' (ferric) *instead of* Fe″ and Fe‴

He thus regarded *two* atoms of aluminium and *two* atoms of ferric iron as tervalent, as indicated by the symbols Al_2''', Fe_2'''. In the same way, Kolbe and Frankland, in a paper in which they foreshadowed the quadrivalency of carbon (*Ann. Chem. Pharm.*, 1857, **101**, 257–265) were only able to discuss the combining-power of a double atom C_2 of atomic weight 2 × 6 (see Japp's "Kekulé Memorial Lecture," *Trans. Chem. Soc.*, 1898, **73**, 97–138; p. 130). Their conceptions of valency or combining-power could not therefore be put forward in the same convincing way as in Kekulé's papers,

where Gerhardt's newer atomic weights were employed. In particular, it must be noticed that if Al_2 is tervalent, Al must be at least quadrivalent, to provide for the linking together of the two aluminium atoms; so also, if C_2 is quadrivalent, the single carbon atoms must be at least quinquevalent, etc.

Kekulé on the "marsh gas type" (1857) and the quadrivalency of carbon (1858).—The problem of molecular structure was almost solved when Gerhardt's types (simple, multiple and mixed) had developed into the conception of valency. It was then seen clearly that oxygen and sulphur might link together *two* radicals, whilst nitrogen and phosphorus might unite *three* radicals. But the inner structure of the radicals themselves remained obscure, until Kekulé detected the secret of their construction in the quadrivalency of carbon; the radicals, in fact, were held together by their carbon atoms, which possessed the remarkable power of uniting *four* other atoms or radicals.

In 1857 he had referred some ten different compounds of carbon to the MARSH GAS TYPE (*Ann. Chem. Pharm.*, 1857, **101**, 204), thus deriving them from a hydrocarbon containing *four* atoms of hydrogen[1] displaceable by other radicals. In the following year, having accepted the atomic weights of Gerhardt and of Cannizzaro, he was in a position to discuss the combining-power of the single carbon atom in a marsh gas of the formula, CH_4, as follows:

"If one considers the simplest compounds of carbon (marsh gas, methyl chloride, carbon chloride, chloroform, carbonic acid, phosgene gas, carbon sulphide, prussic acid, etc.) it appears that the quantity of carbon, which chemists have recognised as the smallest possible, as the *atom*, always binds four atoms of a monatomic, or two atoms of a diatomic element; that in general the sum of the chemical units of the elements combined with an atom is equal to four. This

[1] Kekulé still wrote the formula of marsh gas as C_2H_4, taking the atomic weight of carbon as 6.

leads to the view, that carbon is *tetratomic* (or tetrabasic)" (*Ann. Chem. Pharm.*, 1858, **106**, 153).

"If one introduces carbon as a *tetratomic radical* into the types, one obtains for several of its known compounds relatively simple formulæ" (*ibid.* footnote).

The QUADRIVALENCY of the single carbon atom was shown in the following compounds in which it is combined with

(a) *Four univalent radicals.*	(b) *One bivalent and two univalent radicals.*	(c) *Two bivalent radicals.*	(d) *One tervalent and one univalent radical.*
CH_4	$COCl_2$	CO_2	CNH
CCl_4		CS_2	
CH_3Cl			
$CHCl_3$			

When two carbon atoms were united, the valency of the double carbon atom, C_2, was not $2 \times 4 = 8$, but 6, since two units of combining-power were used in holding the two carbons together, as in :

Ethane . .	C_2H_6	Acetonitrile .	C_2H_3N'''
Ethyl chloride .	C_2H_5Cl	Cyanogen .	C_2N_2'''
Ethylene chloride	$C_2H_4Cl_2$	Aldehyde .	C_2H_4O''
Carbon trichloride	C_2Cl_6	Acetyl chloride	C_2H_3ClO'', etc.

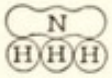
(*ibid.*, p. 154). In reference to such a group of compounds Kekulé suggests that

"If one compares together compounds, which contain the same number of carbon atoms in the molecule and can be converted into one another by simple metamorphoses (*e.g.* alcohol, ethyl chloride, aldehyde, acetic acid, glycollic acid, oxalic acid, etc.) one comes to the conclusion, that they contain the carbon atoms arranged in the same way, and that only the atoms attached to the carbon-skeleton change (*ibid.*, 155–156).

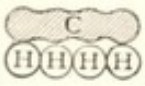
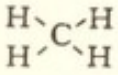
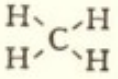
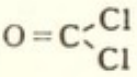
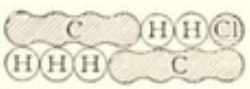
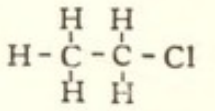
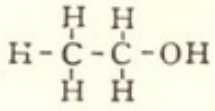
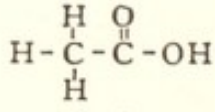
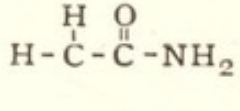
Structural formulæ of organic compounds. Graphic formulæ.—Kekulé's recognition of the quadrivalency of carbon, and of the CARBON-SKELETON as the nucleus of all organic compounds, provided a complete solution of the problem of molecular structure. In order to show the structure of any compound it was only necessary to indicate

the arrangement of the multivalent atoms forming the skeleton, and the method of attachment of the other atoms to this skeleton.

We also owe to Kekulé a revival of the GRAPHIC FORMULÆ, which Dalton had used to indicate the number and the nature of the atoms (p. 295), but which Kekulé proposed to use in order to show also the way in which the atoms were linked together. The univalent atoms were represented by circles, the bivalent atoms by a dumb-bell figure occupying the width of two circles, and so on. In all the simpler compounds, the atoms were arranged in two equal horizontal rows, and every point of contact between the two rows indicated a linkage between two atoms. A number of Kekulé's graphic formulæ (*Lehrbuch*, 1861, I. 160, 162, 164, footnotes) are shown below, together with

Simple Inorganic Compounds.	Kekulé's graphic formulæ.	Modern structural formulæ.	Modern graphic formulæ.
Hydrogen chloride		HCl	H-Cl
Water . . .		HOH	H-O-H
Ammonia . .		NH_3	H-N(-H)-H
Oxygen		O_2	O=O
Sulphuryl radical [1]		SO_2	-O-S-O- or O=S<(=O)
Sulphuryl chloride [1]		$Cl \cdot SO_2 \cdot Cl$	Cl-O-S-O-Cl or O=S(-Cl)-Cl
Sulphuric acid [1] .		$HO \cdot SO_2 \cdot OH$	H-O-O-S-O-OH or O=S(-OH)-OH
Nitric acid [1] . .		$ON \cdot O \cdot OH$ or $NO_2 \cdot OH$	O=N-O-OH or O=N-OH

[1] In these cases the structure given by Kekulé differs from that which is commonly accepted to-day and which is shown as the second of two

Derivatives of Marsh Gas.	Kekulé's graphic formulæ.	Modern structural formulæ.	Modern graphic formulæ.
Marsh gas .		CH_4	
Methyl chloride .		$CH_3 \cdot Cl$	
Carbonyl chloride		$Cl \cdot CO \cdot Cl$	
Carbonic anhydride		CO_2	$O=C=O$
Prussic acid . .		$H \cdot CN$	$H-C\equiv N$
Derivatives of Ethane.			
Ethyl chloride .		$CH_3 \cdot CH_2 \cdot Cl$	
Ethyl alcohol .		$CH_3 \cdot CH_2 \cdot OH$	
Acetic acid . .		$CH_3 \cdot CO \cdot OH$	
Acetamide . .		$CH_3 \cdot CO \cdot NH_2$	

modern structural formulæ, in which dots are used to show the linkages between the radicals, and modern graphic formulæ, in which the linkages are shown in detail by a series of straight lines.

Kekulé's formula for benzene (1865).—The subsequent history of organic chemistry has consisted largely of a search for, and demonstration of structural formulæ for compounds of greater and greater complexity. At first these compounds showed only "open-chains" of carbon atoms, but Kekulé himself in 1865 (*Bull. Soc. Chim.*, 1865,

alternative formulæ. It will be seen that Kekulé regarded sulphur as bivalent in all its compound and nitrogen as tervalent; modern formulæ often show sulphur as quadrivalent or sexavalent and nitrogen as quinquevalent.

3, 98–110; *Ann. Chem. Pharm.*, 1866, **137**, 129) recognised the existence of a "closed chain" or "ring" of carbon atoms in the formula of BENZENE; similar ring-systems are characteristic of nearly all aromatic compounds. Kekulé's graphic formula for benzene was of the same type as those shown above, but may be translated into modern symbols as $HC\begin{matrix}<\\>\end{matrix}\begin{matrix}CH{=}CH\\CH{-}CH\end{matrix}\begin{matrix}>\\<\end{matrix}CH$. Only three valencies are needed to form the ring of carbon-atoms and to hold the six hydrogen atoms, as shown in the symbol $HC<\begin{matrix}CH{-}CH\\CH{-}CH\end{matrix}>CH$; much controversy has therefore arisen as to the way in which the fourth valency is disposed of, but Kekulé's formula is universally recognised as the opening of a new chapter in organic chemistry and was made the subject of a public celebration in 1890.

Position of the atoms in space.—Kekulé represented the four hydrogen atoms of marsh-gas as lying in a row by the side of the carbon atom. More frequently they have been represented as arranged round the carbon atom in such a way as to occupy the four corners of a square. Van t'Hoff's study of the isomerism of carbon compounds, and the crystallographic work of Barlow and Pope, and of Bragg, have shown that they are probably arranged at the corners of an enveloping tetrahedron. This idea, one of the most fertile in modern chemistry, cannot, however, be discussed in the present volume.

Fixed or variable valency.—Is the valency of an atom fixed or variable? Kekulé held strongly to the view that the valency or "atomicity is a fundamental property of the atom, which must be constant and invariable like the weight of the atom itself" (*Comptes rendus*, 1864, **58**, 511). In order to account for the existence of compounds such as ammonium chloride and phosphorus pentachloride in which the valency of nitrogen and phosphorus appears to be increased, he assumed the existence of a class of MOLECULAR

COMPOUNDS, which "do not form vapours, but are decomposed by the action of heat, reproducing the molecules which gave birth to them" (*ibid.* 513). Thus he wrote

$$NH_3 + HCl = NH_3,HCl \quad \textit{not}\ NH_4Cl$$
$$PCl_3 + Cl_2 = PCl_3,Cl_2 \quad \textit{not}\ PCl_5$$

Frankland, on the other hand, in his first note on the combining-power of the elements (1852) had already adopted the idea of variable valency by ascribing to nitrogen and phosphorus a tendency to unite with *three or five* equivalents of other elements. This idea, in one form or another, is now adopted very widely. Odling's attempt to distinguish between "artiads" of even valency and "perissads" of uneven valency (*Phil. Mag.*, 1864, **27**, 115–119) broke down when it was found to lead to purely fictitious formulæ, such as N_2O_2 for nitric oxide, NO, and to unjustified contrasts such as those shown by the formulæ $FeCl_2,Fe_2Cl_6$ (for $FeCl_3$) and $KClO_4,K_2Mn_2O_8$ (for $KMnO_4$).

SUMMARY AND SUPPLEMENT.

A. THE RISE OF ORGANIC CHEMISTRY.

The rapid growth of inorganic chemistry between 1766 and 1816 is paralleled by the rise and development of organic chemistry in the fifty years from 1815 (when Berzelius first assigned formulæ to organic compounds) to 1865 (when Kekulé put forward his structural formula for benzene). The recognition of organic substances as compounds of carbon and hydrogen with oxygen, and sometimes nitrogen and phosphorus, is due to **Lavoisier** (1784–1789), who also made the first organic analyses. He estimated the carbon and hydrogen in charcoal, olive-oil, wax and spirit of wine (1784) and showed (1789) that in *vinous fermentation* there is a balance between the carbon, hydrogen, oxygen, and nitrogen in the materials used (sugar, water, yeast) and in the products obtained (alcohol, carbonic anhydride, etc.). In doing this he enunciated the principle of the CONSERVATION OF MASS in chemical changes and explained the significance of

a *chemical equation*. Other early analyses were made by **Gay-Lussac and Thenard** (1810), who discovered the existence of *carbohydrates*, by Berthollet (1809), by **de Saussure** (1807 and 1814), who analysed alcohol and ether, by **Berzelius** (1815), who first expressed his organic analyses by means of formulæ, and finally by **Liebig** (1831), to whom belongs the credit of perfecting the methods of organic analysis.

B. The Structure of Salts.

Mayow, in 1674, showed that salts contained an acid and a base, which might be set free again by the action of a stronger acid or base. **Lavoisier** regarded salts as compounds of two oxides, namely, the acid oxide of a non-metal and the basic oxide of a metal. **Berzelius** (1819) adopted this dualistic theory, but recognised that binary compounds could be formed which contained no oxygen, and (at a later date) that salts might be formed by uniting two hydrides or two sulphides. He suggested that all compounds were held together by the electrical attraction between oppositely charged components (Berzelius' *dualistic* or *electro-chemical theory*).

C. The Theory of Radicals.

Berzelius's electro-chemical theory could not readily be applied to organic compounds, which were not amenable to electrolysis. In order to bring them into his scheme **Berzelius** (1819) adopted Lavoisier's view that inorganic compounds were derived from simple elementary radicals, but organic compounds from compound radicals, containing two or more different elements. The most important radicals were :

Cyanogen . . .	CN or Cy	Gay-Lussac, 1815.
Ammonium . .	NH_4 or Am	Ampère, 1816.
Ammonia . .	NH_3	
Amide . . .	NH_2 or Ad	Berzelius, 1832
Ethyl . . .	C_2H_5 or Et	Liebig, 1834.
Aetherin (ethylene)	C_2H_4 or Ae	Dumas and Boullay, 1827.
"Acetyl" now C_2H_3O)	C_2H_3	Liebig, 1839.
Methylene . .	CH_2	Dumas and Péligot, 1834.
Methyl . . .	CH_3 or Me	Dumas and Péligot, 1834.
Benzoyl . . .	C_7H_5O or Bz	Wöhler and Liebig, 1832.
Pikramyl . .	C_7H_6 or Pk	Berzelius, 1843.

After the discovery of the benzoyl-radical in 1832, **Liebig** became the champion of the theory of radicals, whilst Berzelius was chiefly concerned that the dissection of organic compounds should be carried out in such a way as to segregate completely the electro-positive and the electro-negative elements. **Dumas**, who had much to do with the development of the theory of radicals, soon broke away from Berzelius's interpretation of that theory and became the chief exponent of the rival theory of "substitution."

D. The Theory of Substitution.

Dumas, in 1834, showed that by a process of *substitution* or *metalepsy* the hydrogen of organic compounds could be replaced by an equivalent quantity of chlorine or oxygen, *e.g.*

Prussic acid . .	$HCN + Cl_2 = HCl + ClCN$	(Gay-Lussac, 1815)
Ethylene chloride	$C_2H_4Cl_2 + 4Cl_2 = 4HCl + C_2Cl_6$	(Faraday, 1821)
Oil of bitter almonds	$C_7H_6O + Cl_2 = HCl + C_7H_5OCl$	(Wöhler and Liebig, 1832).

In some cases, hydrogen was removed without replacement, *e.g.*

Oxalic acid . $H_2C_2O_4 + O$ gave $H_2O + 2CO_2$.

In such cases, it was assumed that hydrogen was present in the form of water : thus in the preparation of chloral by the action of chlorine on alcohol,

Ethylene . .	$C_2H_4 + 3Cl_2$	gave	C_2HCl_3	$+ 3HCl$
Water . .	$H_2O + Cl_2$	gave	O	$+ 2HCl$
therefore				
Alcohol .	$C_2H_6O + 4Cl_2$	gave	$C_2HCl_3O + 5HCl$	

E. Organic Types, Nuclei and Residues.

Laurent, a pupil of Dumas, asserted that substitution was not merely an empirical rule, but, in defiance of all Berzelius' electro-chemical conceptions, that chlorine took the place and *played the part* of hydrogen in organic compounds. **Dumas**, in 1839, adopted this view by suggesting that substitution could take place without any change of type ; this idea was cleverly ridiculed in an anonymous letter written by Wöhler in 1840. Dumas distinguished between *chemical types*, in which

the laws of substitution were obeyed strictly, and *mechanical types*, in which a part of the hydrogen (existing separately from the rest in the form of water) could be removed without replacement by oxygen or chlorine. **Laurent**, in 1837, found an explanation of the same facts in the theory that an organic compound consists of a *nucleus* of atoms geometrically arranged, *e.g.* in the form of a prism; hydrogen atoms in the prism could only be replaced according to the laws of substitution, but other atoms, forming pyramids on the ends of the prism, could be added, or removed without replacement. **Gerhardt**, in 1839, regarded substitution as a particular case of the *copulation* of two *residues* or *radicals*. Thus when chlorine acted on oil of bitter almonds, the former lost a chlorine and the latter a hydrogen atom in the form of hydrogen chloride and the product was formed by the union of the two residues,

$$C_7H_5O\cdot H + Cl\cdot Cl = HCl + C_7H_5O\cdot Cl.$$

In this way the idea of substitution could be extended to include the products obtained by the action of sulphuric acid and nitric acid on benzene, of acetic acid on alcohol, of ammonia on benzoyl chloride, etc. Gerhardt regarded his residues, not as real substances, but as expressions of the changes which a compound could undergo; he therefore distinguished between the radicals H and Cl and the gases H_2 and Cl_2. He also halved the formulæ of nearly all organic compounds and used simple formulæ based on Avogadro's hypothesis.

F. Simple Inorganic Types.

The discovery by **Wurtz**, in 1849, of the primary amines, methylamine, $CH_3\cdot NH_2$, and ethylamine, $C_2H_5\cdot NH_2$, and by **Hofmann**, in 1850, of the secondary and tertiary amines, led to the recognition of *ammonia* as a *simple inorganic type*, from which derivatives could be obtained by replacing one or more of the three hydrogen atoms by organic radicals. The experiments of **Williamson**, in 1852, on etherification, showed that alcohol and ether could be derived from the *water type* by replacing one or both of the two hydrogen atoms by ethyl. **Gerhardt**, in 1856, added the *hydrogen type* and the *hydrochloric acid type*. The *marsh gas type*, CH_4, in which *four* hydrogen

atoms can be replaced by radicals, was introduced by **Kekulé** in 1857.

These simple inorganic types showed only one stage in the construction of the molecule, namely, the linking together of radicals either directly (in pairs), or through an atom of oxygen, nitrogen or carbon, whereby two, three or four radicals could be held together. A further subdivision of the molecule was effected in the *multiple types* of **Williamson** (1852–1855), and **Odling** (1855), the *mixed types* of **Odling** (1855) and **Kekulé** (1857), and finally the *conjugated radicals* of **Gerhardt** (1855).

G. Valency.

Gerhardt's simple inorganic types indicated that the different elements possessed unequal combining-power; thus hydrogen and chlorine could only be linked to one radical, oxygen to two, and nitrogen to three. **Kekulé** therefore suggested, in 1857, that the elements should be described, according to their *substitution-values*, as *monatomic*, *diatomic*, *triatomic*. This idea could also be supplied to radicals, the sulphuryl and carbonyl radicals being diatomic, as in sulphuryl chloride, SO_2Cl_2, sulphuric acid, $SO_2(OH)_2$, and carbamide, $CO(NH_2)_2$, whilst triatomic radicals were present in phosphoric acid, $PO(OH)_3$, glycerine, $C_3H_5(OH)_3$, and trichlorhydrin, $C_3H_5Cl_3$. The diatomic character of the carbonyl radical in potassium carbonate, $CO(OK)_2$, had already been indicated by **Williamson** in 1851. **Frankland**, in 1852, had directed attention to the fact that nitrogen, phosphorus, arsenic and antimony always combined with *three* or *five* equivalents of other elements, and had suggested that each element had a definite *combining-power*. **Odling**, in 1855, had gone further and had represented the combining powers or substitution values of the elements by symbols such as H′, Cl′, O″, S″, N‴, P‴. Frankland and Odling thus set forth clearly the idea now known as *valency*, but they were hampered by an obsolete system of atomic weights, and in the case of many elements could only indicate that the double-atom Al_2 was tervalent, C_2 was quadrivalent, etc. The quadrivalency of the single carbon atom was first postulated by **Kekulé** in 1858; he had already, in 1857, introduced the *marsh gas type*, containing *four* hydrogen atoms,

displaceable by radicals, but was not then convinced that marsh gas contained only one atom of carbon. Kekulé's discovery of the *carbon-skeleton* as the basis of all the hydrocarbon radicals provided a final solution of the problem of the molecular structure of organic compounds; in the fatty-compounds the carbon-skeleton is composed of *open chains* of carbon atoms, but in benzene and aromatic compounds derived from it Kekulé recognised, in 1865, the existence of a *closed chain* or *ring* of carbon atoms.

CHAPTER XVIII

THE CLASSIFICATION OF THE ELEMENTS

A. Metals and Non-Metals

A "sceptical chemist's" views on the elements (Boyle 1661).—Until the close of the alchemistic period, it was universally agreed that all matter was composed of a very small number of "principles" or "elements," *e.g.* the four elements, *earth*, *air*, *fire* and *water* of Aristotle and the Peripatetic School, or the three principles, *mercury*, *sulphur* and *salt*, of Albertus Magnus (1205-1280) and the alchemists. The modern conception of elements is due to **Boyle**, who sets out his views in the first pages of "The Sceptical Chymist"[1] as follows :

"I perceive that divers of my Friends have thought it very strange to hear me speak so irresolvedly, as I have been wont to do, concerning those things which some take to be the Elements, and others to be the Principles of all mixt Bodies. But I blush not to acknowledge that I much less scruple to confess that I doubt, when I do so, than to profess that I know what I do not" (*Sceptical Chymist*, 1661, 1-2).

In discussing "the number of Elements or Principles" it was agreed to use "elements and principles as terms equivalent : and to understand, both by the one and the other, those primitive and simple bodies of which the mixed ones

[1] *The Sceptical Chymist : or Chymico-physical Doubts and Paradoxes touching the Experiments whereby vulgar Spagyrists are wont to endeavour to evince their Salt, Sulphur and Mercury, to be the True Principles of Things.* London, 1661. Compare *Works*, 1725, iii. 261.

are said to be composed, and into which they are ultimately resolved" (*ibid.* p. 16). But Boyle insisted that "a man may rationally enough retain some doubts concerning the very number of those material ingredients of mixed bodies, which some would have us call elements and others principles" (*ibid.* p. 10), and urged that the problem must be settled rather by experiments than by abstract reasoning.

Although Boyle was able to combat very effectively the idea that the number of elements was limited to three or four, more than a century elapsed before it was possible to compile a reasonable list of the chemical elements, or to make any serious attempt to classify them. But as soon as the discovery of oxygen had been followed by the proof of the composite character of water, Lavoisier was able to set out, in 1789, a list of some thirty elements, which was increased to fifty in the hands of Berzelius (1819), and now amounts to more than eighty. These elements, with their atomic weights, are set out in Table F, p. 491.

Lavoisier's classification of the elements (1789).—In his *Elementary Treatise*, Lavoisier classified the elements as follows (*Works*, I. 135):

Simple substances belonging to the three kingdoms, which may be regarded as the elements of bodies.	Light Heat Oxygen Azote Hydrogen
Simple substances, non-metallic, oxidisable, and acidifiable.	Sulphur Phosphorus Carbon Muriatic radical [3] Fluoric radical [3] Boric radical [3]
[1] Simple substances, salifiable, earthy.	Lime Magnesia Baryta Alumina Silica
[2] Simple substances, metallic, oxidisable, and salifiable.	Antimony Silver Arsenic Bismuth Cobalt Copper Tin Iron Manganese Mercury Molybdenum Nickel Gold Platinum Lead Tungsten Zinc

[1] Lavoisier considered it as "probable that the four salifiable earths set out above contain oxygen" (*Works*, I. 126), but he was not able to

The dominant position which Lavoisier assigned to oxygen is seen in the text preceding the table:

"The acidifiable substances, combining with oxygen and being converted into acids, acquire a great tendency to combination; they become capable of uniting with earthy and metallic substances, and it is by this union that neutral salts are produced.

"This manner of viewing the acids does not permit me to regard them as salts, although they have some of their principal properties, such as solubility in water, etc. . . . For the same reason, I shall no longer place the alkalis nor the earthy substances, such as lime, magnesia, etc., in the class of salts, and I shall designate by this name only compounds formed by the union of an oxidised element and a base" (*Works*, I. 115–116).

Lavoisier's broad classification of the elements into three groups, (1) *metals*, (2) *inflammable elements*, yielding acids by combustion, and (3) *oxygen*, the essential constituent of acids, bases and salts, is curiously similar to the alchemistic system in which the three elements were (1) mercury, the typical metal, (2) sulphur, the typical combustible substance, and (3) salt.

Oxygen and chlorine as "supporters of combustion" (Davy, 1812).—Davy, in his *Elements of Chemical Philosophy* (1812), followed Lavoisier's classification but made certain important modifications. His three groups were:

(1) *Elements that support combustion*, — oxygen, and chlorine, which Davy had just shown to be an element.

prove this experimentally. The alkalis were omitted because Lavoisier regarded them as compounds, in view of Berthollet's proof of the composite nature of ammonia. Silica is not mentioned in the text accompanying the table, but seems to have been classified with the earths, rather than with the boric radical, because it was insoluble in water.

[2] Arranged in alphabetical order in French. In the text they are described, by an obvious misprint, as "acidifiable" instead of "salifiable."

[3] Three unknown elements, assumed to be present *as oxides* in muriatic, "fluoric," and boric acids.

(2) *Inflammable or acidiferous elements, not metallic*,—hydrogen, nitrogen, sulphur, phosphorus, carbon, and boron (prepared in a crude state from boric anhydride in 1807).

(3) *Metals*, 38 in number, as contrasted with Lavoisier's 17, including sodium and potassium, barium, strontium, calcium and magnesium; also "aluminum" and "silicum," which Davy had prepared in an impure condition from alumina and silica (*Works*, IV. 165–346).

Elements classified as metals and non-metals.—In Lavoisier's system oxygen occupied a unique position as a supporter of combustion for metals and non-metals alike. Davy was fully justified in putting chlorine in the same class, but Gay-Lussac showed in 1814 (p. 246) that chlorine could not stand alone, since sulphur, chlorine and iodine agreed together in their power of uniting both with hydrogen to form hydracids and with oxygen to form oxy-acids. Berzelius in 1825 grouped together under the name of halogens (p. 247) the three elements chlorine, iodine and fluorine (to which bromine was added in 1826), which united directly with metals to form binary haloid-salts; on the other hand, he grouped together oxygen, sulphur and selenium, all of which could unite with metals and with non-metals to form ternary amphi-salts (p. 248).

After undergoing so many modifications, the attempt to classify the non-metals as "combustibles" and "supporters of combustion" broke down. Later writers were content to distinguish broadly between METALS and NON-METALS, doubtful elements being described sometimes as METALLOIDS. There is not much difficulty in classifying the elements themselves as metals and non-metals, but confusion and difficulty arise when attempts are made to effect an identical classification by studying the basic or acid qualities of the oxides, or the properties of the chlorides and other compounds of the elements.

B. Numerical Relationships and the Periodic Law

Döbereiner's "triads" (1829).—The existence of small groups or "families" of elements became evident at a very early date. The metals of the alkalis and of the alkaline earths formed two of these natural groups. Amongst the non-metals, the group of halogens and the elements of the oxygen group were enumerated by Berzelius as typical constituents of "haloid" and of "amphi" salts respectively.

Döbereiner, in 1829, directed attention to the fact that a determination by Berzelius of the atomic weight of bromine agreed with a prediction of his own "that the atomic weight of bromine would probably be the arithmetic mean of the atomic weights of chlorine and iodine"; thus

$$\frac{35{\cdot}470 + 126{\cdot}470}{2} = 80{\cdot}970$$

where Berzelius found 78·383. So also in the case of sulphur, selenium and tellurium, $\frac{32{\cdot}239 + 129{\cdot}243}{2} = 80{\cdot}741$, where the actual atomic weight of selenium was 79·263.

In the case of the metals, similar relationships were detected in the groups

calcium, strontium, barium
lithium, sodium, potassium

as well as in certain groups where the atomic weights differed but little, as in

nickel, copper, zinc,
platinum, iridium, osmium, etc.

(*Pogg. Ann. der Physik.*, 1829, **15**, 301–307.) These groups of three elements, with atomic weights in arithmetical progression, became known as Döbereiner's TRIADS.

Dumas's "natural series" and "common differences" (1859). The accuracy of the relationship discovered by

Döbereiner was tested by **Dumas** in a memoir "On the Equivalents of the Elements" (*Ann. Chim. Phys.*, 1859, **55**, 129–210), in which he sought to establish an analogy between the "natural families" of elements and the "natural series" of organic radicals. Dumas concluded that :

"In a family of three elements, the equivalent of the intermediate element may be equal to the mean of the equivalents of the two extreme elements ; but the contrary may also occur in regard to the most closely related elements" (*loc. cit.* p. 163).

Thus $\left.\begin{matrix} Cl = 35{\cdot}5 \\ I = 127{\cdot}0 \end{matrix}\right\}$ Mean = 81·25, whereas Br = 80·0.

When dealing with the equivalents of organic radicals, on the other hand, the averages are exact, and may, moreover, be extended throughout a homologous series in the form of arithmetical progression, as represented by the simple formula $a + nd$, *e.g.*

$H = 1, CH_3 = 1 + 14, C_2H_5 = 1 + 2 \times 14, C_3H_7 = 1 + 3 \times 14$, etc.

Dumas suggested that something similar might be recognised in the equivalents of the following families of elements :

		[1]	
F = 19		O = 8	
Cl = 19 + 16·5 =	35·5	S = 8 + 8 =	16
Br = 19 + 2 × 16·5 +	28 = 80	Se = 8 + 4 × 8 =	40
I = 19 + 2 × 16·5 + 2 × 28 + 19 =	127	Te = 8 + 7 × 8 =	64
N = 14		[1] Mg = 12	
P = 14 + 17 =	31	Ca = 12 + 8 =	20
As = 14 + 17 +	44 = 75	Sr = 12 + 4 × 8 =	44
Sb = 14 + 17 + 2 × 44 =	119	Ba = 12 + 7 × 8 =	68
Bi = 14 + 17 + 4 × 44 =	209	Pb = 24 + 10 × 8 =	104 etc.

To Dumas belongs also the credit of recognising the existence of numerical relationships between the equivalents

[1] The equivalents of the oxygen and magnesium families require to be doubled in order to give the modern atomic weights.

of different families of elements, *e.g.* the fluorine and nitrogen families, and the magnesium and oxygen families, thus :

Fluorine	19	Nitrogen	14	Common difference 5
Chlorine	35·5	Phosphorus	31	
Bromine	80	Arsenic	75	
Iodine	127	Antimony	122	
[1] Magnesium	12	[1] Oxygen	8	Common difference 4
Calcium	20	Sulphur	16	
Strontium	43·75	Selenium	39·75	
Barium	68·5	Tellurium	64·5	
Lead	103·5	Osmium	99·5	

These differences were precisely similar to those observed in homologous series of organic radicals, *e.g.*

Ammonium	18	Methyl	15	Common difference 3
Methylammonium	32	Ethyl	29	
Ethylammonium	46	Propyl	43	
Propylammonium	60 etc.	Butyl	57 etc.	

Dumas concluded that

"Since the radicals of mineral chemistry show amongst themselves the same general relations as the radicals of organic chemistry, there is certainly room to bring the two chemistries more closely together than is the case at the present day" (*Ann. Chim. Phys.*, 1859, **55**, 202).

Newlands's "relations between equivalents" (1864).—Dumas was much restricted by using the old equivalents in place of the newer atomic weights which were adopted immediately afterwards in consequence of the work of Deville and of Cannizzaro (pp. 514 and 343). If he had doubled the equivalents of the oxygen and magnesium families, he would have recognised that his scheme of "common differences" could be applied generally to all the elements. Thus the four families which he considered specially would have come together as in columns IV, V, VI and VIII of Table A.

[1] The equivalents of the oxygen and magnesium families require to be doubled in order to give the modern atomic weights.

TABLE A

NEWLANDS'S FIRST TABLE OF THE ELEMENTS[1]

	I.	II.	III.	IV.	V.
	Li 7	B 11	C 12	N 14	O 16
Triads	Mg 24	—	Si 28	P 31	S 32
Triads	Zn 65	—	—	As 75	Se 79·5
Triads	Cd 112	—	Sn 118	Sb 122	Te 129
	—	Au 196	—	Bi 210	Os 199

	VI.	VII.	VIII.	IX.	X.
	F 19	Na 23	Mg 24	—	—
Triads	Cl 35·5	K 39	Ca 40	Mo 96	Pd 106·5
Triads	Br 80	Rb 85	Sr 87·5	V 137	—
Triads	I 127	Cs 133	Ba 137	W 184	Pt 197
	—	Tl 203	Pb 207	—	—

This table, which shows all the triads in a single scheme, was put forward by **Newlands** in 1864 in a paper on "Relations between Equivalents" (*Chem. News*, July 30, 1864, **10**, 59; reprinted in a pamphlet *On the Discovery of the Periodic Law*, London, 1884, p. 8). He had already described a number of relations between the equivalents in continuation of the work of Dumas; but this new table was a direct result of the adoption of Cannizzaro's system of atomic weights. Newlands directed attention to the following features in the table:

(1) There is a constant difference of sixteen to seventeen units between the values for the initial member of each group and the first term of the corresponding triad.

(2) This difference is equal to the value assigned to oxygen; simple multiples of this difference may be recognised in other parts of the table.

(3) "Silicon and tin stand to each other as the extremities of a triad," the "central term or mean of the triad. . . . is at present wanting; thus $\frac{\text{Si } 28 + \text{Sn } 118}{2} = 73$" (*Periodic*

[1] The triads are arranged horizontally in the original table. The following elements would now be assigned to different families: Li, Au, Os, Tl, Pb, V.

Law, p. 8). This missing element (Mendeléeff's eka-silicon) was discovered in 1886 by Winkler, who called it Germanium.

(4) "Palladium and platinum appear to be the extremities of a triad, the mean of which is unknown," and remains unknown at the present day.

Newlands's "Law of Octaves" (1865).—To Newlands belongs also the credit of publishing, in 1864, the first table in which the elements were arranged *in the order of their atomic weights*, and of assigning to the elements thus arranged a series of consecutive *atomic numbers* (*Periodic Law*, pp. 7 and 11). When this arrangement was made, it was seen that:

"The numbers of analogous elements generally differ either by seven or by some multiple of seven; in other words, members of the same group stand to each other in the same relation as the extremities of one or more octaves in music. Thus, in the nitrogen group, between nitrogen and phosphorus there are 7 elements; between phosphorus and arsenic 14; between arsenic and antimony, 14; and lastly between antimony and bismuth, 14 also" (*Chem. News*, Aug. 18, 1865; *Periodic Law*, p. 14).

This peculiar relationship Newlands proposed to term provisionally the LAW OF OCTAVES. It was described at a meeting of the Chemical Society on March 1, 1866, and was criticised "on the score of its having been assumed that no elements remain to be discovered." One Fellow, whose misdirected wit has provided a perennial warning to rash critics, "humorously inquired of Mr. Newlands whether he had ever examined the elements according to the order of their initial letters?" Newlands replied that "he had tried several other schemes" and had found that "no relation could be worked out of the atomic weights under any other system than that of Cannizzaro" (*Periodic Law*, p. 19); but the paper was rejected and failed to secure attention until similar relationships were put forward five or six years later by Mendeléeff and by Lothar Meyer.

It is not necessary to consider in detail the table which Newlands used to illustrate the Law of Octaves. In spite of the larger number of elements, the families were reduced from ten to seven, in order to maintain the idea of octaves.

Table B. Newlands's "Elements arranged in Octaves."

H	1	F	8	Cl	15	Co & Ni	22	Br	29	Pd	36	Te	43	Pt & Ir	50
Li	2	Na	9	K	16	Cu	23	Rb	30	Ag	37	Cs	44	Os	51
G	3	Mg	10	Ca	17	Y	24	Sr	31	Cd	38	Ba & V	45	Hg	52
Bo	4	Al	11	Ti	18	Zn	25	Zr	32	Sn	39	Ta	46	Tl	53
C	5	Si	12	Cr	19	In	26	Ce & La	33	U	40	W	47	Pb	54
N	6	P	13	Mn	20	As	27	Di & Mo	34	Sb	41	Nb	48	Bi	55
O	7	S	14	Fe	21	Se	28	Ro & Ru	35	I	42	Au	49	Th	56

The members of the triads, recurring at intervals of fourteen elements, were separated by unrelated elements occupying the intermediate octaves, thus disguising to some extent the relations indicated so clearly in the first table.

Mendeléeff on "periodicity" (1869).—This fault was remedied in a short note "On the Relationships of the Properties to the Atomic Weights of the Elements," submitted to the Russian Chemical Society in March, 1869, by **D. Mendeléeff.** In Mendeléeff's table the number of families was increased to nineteen, and, in spite of many gaps and a large number of interrogation-marks, all

Table C. Mendeléeff's First Table of the Elements.

			Ti = 50	Zr = 90	? = 180
			V = 51	Nb = 94	Ta = 182
			Cr = 52	Mo = 96	W = 186
			Mn = 55	Rh = 104,4	Pt = 197,4
			Fe = 56	Ru = 104,4	Ir = 198
			Ni = Co = 59	Pd = 106,6	Os = 199
H = 1			Cu = 63,4	Ag = 108	Hg = 200
	Be = 9,4	Mg = 24	Zn = 65,2	Cd = 112	
	B = 11	Al = 27,4	? = 68	Ur = 116	Au = 197?
	C = 12	Si = 28	? = 70	Sn = 118	
	N = 14	P = 31	As = 75	Sb = 122	Bi = 210?
	O = 16	S = 32	Se = 79,4	Te = 128?	
	F = 19	Cl = 35,5	Br = 80	J = 127	
Li = 7	Na = 23	K = 39	Rb = 85,4	Cs = 133	Tl = 204
		Ca = 40	Sr = 87,6	Ba = 137	Pb = 207
		? = 45	Ce = 92		
		?Er = 56	La = 94		
		?Yt = 60	Di = 95		
		?In = 75,6	Th = 118?		

the old relationships were shown clearly. Moreover, new determinations of atomic weights permitted the elements Be 9·4, V 51, Ta 182, to be placed in their correct positions in the table.

Mendeléeff's first table was accompanied by the following statement of the LAW OF PERIODICITY:—

"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 (Pt, Ir, Os), or which increase regularly (K, Rb, Cs).

"3. The arrangement of the 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, *e.g.* Li, Be, B, C, N, O, F.

"4. The elements which are 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.

"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 element. Thus the atomic weight of tellurium must lie between 123 and 126, and cannot be 128.

"8. Certain characteristic properties of the elements can be foretold from their atomic weights" (German trans., *Zeitschr. f. Chemie*, 1869, **5**, 405–406, from *Russ. Chem. Ges.*, **1**, 60. English translation in Mendeléeff's "Faraday Lecture," *Trans. Chem. Soc.*, 1889, **55**, 634–656).

Lothar Meyer on periodicity (1869).—A few months after the publication of Mendeléeff's brief note, a paper appeared on "The Nature of the Chemical Elements as a Function of their Atomic Weights" (Liebig's *Ann. Chem.*

Pharm., 1870, **7**, Suppl., 354–364), in which Mendeléeff's suggestions were developed in a remarkable way by **Lothar Meyer**. Meyer defined the law of periodicity as follows:

"The properties of the elements are largely *periodic* functions of the atomic weight. Identical or similar properties recur, if the atomic weight is increased by a definite amount, which is at first 16, then about 46, and finally 88 to 92 units" (*loc. cit.* p. 358).

Thus there is a difference of 16 units between the alkali-metals lithium and sodium, and again between sodium and potassium. These elements resemble one another closely, but differ widely from all the elements of intermediate atomic weight. "Only the valency rises and falls regularly and equally in the two intervals," thus

Valency	1	2	3	4	3	2	1
Elements	Li	Be	B	C	N	O	F
	Na	Mg	Al	Si	P	S	Cl

(*loc cit.* p. 358).

Meyer's paper includes a complete classification of the elements, which shows all the essential features of the familiar table which Mendeléeff produced two years later, and in some points is in even closer agreement with the modern table on p. 462.

The paper also contains a curve showing the variations of atomic volume as the atomic weight increases (see below, p. 472); this curve remains, even to-day, one of the best illustrations that can be given of the principle of periodicity.

Mendeléeff on "The Periodic Law" (1871).—In his complete paper on "The Periodic Law of the Chemical Elements," *Ann. Chem. Pharm.*, 1872, **8**, Suppl., 133–229), Mendeléeff, following Lothar Meyer, adopted a compromise (compare Table D,[1] p. 462), between Newlands's

[1] This table differs from Mendeléeff's table as follows: (1) An additional column O has been added; (2) Series 2 and 3 are placed in the

system, in which only 7 families were recognised, and his own, in which there were 19.

Nearly all the elements were classified, according to the general scheme of Newlands's octaves, in seven GROUPS, numbered I to VII, arranged in seven vertical columns under the seven TYPICAL ELEMENTS[1] (*loc. cit.* p. 152):

Li Be B C N O F

When the elements, in the order of their atomic weights, had been allotted to their proper families they formed not fewer than thirteen horizontal SERIES or SHORT PERIODS (*loc. cit.* p. 145), of which the first was occupied by hydrogen only, and the second by the seven typical elements referred to above.

Mendeléeff, like Newlands, now found that the chief triads appeared in alternate short periods or octaves, and therefore distinguished between the EVEN SERIES and the ODD SERIES (*loc. cit.* p. 145), *e.g.*

Fourth Series :	K	Ca	—	Ti	V	Cr	Mn
Fifth Series :	*Cu*	*Zn*	—	—	*As*	*Se*	*Br*
Sixth Series :	Rb	Sr	—	Zr	Nb	Mo	—
Seventh Series :	*Ag*	*Cd*	*In*	*Sn*	*Sb*	*Te*	*I*

This difficulty was overcome (again following Lothar Meyer) by placing the members of the even series on the left hand, and the members of the odd series on the right hand side of the vertical columns; in this way the number of columns was virtually increased to fourteen and each group could be

centre of the columns instead of left and right; (3) The four series 8, 9, 10, 11 have been compressed into two lines by clustering 15 rare earth elements into a single space in the table; (4) The elements Sc, Ga, Ge, predicted by Mendeléeff have been inserted, and other missing elements are indicated by numbers of a consecutive series (see below, p. 491).

[1] The phrase was derived from Gerhardt's "simple inorganic types" (p. 425), the chief of which may be recognised in the series

— — — CH_4 NH_3 OH_2 FH (compare ClH).

subdivided into two distinct families. Unfortunately, the distinction between the odd and even series is not a sharp one, since the alkali-metals are found in series two, three, four, six, and the halogens in series two, three, five, seven. This difficulty may be diminished by placing the elements of series two and three either on the right, or on the left according to the relation which they show to the elements of the later series; or the elements of series two and three may all be placed in the centre of the column as in Table D, p. 462.

Mendeléeff also recognised that whilst there were "sharp differences between the last members of the odd series (halogens), and the first members of the even series (metals of the alkalis)," yet "the last members of the even series resemble in many respects. . . . the first members of the odd series" (*loc. cit.* pp. 145, 146). Thus there was a sharp break between Cl and K or Br and Rb, but a gradual transition from Cr and Mn to Cu and Zn. Moreover, even this interval was bridged over by a group of three metals, which Mendeléeff placed together in an additional Group VIII. The even and odd series were thus linked together by a remarkably smooth TRANSITION SERIES of elements (*loc. cit.* p. 146):

Cr = 52, Mn = 55, Fe = 56, Co = 59, Ni = 59, Cu = 63, Zn = 65.

Mendeléeff therefore proposed to describe the triad of Group VIII with the octave or short period on either side as a LONG PERIOD (*loc. cit.* p. 146) of $7 + 3 + 7 = 17$ elements. Similar long periods were recognised on either side of the triads Ru = 104, Rh = 104, Pd = 106 and Os = 193 (?), Ir = 195 (?), Pt = 197.

A periodic classification of the elements.—A modern classification of the elements which embodies all the essential features of the tables of Lothar Meyer and Mendeléeff is set out in Table D.

TABLE D

PERIODIC CLASSIFICATION OF THE ELEMENTS[1]

Full Periods.	Series.	Groups. O.	I.	II.	III.	IV.	V.	VI.	VII.	VIII.
I.	1		H							
II.	2	He	Li	Be	B	C	N	O	F	
III.	3	Ne	Na	Mg	Al	Si	P	S	Cl	
IV.	4	Ar	K	Ca	Sc	Ti	V	Cr	Mn	Fe Co Ni
	5		Cu	Zn	Ga	Ge	As	Se	Br	
V.	6	Kr	Rb	Sr	Y	Zr	Nb	Mo	43	Ru Rh Pd
	7		Ag	Cd	In	Sn	Sb	Te	I	
VI.	8 9 10	Xe	Cs	Ba	15 RARE EARTHS	72	Ta	W	75	Os Ir Pt
	11		Au	Hg	Tl	Pb	Bi	84	85	
VII.	12	Nt	87	Ra	89	Th	91	U		

In this table the number of columns has been increased to nine, in order to include the newly-discovered RARE GASES, shown in Group O.

He 3·99, Ne 20·2, Ar 39·88, Kr 82·92, Xe 130·2, Nt 222·4.

The discovery of these six gases not only adds an additional column to the table, but justifies its subdivision into seven chief periods. These periods are as follows :

(1) **The "hydrogen-period,"** which may perhaps contain one or two other light gases. It may be extended, if desired, to include helium, in which case neon would be transferred to the end of Period II, and so on down the series.

(2) **Two short periods of eight elements.**—Each period starts with one of the rare gases, and both periods are similar and complete. In Table E, the atomic weights are given in round numbers and are seen to differ on the average by 16 units ; if exact atomic weights are taken the average difference is 16·06, agreeing somewhat closely with the atomic weight of oxygen. The average differences between Period III and the initial portion of Period IV is $18\frac{1}{2}$ units.

[1] See footnote, p. 459.

TABLE E.—SHORT PERIODS AND LONG PERIODS

I. H	II. He	Li	Be	B	C	N	O	F
1	4	7	9	11	12	14	16	19
	Differences *16*	*16*	*15*	*16*	*16*	*17*	*16*	*16½*
	III. Ne	Na	Mg	Al	Si	P	S	Cl
	20	23	24	27	28	31	32	35½
	Differences *20*	*16*	*16*	*17*	*20*	*20*	*20*	*19½*

IV.	Ar	K	Ca	Se	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br
	40	39	40	44	48	51	52	55	56	59	59	63	65	70	72½	75	79	80
Differences	*43*	*46½*	*48*	*45*	*43*	*42½*	*44*	—	*46*	*44*	*48*	*45*	*47*	*45*	*46½*	*45*	*48½*	*47*
V.	Kr	Rb	Sr	Y	Zr	Nb	Mo	—	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I
	83	85½	88	89	91	93½	96	—	102	103	107	108	112	115	119	120	127½	127
Differences	*47*	*47½*	*49*	*50*	—	*88*	*88*	—	*89*	*90*	*88*	*89*	*89*	*89*	*88*	*88*	—	—
VI.	Xe	Cs	Ba	RARE EARTHS	—	Ta	W	—	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	—	—
	130	133	137		—	181½	184	—	191	193	195	197	201	204	207	208	—	—
Differences	*92*	—	*89*	—	—	—	*54*	—										
VII.	Nt	—	Ra	—	Th	—	U	—										
	222	—	226	—	232	—	238	—										

(3) **Two long periods of eighteen elements.**—These two periods are again precisely similar to one another, with the single exception of a missing element, of atomic weight about 100, which is required to fill a gap below manganese, and between molybdenum and ruthenium. The average difference between the atomic weights of the long Periods IV and V is nearly 46, a difference which persists between Periods V and VI, until the elements of the rare earths are reached, when the difference between analogous elements jumps suddenly to 89, but finally drops back to 54 when the rare earths are passed. This is shown in Table E, which carries the differences forward to the end of the list of elements.

(4) **A long period of some thirty-two elements, including the elements of the rare earths.**—Mendeléeff assumed that the two long periods, including series 4–5 and 6–7, would be followed by three more long periods of identical type, including series 8–9, 10–11, and 12–13 (?). He therefore left spaces (*loc. cit.* p. 151), for a group of transition-elements of atomic weight about 150, between periods 8 and 9, and for another group of atomic weight about 250, at the end of period 12, to correspond with the group Os, Ir, Pt, of atomic weight about 193 between series 10 and 11. He was also obliged to assume that there was an element missing in each of the following families:

Cu	Zn			As
Ag	Cd	In	Sn	Sb
—	—	—	—	—
Au	Hg	Tl	Pb	Bi

Lothar Meyer, on the other hand (*Ann. Chem. Pharm.*, 1870, **7**, Suppl., 356), suppressed these gaps and assumed that the differences between analogous elements increased abruptly from 16 to 46, and then again from 46 to 90 on passing from Ba—Sr to Ta—Nb (see quotation, p. 459).

None of Mendeléeff's hypothetical transition-elements

have been found nor have the gaps between silver and gold, cadmium and mercury, tin and lead, or antimony and bismuth been filled by the discovery of additional elements belonging to any of these families. It is therefore probable that these gaps do not in fact exist, and that Lothar Meyer was right in his suggestion that the differences in a family of elements may be 16 *or* 46 *or* 90, as in the two series

Li = 7	Na = 23	K = 39	Rb = $85\frac{1}{2}$	Cs = 133
Differences 16	16	$46\frac{1}{2}$	$47\frac{1}{2}$	
N = 14	P = 31	As = 75	Sb = 120	Bi = 208
Differences 17	44	45	88	

There is, however, a gap of about 40 units at the point where the differences undergo this sudden increase. This gap, which extends from barium (Ba – Sr = 137 – 88 = 49) to tantalum (Ta – Nb = 181 – 93 = 88) is filled by a series of RARE EARTH ELEMENTS, derived mainly from monazite sand. In addition to scandium and yttrium, two elements of much smaller atomic weight, fourteen elements of known atomic weight have been separated (see Table F, p. 492) as follows :

La	Ce	Pr	Nd	Sa	Eu	Gd	Tb	Ds	Ho	Er	Tm	Yb	Lu
139·0	140·25	140·6	144·3	150·4	152·c	157·3	159·2	162·5	163·5	167·7	168·5	172·0	174·0

These elements exhibit a remarkable resemblance to one another; their compounds are so similar that their separation has occupied more than a century, and even now may not be quite complete. They differ far less than Mendeléeff's transition-elements and cannot possibly be scattered over the eight families of the short periods, or the eighteen families of the long periods of the conventional classification. With unmistakable clearness these elements all claim a place in the same family as scandium and yttrium and must be placed with these elements in Group III of Tables D and E.[1] The regular periodic change in the

[1] Armstrong, *Encycl. Brit.*, Ninth Edition, 1902, XXVI, 712; compare Biltz, *Ber.*, 1902, **35**, 562–568.

properties of the elements is evidently checked at this point and only goes forward again after some 40 units have been added to the atomic weight.

There is reason to think (see later, p. 492) that there may be *sixteen* elements between barium and tantalum, of which fourteen are now known; if this be correct, the total number of elements in this period would be *thirty-two*.

(5) **A period composed of radioactive elements.**—The last period is a mere fragment, but includes four well-defined elements of known atomic weight, occupying alternate columns in the first octave of Period VII. and corresponding closely in their properties with the earlier members of these four families. These four elements are

Niton	Nt 222	Thorium	Th 234
Radium	Ra 226	Uranium	Ur 238

They differ from the lighter elements in that they are all RADIOACTIVE, *i.e.* they constantly liberate energy, which appears to be derived from the DISINTEGRATION of the atom. In the absence of any known synthetic process, a radioactive element must either decay very slowly, or must be reproduced continuously from some element of greater atomic weight. Uranium and thorium, the two elements of greatest atomic weight, show very slight radioactivity and are credited with a very slow rate of decay. All other radioactive substances appear to be derived, directly or indirectly, from these TWO PARENT ELEMENTS.

Some of these radioactive elements, or, more briefly, RADIO-ELEMENTS,[1] which enjoy a relatively long life, are found in appreciable quantities in the ores from which the parent-elements are derived, and can be separated by ordinary chemical methods. Thus the Bohemian pitchblende of Joachimsthal (crude U_3O_8) has given radium, polonium and actinium, in the uranium series, whilst thorium-

[1] Soddy, *The Chemistry of the Radio-Elements*, Parts I and II, London, 1914.

minerals have given mesothorium and radiothorium. Radium has been prepared in sufficient quantity for an ordinary determination of atomic weight, and the atomic weight of niton, a gaseous emanation produced during the decay of radium, has been determined by special modifications of ordinary methods (Gray and Ramsay, *Proc. Roy. Soc.*, 1911, A, **84**, 536–550). The chemical properties of other radio-elements can be inferred from the readiness or otherwise with which they are carried down with, or can be separated from, typical elements of smaller atomic weight. On these grounds *polonium* has been placed in the same family as tellurium, in a vacant space immediately after bismuth. In the same way, *actinium* is assigned to the same family as lanthanum, the first of the rare-earth elements, and probably occupies the vacant place between radium and thorium. The vacant place between thorium and uranium is perhaps occupied by one of the disintegration-products of uranium (UrX_2) with an average life of only 1·65 minutes; but no radioactive element, however transient, has been found to occupy the vacant places below cæsium and iodine in the families of the alkali-metals and the halogens respectively.

The total number of radio-elements that have been scheduled is about 40. These are all crowded into the narrow range from thallium (204) to uranium (238), covering only 12 places in the periodic classification of the elements. It is already occupied by three ordinary elements (thallium, lead and bismuth) in addition to the four radio-elements of known atomic weight (niton, radium, thorium and uranium). As none of the radio-elements are allied to the alkali-metals or the halogens there are really only 10 places, of which 7 are clearly occupied, leaving only 3 vacancies for the 36 remaining radio-elements. This crowding is explained by the existence of ISOTOPIC ELEMENTS, having similar (or perhaps identical) chemical properties (and

perhaps identical spectra), but differing in atomic weight by a very small number of units. The story of the rare-earth elements is, in fact, assumed to be repeated at almost every stage of the progress from thallium to uranium. The 40 radio-elements are distributed as follows :

Groups.	0.	I.	II.	III.	IV.	V.	VI.	VII.
Period VI.	—	—	—	Tl(3)	Pb(9)	Bi(4)	–(7)[1]	–(0)
Period VII.	Nt(3)	–(0)	Ra(4)	–(2)[2]	Th(5)	–(1)	Ur(2)	—

The ultimate products of disintegration appear to be helium and lead, but the existence is indicated of 5 isotopic forms of lead, devoid of radioactivity, in addition to 4 radioactive forms. The theory of isotopic elements has received confirmation from the fact that samples of "lead" derived from different sources have been found to show marked differences of atomic weight (p. 303)

C. Illustrations and Applications of the Periodic Law.

Periodicity of valency.—The ebb and flow of valency, which was described by Meyer in 1869 (p. 459), was discussed more fully in 1871 by Mendeléeff. He suggested (*loc. cit.* p. 141) that whilst the valency in the hydrides varied in the order indicated by Meyer (p. 459), the valency in the oxides was identical with the group-number, and varied in the order 1 2 3 4 5 6 7 8. The typical hydrides and oxides may therefore be tabulated as follows :—

Group	I.	II.	III.	IV.	V.	VI.	VII.	VIII.
	1	2	3	4	3	2	1	—
Hydrides[3]	LiH	—	BH_3	CH_4	NH_3	OH_2	FH	—
	NaH	[CaH_2[4]]	—	SiH_4	PH_3	SH_2	ClH	—

[1] Including polonium. [2] Including actinium.
[3] The hydrides of the earlier groups were not known to Mendeléeff.
[4] MgH_2 is not known.

	1	2	3	4	5	6	7	8
Oxides	Li_2O	BeO	B_2O_3	CO_2	N_2O_5	—	—	—
	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	Cl_2O_7	includes RuO_4, OsO_4

The "typical" hydrides and oxides at the head of Mendeléeff's tables were selected so as to fit into a regular series. Thus in Group I. the higher oxides of sodium and potassium, Na_2O_2 and K_2O_4, were rejected as "peroxides" (which did not form salts); but the typical salt-forming oxides, cupric oxide, CuO, and auric oxide, Au_2O_3, were also set aside in favour of the less stable oxides Cu_2O and Au_2O. The regular ebb and flow of valency with increasing atomic weight is, however, one of the most striking features of the periodic classification, and is set out in a very effective way in a chart attached to the Faraday Lecture which Mendeléeff delivered before the Chemical Society in 1889 (*Trans. Chem. Soc*, 1889, **55**, facing p. 656), where all the salt-forming oxides are tabulated in a series of well-defined waves. These regular changes of valency afford the sole justification for crowding the elements into eight groups, to which a new Group 0 is now added to include the inert gases of the helium family, which appear to be devoid of all combining-power. Moreover, no excuse, but those arising from identity of valency in selected compounds, can be given for including in the same column elements so diverse as sulphur and chromium, chlorine and manganese, or potassium and copper.

Periodicity of atomic volumes (L. Meyer, 1869).—The most remarkable feature of Lothar Meyer's paper is a diagram, which shows the ebb and flow of the ATOMIC VOLUME[1] of the solid elements as the atomic weight increases.

[1] The atomic volume = At. wt. × specific volume *or* At. wt. ÷ density.

"The curve . . . is divided by five maxima[1] into six sections, which have somewhat the form of a series of suspended chains, of which the second and third, and likewise the fourth and fifth, are similar to one another and occupy nearly equal portions of the horizontal axis.

"If one considers now the placing of the elements on the curve, one finds in corresponding places on similar portions of the curve elements with similar properties.

"All *easily melted*, *volatile* and *gaseous* elements are on *ascending* branches of the curve; those *fusible with difficulty* . . . on *descending* branches. . . near the minimum," where also are found the few elements that do not obey the law of Dulong and Petit, and so forth (*Ann. Chem. Pharm.*, 1870, **7**, Suppl., 359–363).

The chief feature of the atomic volume curve (Fig. 52, pp. 472—473), as Lothar Meyer points out, is its subdivision into a series of six catenary curves, which correspond with the first six periods of the modern table of the elements shown on p. 462. In the region covered by the two short catenaries II and III, Newlands's Law of Octaves may be applied with little modification, but the long catenaries IV and V (which form an equally close pair), indicate clearly that the interval between analogous elements is now much greater than an octave; the atomic volume curve thus makes the distinction between the short and long periods compulsory rather than optional.

The subsequent course of the curve is less certain. Lothar Meyer represented the whole of the elements from cæsium 133 to bismuth 208, as lying upon a single big catenary VI, corresponding with the big period VI of 32 elements shown in Tables 2, 3 and 4. Later writers, following Mendeléeff, have assumed that there are two long periods here, separated by a maximum occupied by an unknown alkali-metal. But there is no experimental

[1] Corresponding, in Lothar Meyer's curve, with the five alkali-metals.

evidence to support this view; on the contrary, the few measurements that have been made of the atomic volumes of rare-earth elements suggest that these would fall on a smooth curve running down gently from barium to tantalum and tungsten. It is remarkable that Lothar Meyer, with the help of his atomic volume curve should have anticipated at so early a date the modern classification of the elements into five complete periods and two fragments.

Later measurements have added a number of additional points to the curve. The cæsium peak has been realised experimentally, and the discovery of niton and radium has rendered probable the existence of yet another peak beyond the region covered by Lothar Meyer's curve. The most striking additions to the curve are points corresponding with 10 elements which are gaseous at ordinary temperatures.[1] Some risk attaches to the inclusion of liquefied gases in a comparison which is primarily concerned with solid elements, but the additional points are by no means devoid of interest. Thus the inert gases of Group 0 are found on the ascending portions of the curves, just below the alkali metals, with the solitary exception of helium, which rises above and dominates the point representing lithium. If the atomic volume were the only periodic property, it would be convenient to place the inert gases at the *ends* of Periods I to VI, instead of at the *beginning* of Periods II to VII, but the point is not important and there are definite advantages in placing the gases of zero valency at the beginning of the table. Liquid oxygen and fluorine fall into position on the second catenary, but liquid nitrogen produces a small secondary peak on the curve.

Periodicity of atomic heat (Dewar, 1913).—According to the Law of Dulong and Petit, the ATOMIC HEAT is a constant quantity which does not vary with the atomic weight of the element. No better illustration could be

[1] Chlorine was the only substance studied by Meyer in the *liquid* state.

given of the occasional absence of periodicity than the specific heat, which can be plotted against the atomic weight in the form of a rectangular hyperbola, or the atomic heat, which gives a straight line parallel to the axis of atomic weight. But this simple law ceases to hold at low tempera-

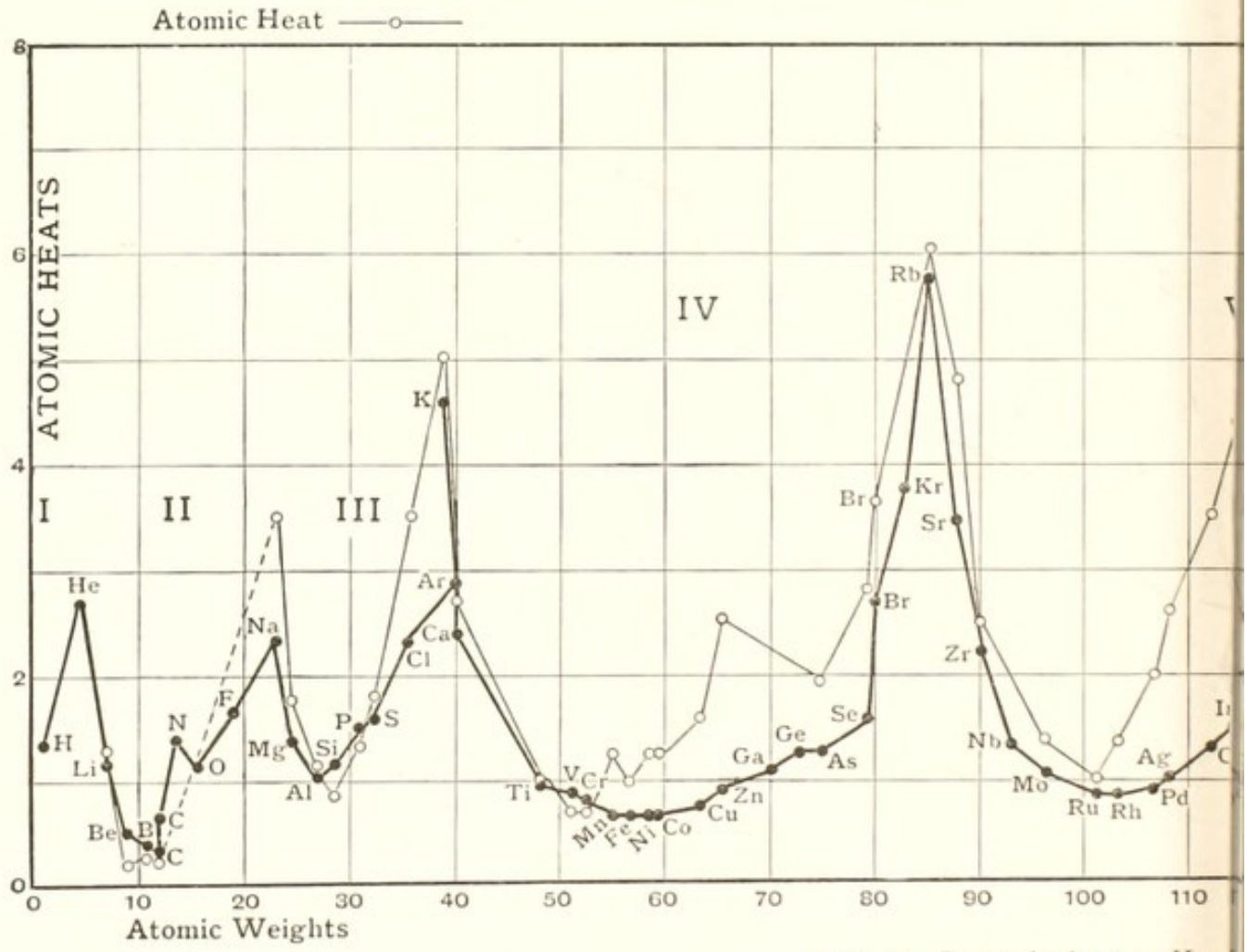


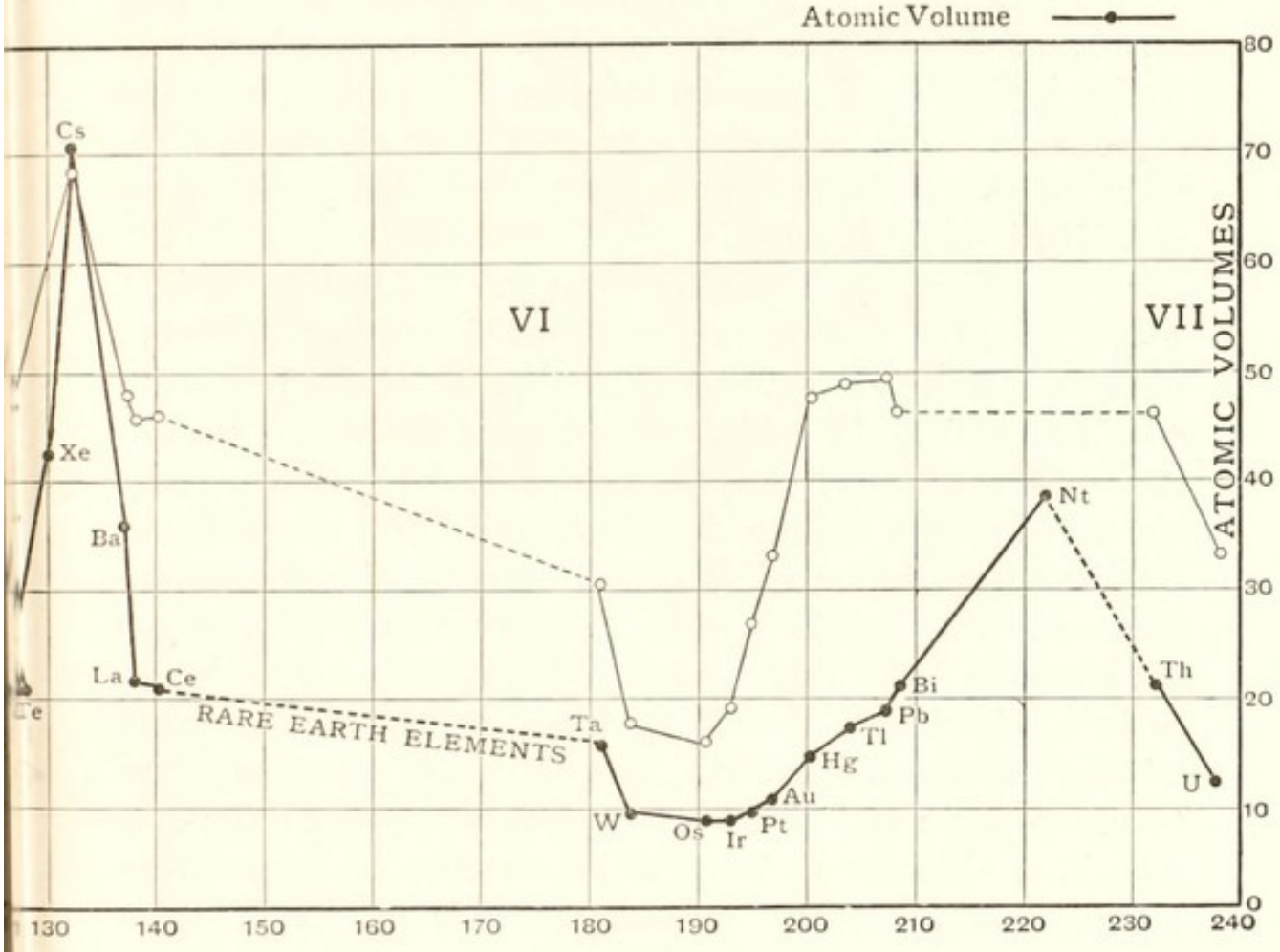
FIG. 52. DEWAR'S ATOMIC HEA

tures. Thus the average values and average errors for twenty-four elements from Mg to Bi (p. 365) are as follows:

Temperature.	Atomic heat.
100° to 20°C.	6·2 ± 0·2
20° to −188°C.	5·2 ± 0·5
−195° to −253°C.	2·2 ± 1·0

Dewar, to whom the measurements in the lowest range of

temperatures are due, points out that "when plotted in terms of their atomic weights, they reveal definitely a periodic variation resembling generally the well-known Lothar Meyer atomic volume curve for the solid state" (*Proc. Roy. Soc.*, 1913, A., **89**, 167). The striking character of this resem-



A CURVE OF ATOMIC VOLUMES.

blance is well shown in Fig. 52, above. The similarity of the two curves suggests that, at low temperatures, *equal volumes* of different elements have the same heat capacity, instead of equal numbers of atoms, as required at higher temperatures by the law of Dulong and Petit.

Correction of atomic weights. (*a*) **Valencies corrected or confirmed**.—When the equivalent of a metal has been

determined there is often some doubt as to its valency and therefore as to its atomic weight. If the metal can be separated, its specific heat will give the information required. If not, the isomorphism of its compounds is the most trustworthy guide; but there are so many exceptions to the law of isomorphism (*e.g.* Ag_2S and PbS are isomorphous) that further confirmation is often needed. It is just here that the periodic classification finds its most important practical application. The following examples show also the advantages of the periodic system over the earlier system of classification into families.

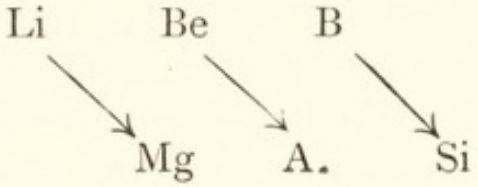
1. *Beryllium.* Equivalent 4·55. Atomic weight $4{\cdot}55 \times 2 = 9{\cdot}1$. The compounds of beryllium resemble those of aluminium, *e.g.* the hydroxide is soluble in caustic alkalis as well as in acids, the carbonate decomposes spontaneously at ordinary temperatures, the metal is prepared by electrolysing the fusible double fluoride and dissolves in alkalis with liberation of hydrogen. Beryllium was therefore assumed, like aluminium, to be tervalent, with atomic weight $3 \times 4{\cdot}55 = 13{\cdot}65$.[1] But there is no vacant place here in the periodic classification, and Newlands in his first complete table of the elements (p. 457) was obliged to place beryllium (with valency 2 and atomic weight 9) above magnesium, in a position which he had assigned a few months before (from a consideration of the individual family relationships) to lithium (p. 455). Mendeléeff (*Ann. Chem. Pharm.*, 1872, **8**, Suppl., p. 166) was able to justify the position thus assigned to beryllium by showing that

(*a*) there was a steady gradation in the series Li, Be, B;
(*b*) the differences between beryllium and magnesium were of the same character as in the corresponding members of the two adjacent families,

Li	Be	B
Na	Mg	Al

[1] Equivalent 6·8, if O = 8.

(*c*) the resemblance between beryllium and aluminium was similar to that which Newlands had detected between lithium and magnesium and that which is found between boron and silicon, thus :



The correctness of the smaller atomic weight was proved finally by determinations of the vapour-density of beryllium chloride, which gave the molecular weight as 81·7 (Be = 9, $Cl_2 = 71$) between 686° and 812° (Nilson and Pettersson, *Comptes rendus*, 1884, **98**, 988–990).

2. *Indium.* Equivalent 38·27. Atomic weight $3 \times 38{\cdot}27 = 114{\cdot}8$. This element, discovered by spectrum analysis [1] in the Freiburg zinc ores, by Reich and Richter in 1863, was regarded by Newlands as divalent, but was placed correctly by Lothar Meyer, with the help of his atomic volume curve. Mendeléeff (*loc. cit.* p. 178) confirmed the higher atomic weight for the element by measuring its specific heat, which he found to be 0·055 (agreeing closely with a number 0·057 given by Bunsen), whence the approximate atomic weight equals $6{\cdot}3 \div 0{\cdot}055 = 115$.

3. *Uranium.* Equivalent 59·6. Atomic weight $59{\cdot}6 \times 6 = 238{\cdot}5$. This element was regarded by Newlands as divalent, at. wt. $60 \times 2 = 120$. Lothar Meyer showed that it could not be placed on the atomic volume curve at this point, and suggested $Ur = 60 \times 3 = 180$. Mendeléeff (*loc. cit.* pp. 178–184), after tracing its analogies with chromium, molybdenum and tungsten, assigned to it the atomic weight $60 \times 4 = 240$. Its recently-discovered radioactivity has fully justified the view that uranium should be placed at the end

[1] Compare thallium, discovered in pyrites by Crookes (1861) and gallium (p. 477), discovered in zinc blende from the Pyrenees by Boisbaudran (1875).

of the table as the element having the greatest atomic weight that is known.

Correction of atomic weights. (*b*) **Equivalents corrected.**—Certain elements, which were found to be misplaced, when arranged strictly in the order of their atomic weights, could be restored to their own families by assuming smaller errors, due to the use of inexact equivalents. Thus gold (196·2) was placed after osmium, iridium and platinum (198·6, 196·7, 196·7); later measurements have proved the correctness of this sequence, thus :

Os	Ir	Pt	Au
190·9	193·1	195·2	197·2

On the other hand, three cases are known in which the atomic weights refuse to conform to the order suggested by the periodic classification. These are

A	K	Co	Ni	Te	I
39·88	39·10	58·97	58·68	127·5	126·92

The significance of these deviations is discussed below (p. 494).

Prediction of missing elements.—Mendeléeff was so convinced of the validity of the periodic law that, unlike Newlands and Lothar Meyer, he altered atomic weights that did not conform to his system and made detailed predictions of the properties of unknown elements, which could be verified or disproved by experiment. Missing elements, were named by prefixing the Sanskrit numerals *eka-*, *dwi-*, *tri-* to the element in the odd or even series below which vacancies were found. Detailed predictions were made of the properties of

ekaboron = 44, *ekaaluminium*[1] = 68, *ekasilicon* = 72.

[1] Mendeléeff gave a more detailed prediction of the properties of ekaaluminium (*Comptes rendus*, 1875, **81**, 970–971) after the discovery of gallium had been announced by Lecoq de Boisbaudran.

These were vindicated in a striking way by the discovery of the three patriotically-named elements

scandium,	*gallium*,	*germanium*,
(Nilson, 1879)	(Boisbaudran, 1875)	(Winkler, 1886)

Some of the chief predictions, and their verification, are set out below. In the case of scandium or ekaboron, the properties of the metal and its anhydrous chloride were predicted by Mendeléeff, but are still unknown. The narrative shows the most important points of agreement between Mendeléeff's predictions and the observed properties of the three elements.

	Ekaboron.	Scandium.
Atomic Weight	Eb = 44	Sc = 44·1
Formula of Oxide	Eb_2O_3	Sc_2O_3
Density of Oxide	3·5	3·8

The oxide is a weak base, intermediate between alumina and magnesia. It forms a gelatinous hydrate, carbonate and phosphate. The sulphate is soluble (but less so than aluminium sulphate). The chloride is more easily hydrolysed than $MgCl_2$, liberating HCl. The salts are colourless.

	Ekaaluminium.	Gallium.
Atomic Weight	68	69·9
Density	5·9	5·93
Melting-point	"low temperature"	30·1° C.
Formula of Oxide	Ea_2O_3	Ga_2O_3
Density of Oxide	5·5	—

The metal is not volatile; it is attacked slowly by air and water, by acids and by alkalis. The oxide being more basic than Al_2O_3 and less basic than MgO, it is precipitated by barium carbonate. The gelatinous hydroxide is soluble in acids and alkalis. The sulphide is precipitated by sulphuretted hydrogen and is not

soluble in ammonium sulphide. The metal forms a soluble trichloride, a soluble sulphate and an alum.

	Ekasilicon.	Germanium.[1]
Atomic Weight	Es = 72	Ge = 72·5
Density	Es, 5·5	Ge, 5·469
Density of Oxide	EsO_2, 4·7	GeO_2, 4·703
Density of Chloride	$EsCl_4$, 1·9	$GeCl_4$, 1·887
B.P. of Chloride	$<$100°	86°C.
Density of Ethide	$Es(C_2H_5)_4$, 0·96	$Ge(C_2H_5)_4$, $<$1
B.P. of Ethide	160°	160°

The metal, prepared by reducing the oxide, or by the action of sodium on the double fluoride, is not easily fusible, but burns to a very refractory white dioxide. The oxide is feebly basic; on adding acid to its alkaline solutions, it may remain in solution as a soluble hydrate or be precipitated as an insoluble metahydrate. The disulphide is insoluble in water, but dissolves in ammonium sulphide. The fluoride, like the chloride, is a volatile liquid.

In the range covered by the rare-earth elements Mendeléeff's predictions were less successful, thus Ekacæsium, Ec = 175, and Ekaniobium, En = 146, are still unknown; but Mendeléeff was struck by "the absence . . . of almost a whole long period (beginning from Ce = 140)" and concluded that this "can scarcely be regarded as accidental and probably has its origin in the nature of the elements" (*Ann. Chem. Pharm.*, 1872, **8**, Suppl., 205). On the other hand his Ekamanganese, Em = 100, and Trimanganese, Tm = 190, are still to be looked for, whilst his Dwicæsium, Dc = 220, and Ekatantalum, Et = 235, correspond with two of the three gaps at the commencement of the radioactive Period VII.

Secondary relationships in the periodic system.—The classification of the elements by vertical columns into groups and families has come to be regarded as the

[1] For a more detailed comparison, see Freund, *Study of Chemical Composition*, pp. 480–481.

dominant property of the periodic system, and has been made the basis for the descriptive portion of many text-books. The undue emphasis of this property, which is mainly an expression of valency-relationships, has created an artificial atmosphere, in which the close similarity between manganese and iron or between the compounds of copper and mercury, is overlooked in favour of a strained analogy between manganese and chlorine, or between cuprous chloride and common salt. In the same way the two combustible elements, sulphur and phosphorus, are only rarely mentioned together, since they have the misfortune to differ in valency.

For this fault Mendeléeff cannot be blamed, since he insisted quite as much on the analogy between adjacent elements in the same *horizontal* series as on that between alternate elements in the same *vertical* group and used both of these "atomic analogies" in predicting the properties of missing elements. He was also careful to point out the relationships which are observed between certain elements lying on the same *diagonal* line (see above, p. 475.).

Some of these *diagonal* analogies are strong enough to overcome the limitations imposed by unequal valencies, as in the case of boron and silicon, their fluorides and double fluorides, BF_3, SiF_4, KBF_4, K_2SiF_6, and the glass-forming borates and silicates. In other cases valencies are developed in defiance of the simpler rules of periodicity, as when boron becomes quadrivalent in the hydrides B_2H_6 and B_4H_{10}, as if in protest against its separation from the non-metals carbon and silicon. Many similar cases might be quoted of unexpected resemblance between elements lying diagonally on lines sloping down from left to right in the table.

The importance of the *horizontal* relationships is seen most clearly in Mendeléeff's group of transition-elements. Metallurgists will recognise in the series

V, Cr, Mn, Fe, Co, Ni,

almost the whole of the elements, apart from carbon, silicon, and tungsten, which are used in the manufacture of modern special-steels. Equally remarkable is the series of isomorphous bivalent sulphates studied by Mitscherlich (p. 372),

$$MnSO_4,\ FeSO_4,\ CoSO_4,\ NiSO_4,\ CuSO_4,\ ZnSO_4,$$

which run right across a series of columns labelled VII, VIII, I, and II, and headed by the symbols R_2O_7, RO_4 R_2O and RO. The horizontal relationship reaches its climax in the case of the rare-earth elements which run consecutively, with identical valency and almost identical properties, over a range of 40 units of atomic weight.

If injustice is not to be done to the memory of Mendeléeff, it is important that these secondary relationships should be recognised and emphasised.

D. Atomic Weights and Atomic Numbers.

Prout's hypothesis (1815).—Almost immediately after the first atomic weights had been determined, attempts were made to discover numerical relationships between them. The most important of these, now known as PROUT'S HYPOTHESIS, was put forward anonymously in a paper "On the Relation between the Specific Gravities of Bodies in their Gaseous State and the Weights of their Atoms" (*Annals of Philosophy*, 1815, **6**, 321–330). It is generally expressed by a statement that

"*The atomic weights of the elements are exact multiples of the atomic weight of hydrogen.*"

The view first put forward by Prout was :

"That all the elementary numbers, hydrogen being considered as 1, are divisible by 4, except carbon, azote, and barytium [1], and these are divisible by 2" (*loc. cit.* p. 330).

[1] *i.e.* barium.

This view was supported by tables showing the actual densities of various gases relatively to hydrogen, and the hypothetical densities of many solid elements and compounds; from these the "specific gravities" or equivalents of the elements were deduced as a series of integral numbers, thus:

H	C	N	P	O	S	Ca	Na	Fe	Zn	Cl	K	Ba	I
1	6	14	14	16	16	20	24	28	32	36	40	70	124

Hypothetical values for 23 other elements were all shown as multiples of 4.

Prout on the specific gravity of hydrogen (1815).—Whilst the idea that all the atomic weights are even multiples of the atomic weight of hydrogen is obviously untrue, credit must be given to Prout for determining for the first time the correct density of hydrogen, by an indirect method, as follows:

"The specific gravity of hydrogen, on account of its great levity, and the obstinacy with which it retains water, has always been considered as the most difficult to take of any other gas. . . . It occurred to me that its specific gravity might be much more accurately obtained by calculation from the specific gravity of a denser compound into which it entered in a known proportion. Ammoniacal gas appeared to be the best suited to my purpose, as its specific gravity had been taken with great care by Sir H. Davy, and the chance of error had been much diminished from the slight difference between its specific gravity and that of steam. . . . The specific gravity of ammonia, according to Sir H. Davy, is ·590164, atmospheric air being 1·000. We shall consider it as ·5902. . . . Now ammonia consists of three volumes of hydrogen and one volume of azote condensed to two volumes. Hence the specific gravity of hydrogen will be found to be ·0694,[1] atmospheric air being 1·0000. It will be also observed that the specific gravity of

[1] "Let x = sp. gr. of hydrogen, then $\frac{3x + ·9722}{2} = ·5902$.

Hence $x = \frac{1·1804 - ·9722}{3} = ·0694$."

oxygen as obtained above is just 16 times that of hydrogen as now ascertained, and the specific gravity of azote just 14 times"[1] (*loc. cit.* p. 322).

Hydrogen as "protyl" (Prout 1816).—This correct determination of the density of hydrogen[2] was essential for the development of the stimulating and suggestive hypothesis of integral[3] atomic weights, which led Prout to conclude that :

"If the views we have ventured to advance be correct, we may almost consider the πρώτη ὕλη of the ancients to be realised in hydrogen ; an opinion, by the by, not altogether new. If we consider this to be the case. . . the specific gravities, or absolute weights of all bodies in the gaseous state, must be multiples of the specific gravity or absolute weight of the first matter (πρώτη ὕλη), because all bodies in a gaseous state which unite with one another unite with reference to their volume" (*Annals of Philosophy*, 1816, **7**, 113).

Atomic weights in relation to oxygen.—Two years before Prout's paper appeared, **Thomas Thomson** pointed out (*Annals of Philosophy*, 1813, **2**, 114) that if *oxygen* be taken as unity "there are eight atoms of simple bodies whose weights are denoted by whole numbers ; namely

Oxygen	1	Sulphur	2	Potassium	5	Arsenic	6
Copper	8	Tungsten	8	Uranium	12	Mercury	25."

The first of these ratios was confirmed by Dumas, but most of the others are obviously incorrect. Dumas concluded that :

"If oxygen be represented by 8, sulphur must be represented by 16. There exists then between these equivalents the simple ratio 1 : 2, of which organic chemistry presents so many examples" (*loc. cit.* p. 148).

[1] "1·11111 ÷ ·0694 = 16 and ·9722 ÷ ·0694 = 14."

[2] Thomson in 1813 using an earlier value for the density of hydrogen, had only been able to find one integral multiple.

[3] No longer even numbers in the second (1816) paper.

The average of five experiments actually gave the ratio 8 : 16·01, agreeing closely with the modern ratio *oxygen* : *sulphur* = 16 : 32·07. Dumas (still using equivalents rather than atomic weights) also gave

Co : Ni : Sn = 29·5 : 29·5 : 59 = 1 : 1 : 2 and
N : Fe : Cd = 14 : 28 : 56 = 1 : 2 : 4 ;

these numbers may be compared with Crookes' suggestion (*Phil. Trans.*, 1908, A. **209**, 44) that

B : Sc : Y : Yb = 11·0 : 44·1 : 89·0 : 173·0 = 1 : 4 : 8 : 16

No special importance is now attached to the fact that the atomic weight tables do actually show some very close multiples of the atomic weight of oxygen, or that this number, as Newlands pointed out in 1864 (*The Periodic Law*, p. 6) is even more common amongst the differences ; thus, when O = 16,

S = 32·07 Ti = 48·1 Br = 79·92 Mo = 96·0
S – O = 16·07 K – Na = 16·10 Na – Li = 16·06, etc.

It is, however, remarkable that integral atomic weights are much more common when O = 16 and H = 1·008 than when H = 1 and O = 15·88.

Experiments to test Prout's hypothesis.—Thomson, who gave to Prout's paper the place of honour in his annual review of the progress of Chemistry for 1815 (Thomson's *Annals of Philosophy*, 1816, **7**, 17) confirmed Prout's hypothesis by a series of experiments carried out between 1819 and 1825 (*An Attempt to Establish the First Principles of Chemistry by Experiment*, London, 1825). But he appears to have had an unconscious bias in favour of those experiments which gave "correct" or integral values for the atomic weights. In the words of Berzelius :

"He reduces all the numbers found by his predecessors to the nearest multiple of the atomic weight of hydrogen, calculates therefrom the atomic weights of their compounds, and precipitates them in weighed quantities corresponding with the corrected atomic weights, when they always

decomposed one another exactly." Berzelius, whose own numbers had been criticised adversely by Thomson,[1] added that "This investigation belongs to that very small class, from which science can derive no advantage whatever . . . and the greatest consideration which contemporaries can show to the author is to treat this work as if it had never appeared" (*Jahresbericht*, 1827, **6**, 77).

But Prout's hypothesis was not to be got rid of so easily. Dumas and Stas (p. 150) by bringing down the atomic weight of carbon from 12·25 to 11·97 (H = 1) obtained striking evidence that Berzelius's deviations from integral ratios might be due largely to unsuspected experimental errors. So, also, Dumas's experiments on the composition of water (p. 127) which brought down the atomic weight of oxygen from 16·03 to 15·96, left it still very close to an integral ratio. Many years later, after completing his experiments on the equivalents of the elements, **Dumas** concluded "that the equivalents of the elements are often integral multiples of the equivalent of hydrogen taken as unity," but that in the case of chlorine[2] and certain other elements "the unit with which they must be compared is only 0·5 of the equivalent of hydrogen" (*Ann. Chim. Phys.*, 1859, **55**, 141). **Stas**, on other hand, who for many years devoted all his leisure to the elucidation of this problem, began his experiments with "an almost absolute confidence in the exactness of the law of Prout," but when they were completed had "arrived at the complete conviction, the entire certainty, so far as certainty is possible on such a subject, that the law of Prout . . . is only an illusion, a pure hypothesis definitely contradicted by experiment" (*Works*, I. 311).

[1] "Berzelius's numbers are in general very near approximations to the truth; though I am persuaded that in very few instances he has actually reached it" (*First Principles*, I. xvii.). For a fuller discussion see Mallet's "Stas Memorial Lecture" (*Trans. Chem. Soc.*, 1893, **63**, 1–56), and Freund, *Chemical Composition*, chap. xix.

[2] Following Pelouze, *Actes Soc. Helv. Sci. Nat.*, 1843, 64.

Prout's hypothesis and the law of probabilities.—Although it is universally admitted that the atomic weights do not conform to Prout's hypothesis, and cannot be calculated or corrected by means of that hypothesis, the frequent approximation of the atomic weights towards integral numbers shows clearly that, as Stas admitted in 1887, "there must be something in it" (Mallet, *loc. cit.* p. 35). Marignac, in reviewing Stas's paper, pointed out that the average difference between Stas's nine atomic weights and those required by Prout's hypothesis (as modified by Pelouze and by himself) was only 0·056 (*Geneva Archives*, 1860, **9**, 105). He concluded that the law of Prout, like the laws of Boyle and of Charles, had been proved to be inexact, but that such laws had still a practical value in supplying useful approximations for everyday use, and were theoretically important as affording an ideal standard or rule, the deviations from which demanded very careful study.

The same idea has been expressed in a mathematical form by Strutt in a paper "On the Tendency of the Atomic weights to approximate to Whole Numbers" (*Phil. Mag.*, 1901, [vi], **1**, 311–314). Taking a series of eight atomic weights given by Richards to three decimal places, he showed that the sum of the differences from integral numbers was 0·809, three-fourths of this difference being due to the two elements chlorine and potassium. The probability of this total deviation is 0·001159, or about 1 chance in 1000, so that "the atomic weights tend to approximate to whole numbers far more closely than can reasonably be accounted for by any accidental coincidence."

Newlands on atomic numbers (1864 to 1878).—Prout's hypothesis is perhaps responsible for the introduction of the idea of ATOMIC NUMBERS, *i.e.* of representing the elements by a series of integral numbers. The publication by Newlands, in 1864, of a table showing the elements in the order of their atomic weights (*Periodic Law*, p. 7) was followed

within a month by the addition to the table of a series of consecutive numbers (p. 457), and by the discovery of the Law of Octaves as applied to these integers.

In these early atomic numbers no space was left for undiscovered elements and the correctness of the numbers could only be checked by the vague indications of the Law of Octaves. Newlands attempted to overcome this difficulty by tabulating the ratios of the atomic weights to the atomic numbers and showing that the ratios increased from 2·5 to 2·75 to 3 to 4 approximately (*Periodic Law*, p. 15). But it was not until Mendeléeff's prediction of missing elements had been justified by the discovery of gallium in 1875 that Newlands attempted a more open spacing of the atomic numbers. Two tables were published in 1878 (*Periodic Law*, facing p. 32) to illustrate the new system of atomic numbers. In the first the atomic weights were divided by 2·3, so that Na = 10; the elements were arranged in sixteen octaves, separate columns being assigned to hydrogen, to the groups of transition elements, and at the end of the table to the two elements thorium and uranium, whilst two octaves were left vacant in the region now occupied by the rare-earth elements. In this scheme of atomic numbers

$$\mathrm{H}(1) = 0{\cdot}435,\ \mathrm{Au}(86) = 85{\cdot}65,\ \mathrm{Ur}(105) = 104{\cdot}35,$$

the number in brackets being the atomic numbers, and the numbers in italics the reducd atomic weights; the reduced atomic weights and the atomic numbers usually agreed within a few units and there were forty vacant spaces. In the second table the atomic numbers were divided by 2·37, so that Cl = 15; hydrogen, and the octaves beginning with sodium and lithium, were followed by nine columns of ten elements, the transition elements being placed below the octaves in the longer columns. In this scheme

$$\mathrm{H}(1) = 0{\cdot}422,\ \mathrm{Au}(86) = 83{\cdot}12,\ \mathrm{Ur}(101) = 101{\cdot}27;$$

the agreement between the reduced atomic weights and the atomic numbers was closer and the number of vacant spaces was reduced to thirty-seven.

Experimental determination of atomic numbers.—Atomic numbers have acquired great importance in recent years, owing to the discovery that several properties of the atom, which are not directly related to the irregularly-distributed atomic weights, are related in a very simple way to integral ATOMIC NUMBERS closely analogous with those put forward by Newlands in 1878, but showing seven places less between hydrogen and gold. Amongst these properties are

(1) The scattering of α-particles by gases.
(2) The absorption of X-rays by different elements.
(3) The high-frequency spectra of the elements.

Of these methods, the last is the simplest to explain, and appears to give the most exact results: it may therefore be described as a type of the new methods of determining atomic numbers experimentally.

Moseley (1914) on the high-frequency spectra of the elements.—When X-rays fall upon a crystal, a diffraction-spectrum is produced, in just the same way as when ordinary light falls upon a ruled diffraction-grating. The two phenomena are very similar to one another, but in the case of X-rays the linear dimensions are about 10,000 times smaller. Thus while the yellow light of sodium consists of two radiations of wave length 5890 and 5896×10^{-8} cm., the radiation from a rhodium target in an X-ray bulb gives radiations of wave-length $0{\cdot}54$ and $0{\cdot}61 \times 10^{-8}$ cm., the latter in its turn being a doublet of wave-lengths $0{\cdot}614$ and $0{\cdot}619 \times 10^{-8}$ cm. (Bragg, *Royal Institution Lecture*, June 5, 1914). The nature of the X-ray spectrum depends on the nature of the elements composing the target (Moseley, *Phil. Mag.*, Dec. 1913, **26**, 1024–1034; April, 1914, **27**, 703–713). The

spectra (Fig. 53) are extremely simple, consisting, in the case of fourteen elements from aluminium to zinc, of two principal lines, decreasing in wave-length and increasing in frequency as the atomic weight increases. The increase of

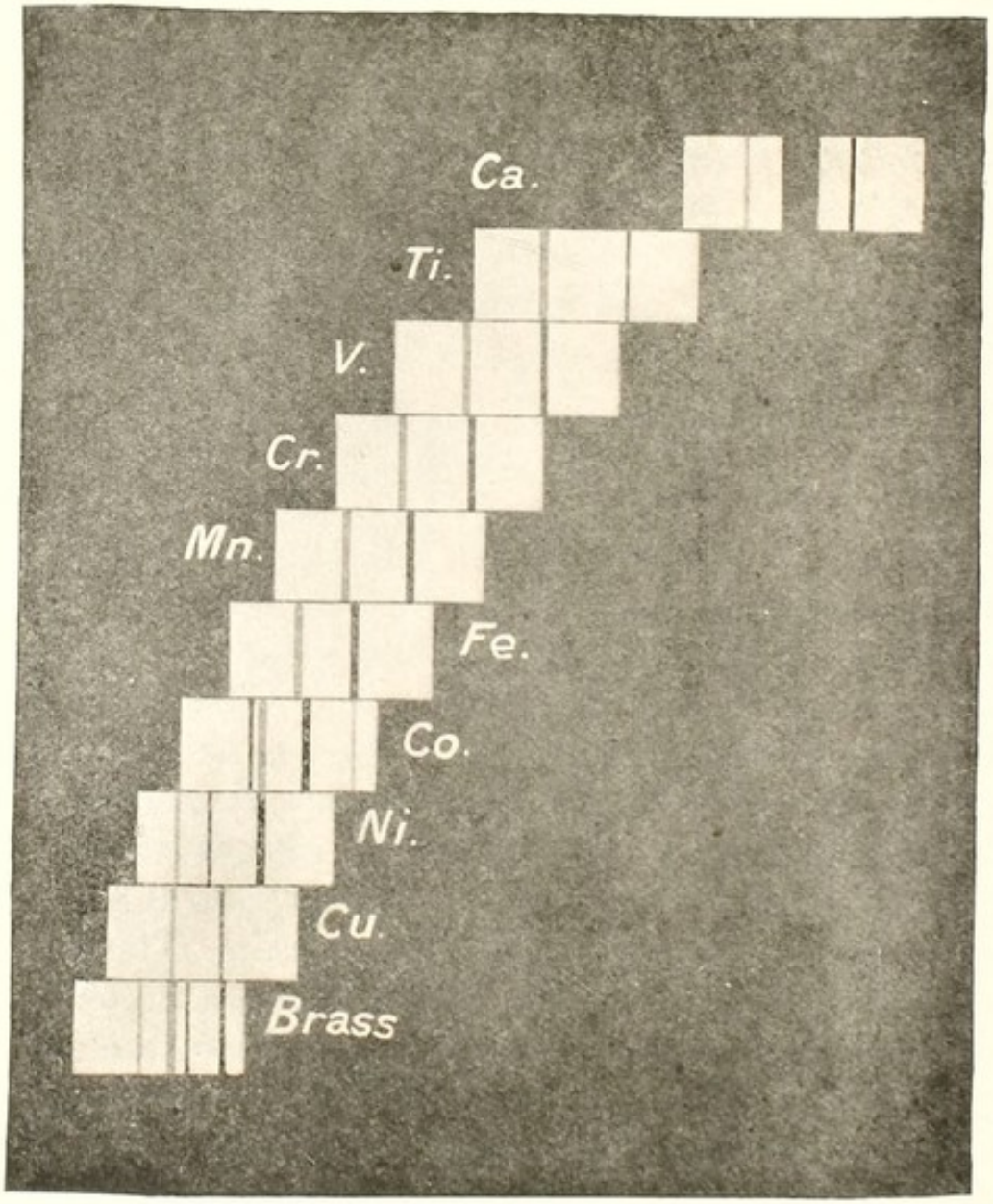


FIG. 53.——HIGH-FREQUENCY SPECTRA.

frequency is perfectly regular, the square-root of the frequency increasing by equal amounts between consecutive elements; thus by selecting a suitable constant the square-roots of the wave-lengths can be plotted out against a series of integral numbers (Fig. 54). The exactness of the relationship is

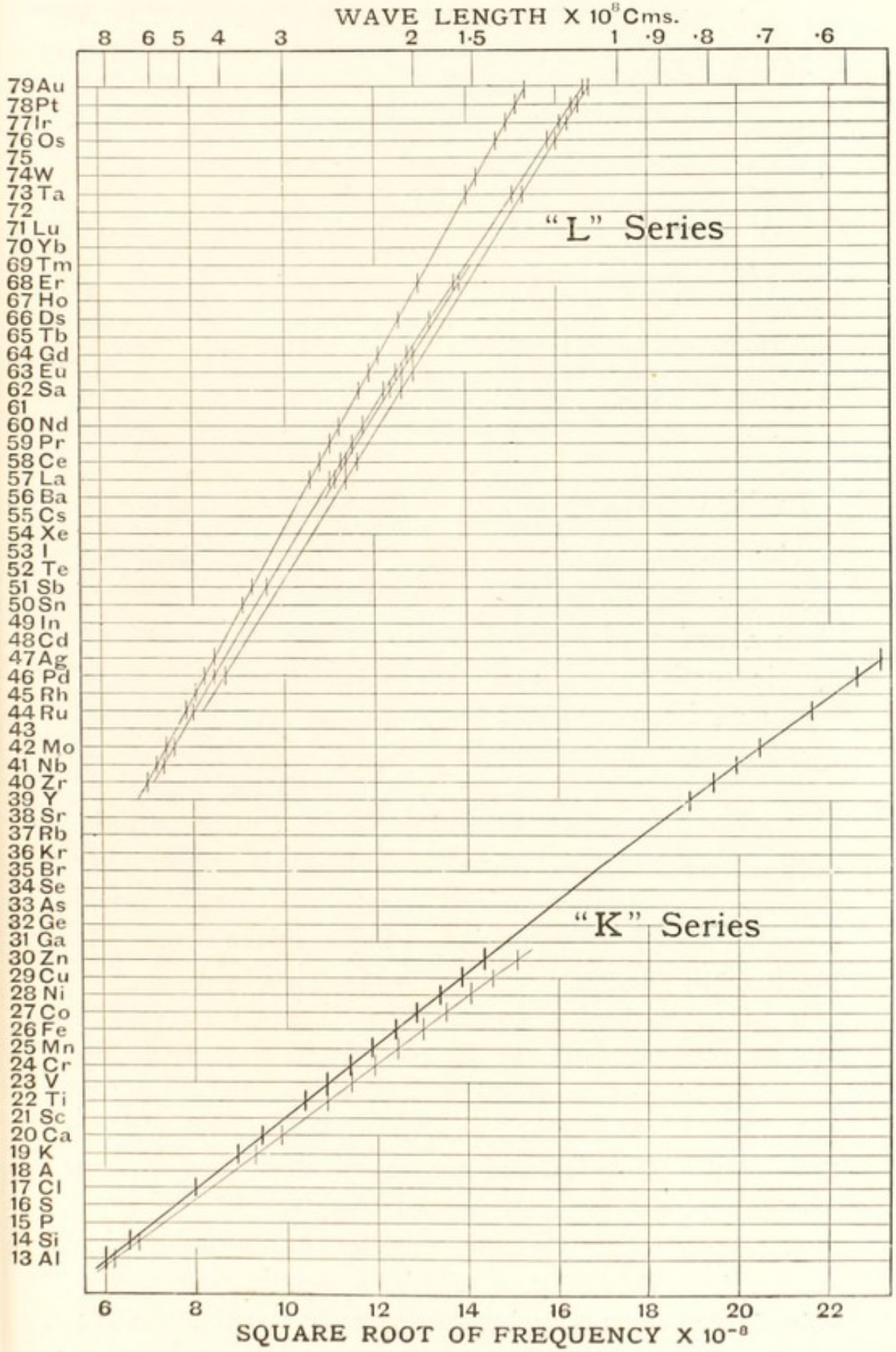


FIG. 54.—HIGH FREQUENCY SPECTRA OF THE ELEMENTS.

shown in the following table (Moseley, *Phil Mag.*, Dec. 1913, **26**, 1028):

Element.	Wave-lengths. $\times 10^{-8}$.		Ratio.	Q.	Atomic Number.	Atomic Weight.
Ca	3·094	3·368	1·089	19·00	20	40·07
Sc	—	—	—	—	21	44·1
Ti	2·524	2·758	1·093	20·99	22	48·1
V	2·297	2·519	1·097	21·96	23	51·0
Cr	2·093	2·301	1·100	22·98	24	52·0
Mn	1·918	2·111	1·101	23·99	25	54·93
Fe	1·765	1·946	1·103	24·99	26	55·84
Co	1·629	1·798	1·104	26·00	27	58·97
Ni	1·506	1·662	1·104	27·04	28	58·68
Cu	1·402	1·549	1·105	28·01	29	63·57
Zn	1·306	1·445	1·106	29·01	30	65·37

In this table $Q = \left\{ \frac{\nu}{\frac{3}{4}\nu_0} \right\}^{\frac{1}{2}}$, where ν is the frequency of the line of longer wave-length and ν_0 is a constant derived from the study of ordinary series spectra. It will be seen that Q gives a series of integral numbers one unit less than the atomic numbers reckoned from H 1, He 2, Li 3, etc., that it leaves an integer vacant for scandium, and finally that the Q-numbers show precisely that exact relationship which Prout postulated incorrectly in the case of the atomic weights. It is further of interest to notice that the value of Q is one unit greater for nickel than for cobalt, although nickel has the smaller atomic weight, thus justifying Mendeléeff's arrangement of the transition-elements in the order Cr, Mn, Fe, Co, Ni, Cu, Zn.

This "K series" of spectra is continued up to Ag(47) = 107·88. But already at Zr(40) = 90·6, an "L series" of spectra begins; this is more complex, containing some five chief lines, but the same laws apply to these lines as to the two lines of the K series, and the atomic numbers can thus be carried forward as far as Au(79) = 197·2.

A complete list of atomic numbers and atomic weights is shown in Table F, p. 491. The atomic numbers determined experimentally by Moseley in 1913 and 1914 are

shown in heavy type. It should be noticed that Cl(17) and K(19), both determined experimentally, leave a gap for Ar(18), although argon has a greater atomic weight than potassium ; corresponding data for tellurium and iodine are not given. In the case of the rare earths, all the numbers from 57 to 72 were observed, either with pure preparations or with mixed fractions, with the exception of 61 and 72, which appear to be entirely wanting in these materials.

TABLE F.—Atomic Numbers and Atomic Weights.

I	1	Hydrogen	H	1·008			
II	2	Helium	He	3·99	III	10 Neon	Ne 20·2
	3	Lithium	Li	6·94		11 Sodium	Na 23·00
	4	Beryllium[1]	Be	9·1		12 Magnesium	Mg 24·32
	5	Boron	B	11·0		**13** Aluminium	Al 27·1
	6	Carbon	C	12·00		**14** Silicon	Si 28·3
	7	Nitrogen	N	14·01		15 Phosphorus	P 31·04
	8	**Oxygen**	**O**	**16**		16 Sulphur	S 32·07
	9	Fluorine	F	19·0		**17** Chlorine	Cl 35·46
IV	18	Argon	Ar	39·88	V	36 Krypton	Kr 82·92
	19	Potassium	K	39·10		37 Rubidium	Rb 85·45
	20	Calcium	Ca	40·07		38 Strontium	Sr 87·63
	21	Scandium	Sc	44·1		**39** Yttrium	Yt 89·0
	22	Titanium	Ti	48·1		**40** Zirconium	Zr 90·6
	23	Vanadium	V	51·0		**41** Niobium[2]	Nb 93·5
	24	Chromium	Cr	52·0		**42** Molybdenum	Mo 96·0
	25	Manganese	Mn	54·93		43 —	— —
	26	Iron	Fe	55·84		**44** Ruthenium	Ru 101·7
	27	Cobalt	Co	58·97		**45** Rhodium	Rh 102·9
	28	Nickel	Ni	58·68		**46** Palladium	Pd 106·7
	29	Copper	Cu	63·57		**47** Silver	Ag 107·88
	30	Zinc	Zn	65·37		48 Cadmium	Cd 112·40
	31	Gallium	Ga	69·9		49 Indium	In 114·8
	32	Germanium	Ge	72·5		**50** Tin	Sn 119·0
	33	Arsenic	As	74·96		**51** Antimony	Sb 120·2
	34	Selenium	Se	79·2		52 Tellurium	Te 127·5
	35	Bromine	Br	79·92		53 Iodine	I 126·92

[1] Or Glucinum Gl. [2] Or Columbium Cb.

TABLE F.—ATOMIC NUMBERS AND ATOMIC WEIGHTS—*cont.*

VI	54	Xenon	Xe 130·2		72	—	— —
	55	Cæsium	Cs 132·81		**73**	Tantalum	Ta 181·5
	56	Barium	Ba 137·37		**74**	Tungsten	W 184·0
RARE EARTH ELEMENTS	**57**	Lanthanum	La 139·0		75	—	— —
	58	Cerium	Ce 140·25		**76**	Osmium	Os 190·9
	59	Praseodymium	Pr 140·6		**77**	Iridium	Ir 193·1
	60	Neodymium	Nd 144·3		**78**	Platinum	Pt 195·2
	61	—	— —		**79**	Gold	Au 197·2
	62	Samarium	Sa 150·4		80	Mercury	Hg 200·6
	63	Europium	Eu 152·0		81	Thallium	Tl 204·0
	64	Gadolinium	Gd 157·3		82	Lead	Pb 207·10
	65	Terbium	Tb 159·2		83	Bismuth	Bi 208·0
	66	Dysprosium	Ds 162·5		84	—	— —
	67	Holmium	Ho 163·5		85	—	— —
	68	Erbium	Er 167·7	VII	86	Niton	Nt 222·4
	69	Thulium	Tm 168·5		88	Radium	Ra 226·4
	70	Ytterbium	Yb 172·0		90	Thorium	Th 232·4
	71	Lutecium	Lu 174·0		92	Uranium	Ur 238·5

Atomic weights and atomic numbers. Total number of missing elements.—The discovery of a real system of integral atomic numbers has supplied just that element of mathematical exactness which was lacking in the relationships put forward by Prout, by Döbereiner, by Dumas, and others. The agreement between these atomic numbers and the consecutive numbering of the elements is such that every confidence may be felt in an enumeration of the elements on this new basis. Thus between Ba(56) and Ta(73) there are sixteen places, of which fourteen are filled by rare-earth elements of known atomic weight; Mendeléeff was probably wrong when he assumed nineteen[1] vacancies in this interval. Apart from one gap at 61 in the rare earth series, and one gap at 72 between the rare-earth elements and tantalum, the new atomic numbers admit only two vacancies between aluminium and gold, namely, Mendeléeff's

Ekamanganese(43) = 99 (?) between Mo(42) and Ru(44)
Trimanganese (75) = 187 (?) between W(74) and Os(76).

[1] The discovery of the gases of the helium family would have increased Mendeléeff's estimate to *twenty*.

There are, however, two vacant places, 84 and 85, between Bi(83) and Nt(86), and three others, 87, 89, 91, between Nt(86), Ra(88), Th(90), U(92), in a region in which the atomic numbers have not yet been determined by experiment. The total number of vacancies between hydrogen and uranium is thus increased to *nine*.[1]

The existence of two light gases, "coronium" and "nebulium," between hydrogen and helium has been suggested by Rydberg (see *Phil. Mag.*, July, 1914, **28**, 139) on the following grounds. The two short periods, from Li to Ne and Na to Ar, contain $2 \times 8 = 4^2$ elements. The two long periods, from K to Kr and Rb to Xe contain $2 \times 18 = 6^2$ elements. These should be followed by two very long periods containing $2 \times 32 = 8^2$ elements, of which 27 out of 32 are known in the range from Cs to Nt, and 3 beyond. On the other hand, the two short periods should be preceded by periods containing $2 \times 2 = 2^2$ elements, so that helium would be the fourth [2] element instead of the second.

The existence of a series of integral atomic numbers proves "that there is in the atom a fundamental quantity, which increases by regular steps as we pass from one element to the next. This quantity can only be the charge on the central positive nucleus" (Moseley *Phil. Mag.*, 1913, **26**, 1031). The atomic weights are determined mainly by the atomic numbers, but there is evidently some secondary factor at work which may modify the atomic weight by at least a unit. Thus in the two short periods the atomic weights are just twice the atomic numbers in the case of He, C, N, O, Ne, S; but they are one unit

[1] Not counting the hypothetical gases "coronium" and "nebulium" of atomic weight perhaps less than hydrogen.

[2] On these grounds Rydberg suggests that the atomic numbers should be converted into ORDINALS by adding two units to all the elements but hydrogen (*Phil. Mag.*, July, 1914, **28**, 144). This would not affect Moseley's data, but measurements of the scattering of X-rays by gases indicate consecutive numbers for hydrogen and helium (*Phil. Mag.*, Oct. 1914, **28**, 631); this difficulty could be overcome by placing the two hypothetical gases before hydrogen instead of after.

less for hydrogen, and almost exactly a unit greater for Li, Be, B, F, Na, Al, P. The nature of this secondary factor is not yet known, but if it exists, there is no reason why the atomic weights should not occasionally overlap, as in the case of Ar and K, Co and N, Te and I; it need not therefore be assumed that the atomic weights now given for these elements are incorrect, as Mendeléeff asserted.

Summary and Supplement.

A. Metals and Non-Metals.

The idea that all bodies were composed of four "elements" or three "principles" was opposed by **Boyle,** who urged that the number of elements could only be determined by experiment (*Sceptical Chymist*, 1661). **Lavoisier,** in 1789, gave a list of 30 elements; **Berzelius,** in 1819, described 50; the number now known exceeds 80.

Lavoisier classified the elements in three chief groups: (a) *Oxygen*, with light and heat, azote and hydrogen, (b) *Metals*, forming basic oxides, and (c) *Non-metals*, forming acid oxides. Davy classified chlorine with oxygen as a "supporter of combustion," and also described the elements as "positive" or "negative" according as they were attracted to the negative or to the positive pole in electrolysis. Berzelius classed fluorine and iodine with chlorine, and sulphur and selenium with oxygen. Finally the oxygen-group ceased to be distinguished from the other non-metals, and the elements were divided into two groups, as metals and non-metals.

B. Numerical Relationships and the Periodic Law.

Döbereiner, in 1829, showed that the atomic weight of bromine was approximately the mean of the atomic weights of chlorine and iodine. Other *triads* were S, Se, Te; Ca, Sr, Ba; Li, Na, K; also Ni, Cu, Zn and Pt, Ir, Os, where the atomic weights differed very little. **Dumas,** in 1859, discovered regular increments of atomic weights in families of 4 or 5

elements, and showed that these might be identical in different families; thus there was a *common difference* between the equivalents in the families F, Cl, Br, I and N, P, As, Sb, as well as between those of Mg, Ca, Sr, Ba, Pb and O, S, Se, Te, Os.

Newlands, in 1864, using Cannizzaro's atomic weights, arranged Döbereiner's triads and Dumas's families in a single table. In 1865, after tabulating the elements in the order of the new atomic weights, he found that similar elements occurred, as in music, at intervals of 7 or 14 places. This *law of octaves* failed to attract attention until similar schemes were put forward by **Mendeléeff** in 1869 and in 1871 and by **Lothar Meyer** in 1869 to illustrate the law of *periodicity*, which states that "*The properties of the elements are periodic functions of their atomic weight.*" In Mendeléeff's classification, Newlands's octaves appear again as 12 *series* or *short periods*, the first containing hydrogen only, whilst the second contains the 7 *typical elements*, Li, Be, B, C, N, O, F, of Groups I to VII. A Group VIII was added to take the triads of *transition-elements*, which bridge the gap between the *even series* and the *odd series*, 4 to 5, 6 to 7, and 10 to 11; each of these triads, with the octaves on either side, constituted a *long period* of $7+3+7=17$ elements. A "Group 0" is now added to take the rare-gases of the helium series. The main periods, as now recognised, are:—

Period I.	(=series 1)	Hydrogen.
Period II and III.	(=series 2 and 3)	Eight elements each.
Periods IV and V.	(=series 4 to 7)	Eighteen elements each.
Period VI.	(=series 8 to 11)	Thirty-two elements.
Period VII.	(=series 12 etc.)	Radioactive elements.

The sixth period is extended to 32 elements by a cluster of some 15 *rare-earth elements*, crowded together in the boron-group. The end of the sixth period and the fragmentary beginning of the seventh period contain 7 elements of known atomic weight from lead to uranium, but the whole space is crowded with some 40 transient *radio-elements*, four of these occupying well-defined places at the beginning of the seventh period; others are clustered together in small swarms of *isotopic elements* having similar chemical properties and nearly equal atomic weights.

C. Illustrations and Applications of the Periodic Law.

The periodic law was illustrated by **L. Meyer** (1869) in reference to the *valency* and the *atomic volumes* of the elements; the former property justifies the classification into octaves or *short periods*, the latter property proves the existence of *five main periods* and two fragments. **Dewar** (1913) has shown that the *atomic heats at low temperatures* exhibit the same periodic variations as the atomic volumes. Other periodic properties are *melting-point*, *compressibility*, *heat of formation of oxides and chlorides*, etc.

The periodic system has been used to correct certain atomic weights, in which there was doubt as to the equivalent, as in the case of *gold*, or the valency, as in the cases of *beryllium*, *indium* and *uranium*; but the atomic weights of argon and potassium, cobalt and nickel, tellurium and iodine do not conform to the order suggested by the periodic classification. Mendeléeff also used the periodic classification to predict the properties of missing elements, of which three have since been discovered, thus

Eka-boron	*Eka-aluminium*	*Eka-silicon*
= Scandium, 44·1	= Gallium, 69·9	= Germanium, 72·5
(Nilson, 1879)	(Lecoq de Boisbaudran, 1875)	(Winkler, 1886)

His predictions in the range covered by the rare-earth elements were incorrect, but his *eka-manganese* = 100 and *tri-manganese* = 190 are still regarded as vacant places in the periodic classification.

D. Atomic Weights and Atomic Numbers.

Prout, in 1815–1816, suggested that the atomic weights of the elements were integral multiples of the atomic weight of hydrogen. "Prout's hypothesis" has not been confirmed by experiment, but **Strutt** has shown that the tendency of the atomic weights to approximate to whole numbers is greater than can be accounted for by the law of probability in the ratio of 1000 : 1.

Newlands, in 1864, attached to the elements a series of consecutive *atomic numbers*, and thereby discovered the law

of octaves. In this arrangement hydrogen was 1 and gold was 49, but in 1878 a more open system was used, in which gold was 86. **Moseley** in 1913–1914 showed that integral atomic numbers could be determined experimentally by studying the high-frequency spectra emitted by different elements when used as targets in an X-ray bulb. In this system, if aluminium be taken as 13, then gold is 79, and there are only four vacant places between these two elements after filling in all elements of known atomic weight. The total number of missing elements between hydrogen and uranium appears to be *nine*, namely, numbers 43, 61, 72, 75, 84, 85, 87, 89, and 91. The atomic number for nickel was found to be one unit greater than for cobalt, in spite of its smaller atomic weight, thus justifying Mendeléeff's view that nickel should be placed between cobalt and copper; in the same way the atomic numbers for chlorine and for potassium were found to be separated by two units, leaving a place between them for argon, the atomic weight of which is greater than that of potassium. Atomic numbers may also be deduced from the absorption of X-rays by solid elements and the scattering of X-rays by gases. These atomic numbers satisfy all the requirements of Prout's hypothesis, but the irregularities shown by the atomic weights are still unexplained.

CHAPTER XIX

BALANCED ACTIONS

Mayow (1674) on the displacement of nitric acid by oil of vitriol.—Like many other important theories, the idea of reversible or balanced actions had its origin in the study of acids, bases, and salts. Mayow (A.C.R. XVII, 161 ; quoted on p. 22) showed in 1674 that, when oil of vitriol was added to nitre, the nitric acid could be distilled out under a heat no greater than is required for the rectification of the free acid. This easy distillation was explained by supposing that the nitric acid had been "expelled from the society of the [alkali] by the more fixed vitriolic acid."

Similarly, it was noticed that the volatile alkali could be displaced from any of its salts by the fixed alkalis, the reason being given "that the acid . . . is capable of entering into closer union with any fixed salt than it is with a volatile salt."

Baumé (1760) on the decomposition of vitriolated tartar by nitric acid.—Whilst nitric acid is expelled from nitre by sulphuric acid with the aid of gentle heat, the opposite change may take place when the mixture is kept cold. This fact was discovered in 1760 by Baumé, who described the action as follows :

"I took four gros of vitriolated tartar,[1] reduced to a fine powder, I mixed it with three gros of very pure fuming spirit of nitre ; . . . the mixture became pasty, I diluted it

[1] Potassium sulphate.

with a sufficient quantity of water to dissolve the saline mass, and I set the liquid to crystallise: the salt which I obtained proved to be very pure nitre, crystallised partly in needles and partly in small cubic crystals; I set it to drain on grey paper . . .; the nitre thus drained, showed just the same phenomena as nitre prepared by the combination of nitric acid with fixed alkali"[1] (*Mem. Math. Phys.*, 1774, VI. 231-236; paper read before the Paris Academy of Sciences, Dec. 23, 1760).

Thus under one set of conditions, sulphuric acid may expel nitric acid from its salts, but under other conditions nitric acid expels sulphuric acid.

Reversible actions.—This reversal of the action may be shown by writing two equations, thus:

Mayow found that:

$$\underset{\text{Nitre}}{2KNO_3} + \underset{\substack{\text{sulphuric}\\\text{acid}}}{H_2SO_4} \rightarrow \text{gave} \rightarrow \underset{\substack{\text{potassium}\\\text{sulphate}}}{K_2SO_4} + \underset{\text{nitric acid}}{2HNO_3}$$

Baumé found that:

$$\underset{\substack{\text{Potassium}\\\text{sulphate}}}{K_2SO_4} + \underset{\text{nitric acid}}{2HNO_3} \rightarrow \text{gave} \rightarrow \underset{\text{nitre}}{2KNO_3} + \underset{\substack{\text{sulphuric}\\\text{acid}}}{H_2SO_4}$$

These two equations may then be combined into a single equation in which arrows pointing in opposite directions show the direction taken by the action under different conditions, thus:

$$2KNO_3 + H_2SO_4 \underset{\text{Cold}}{\overset{\text{Hot}}{\rightleftharpoons}} K_2SO_4 + 2HNO_3$$

Bergman's tables of affinity (1775).—Mayow's idea that a "closer union" existed between fixed than between volatile acids and alkalis was extended to series of acids and bases in the "tables of affinity" drawn up by Geoffroy in 1718, by Stahl in 1720, and finally by Bergman in 1775 (*A Dissertation on Elective Attractions*, tr. T. Beddoes, London, 1785). In these tables one acid or base was selected and the different bases or acids were arranged under it in the order

[1] Potassium carbonate.

of their decreasing affinity. But Bergman was obliged to recognise that the order of affinity was not quite constant, and in particular that different results were often obtained when the affinities were compared: (1) in the dry way, by heating the substances together (as Mayow had done) and discovering which combination remained fixed in the product and (2) in the moist way, by mixing the substances in solution (as Baumé had done) and finding which base secured possession of the acid.

Whilst, therefore, there was a fixed order of affinity of acids for bases and *vice versa*, this order might be altered considerably by changing the conditions of the experiment.

Thus, in the case of sulphuric acid (using modern names) the affinities of the different bases were as follows:

SULPHURIC ACID

In the Moist Way	*In the Dry Way*
Baryta	Potash
Potash	Soda
Soda	Baryta
Lime	Lime
Magnesia	Magnesia
Ammonia	Metallic calces
Alumina	Ammonia
Metallic calces	Alumina

From this table it is seen that ammonia, added "in the moist way" to a solution of a metallic salt, precipitates the calx of the metal and secures possession of the acid with which it was combined. On the other hand, when a metallic calx is heated with an ammonium salt "in the dry way," the volatile alkali is expelled, whilst the acid remains behind in combination with the calx.

This reversal of the action can again be shown by writing two equations, thus:

In the moist way :

$$2NH_3 + PbCl_2 + 2H_2O \rightarrow 2NH_4Cl + Pb(OH)_2$$

Ammonia + lead chloride + water gives ammonium chloride + lead hydroxide

In the dry way :

$$2NH_4Cl + Pb(OH)_2 \rightarrow 2NH_3 + PbCl_2 + 2H_2O$$

Ammonium chloride + lead hydroxide gives ammonia + lead chloride + water

Combining these equations, we may write :

$$2NH_3 + PbCl_2 + 2H_2O \underset{\text{Dry}}{\overset{\text{Moist}}{\rightleftharpoons}} 2NH_4Cl + Pb(OH)_2.$$

Berthollet (1799) investigates the laws of chemical affinity.—Bergman had recognised the influence of temperature on the order of affinity, and had shown that this order was altered considerably when substances were ignited together instead of being merely mixed in solution or in presence of water. To Berthollet belongs the credit of directing attention to the influence on chemical action of the *quantities* of the interacting substances, an influence which is now described as MASS-ACTION.

In his *Researches into the Laws of Chemical Affinity* (read in Cairo in 1799; published 1801; tr. M. Farrell, London, 1804) he criticises Bergman's method in the following terms :

"He prescribes then, for determining the elective affinity of two substances, to try if one of them can remove the other from its combination with a third, and *vice versa*. He takes it for granted, that that body which has removed another from its combination, cannot, in like manner, be expelled by that other, and that both experiments will concur to prove that the first has a greater elective affinity than the second. He adds at the same time, that it may be necessary to employ six times as much of the decomposing substance as would be necessary to saturate immediately the substance with which it tends to combine."

"The doctrine of Bergman is founded entirely on the

supposition that elective affinity is an invariable force, and of such a nature that a body which expels another from its combination, cannot possibly be separated from the same by the body which it eliminated" (*loc. cit.* pp. 3–4).

"It is my purpose to prove in the following sheets, that elective affinity, in general, does not act as a determinate force, by which one body separates completely another from a combination; but that, in all the compositions and decompositions produced by elective affinity, there takes place a partition of the base, or subject of the combination, between the two bodies whose actions are opposed; and that the proportions of this partition are determined, not solely by the difference of energy in the affinities, but also by the difference of the quantities of the bodies; so that an excess of quantity of the body whose affinity is the weaker, compensates for the weakness of affinity" (*loc. cit.* pp. 4–5).

"I shall prove . . . that, in opposing the body A to the combination BC, the combination AC can never take place; but that the body C will be divided between the bodies A and B, proportionally to the affinity and quantity of each" (*loc. cit.* p. 6).

Berthollet illustrates the law of mass-action.—Several examples, of which two may be quoted, are given of the influence of mass in compensating for weakness of affinity.

"I have kept an equal quantity of potash, and of sulphate of barytes, in a small quantity of boiling water. The potash had been prepared by alcohol,[1] and contained no carbonic acid . . . The operation was performed in a retort, and . . . was continued until the mixture was desiccated: the residue was washed with alcohol, which dissolved the potash, and after that with water, which also produced an alkaline solution, the alkali of which I saturated with acetic acid; after which, by evaporation, the solutions yielded crystals possessing all the characters and qualities of the sulphate of potash. Whence it appears that the sulphate of barytes was

[1] This dissolves caustic potash, but leaves the carbonate, sulphate, &c., undissolved.

partially decomposed by the potash, and that the sulphuric acid was divided between the two bases" (pp. 8–9).

"Equal weights of potash and of carbonate of lime, finely pulverised, were boiled in a small quantity of water, which, after being filtered and rendered transparent, effervesced strongly with acids; and the residue, after evaporation, having been treated with alcohol, in order to dissolve the alkali, furnished a substance that had all the qualities or characters of the carbonate of potash" (pp. 10–11).

Balanced actions.—All the cases quoted by Berthollet are examples of BALANCED ACTIONS, *i.e. reversible actions in which chemical change proceeds in both directions at the same time and under the same conditions.* Such actions may be represented by equations in which the opposing actions are shown by two arrows, but without any signs to suggest that different conditions are required to produce reversal. The cases quoted above are shown thus:

$$Ba(OH)_2 + K_2SO_4 \rightleftharpoons 2KOH + BaSO_4.^1$$
$$Ca(OH)_2 + K_2CO_3 \rightleftharpoons 2KOH + CaCO_3.$$

In the first case, it had been supposed that baryta and potassium sulphate interacted to form caustic potash and barium sulphate by an interaction that was non-reversible and complete. Berthollet showed that the action could be reversed, and was, in fact, incomplete, the acid being shared to some extent between the two bases. In the second case it had been supposed that carbonate of potash was deprived of all its carbonic acid and rendered completeiy caustic by the action of lime; Berthollet proved that the converse change could be brought about, and that the action was "balanced" and incomplete. He concludes:

"It is evident, from the preceding experiments, that the bases which are supposed to form the strongest combinations with the acids, may be separated from them by others, whose affinities are supposed to be weaker, and that the acid

[1] It is probable that carbonic anhydride was absorbed from the air, and that the balanced action was really $BaCO_3 + K_2SO_4 \rightleftharpoons K_2CO_3 + BaSO_4$.

divides itself between the two bases. It also appears, that acids may be partially separated from their bases by other acids, whose affinities were supposed to be weaker; in which case, the base is divided between the two acids" (*loc. cit.* p. 11).

Mass-action.—Berthollet's method for detecting the reversed action in the cases quoted above depended on using a solution of potash which was concentrated by evaporating finally to dryness. In this way the action of mass, which was the chief subject of his research, was made use of to the fullest extent. On this point he writes:

"If but a small quantity of the decomposing substance be employed, the effect will not be perceptible; but if, on the contrary, a large quantity be employed, as for instance, if I had treated the sulphate of barytes successively with additional quantities of potash, and removed, by repeated washing, the disengaged barytes, I should have ultimately decomposed the sulphate of barytes almost entirely.[1] The greater then the relative quantity of the decomposing substance, the greater will be the effect produced" (*loc. cit.* p. 12).

Effect of precipitation on balanced actions.—In considering balanced actions in solution, Berthollet recognised that the action of mass was seriously limited in the case of insoluble substances, since "If an insoluble substance be opposed to a combination, it is evident that only a very small quantity of it can act" (*loc. cit.* p. 32). This is expressed in modern terms by saying that the "active mass" of a solid is constant, no further increase of activity being produced by increasing the quantity of solid beyond the point at which it suffices to saturate the liquid.

When one acid is being competed for by two bases or one base by two acids, the result is influenced mainly by the relative strengths of the competing bases or of the competing acids. But when two acids are present in sufficient

[1] In order to do this, carbonate of potash must be used.

quantity to neutralise the whole of two bases, or conversely, the competition is less keen, and the course of the action is determined mainly by the order in which the salts are precipitated from solution. In their aqueous solutions, all neutral salts are almost equally strong or equally stable; moreover, unlike the neutralisation of an acid by an alkali, no marked liberation of heat occurs when two soluble salts are formed by "double decomposition" from two others (Hess's "Law of Thermoneutrality," *Ann. de Chim.*, 1842, [iii], **4**, 222). The nature of the salts that separate on evaporating the solution is therefore determined more by their relative solubilities than by any factor depending on chemical affinity.

Berthollet's experiments (1804) on the interaction of neutral salts.—In his *Essay on Chemical Statics* (1803; tr. B. Lambert, 1804), Berthollet made a very careful study of the balanced interactions of pairs of neutral salts. Amongst other cases he studied the following:

(a) *One of the four salts is almost insoluble in water.*—In this case it is precipitated almost completely when the alternative pair of soluble salts is mixed.

"If sulphate of potash and nitrate of lime are mixed, in any proportions, the sulphate of lime which is formed separates by the excess of its insolubility compared with that of nitrate of potash" (*Chemical Statics*, I. 70):

$$K_2SO_4 + Ca(NO_3)_2 \rightleftharpoons \underset{\text{(precipitated)}}{CaSO_4} + 2KNO_3.$$

Barium sulphate, which is even less soluble than calcium sulphate, is precipitated so completely that it can be filtered off and weighed in order to estimate either the amount of barium or the quantity of sulphates present in a solution:

$$K_2SO_4 + Ba(NO_3)_2 \rightarrow \underset{\text{insoluble}}{BaSO_4} + 2KNO_3.$$

(b) *Two salts are almost equally sparingly soluble.*—If these two salts are on opposite sides of the equation, either

may crystallise out first according to the composition of the solution.

"A mixture of nitrate of potash and muriate of lime yields also a result, in which the influence of the proportions is still more marked, because the two least soluble salts which can be formed, the nitrate of potash and the muriate of potash, differ but little in this property: either of these salts may also be obtained at the first crystallisation by a little variation in the proportions of the nitrate of potash and muriate of lime" (*Chemical Statics*, I. 70-71):

$$2KNO_3 + CaCl_2 \rightleftharpoons 2KCl + Ca(NO_3)_2.$$

If potassium nitrate is in excess, the potash will crystallise out as nitrate, but an excess of calcium chloride will displace the equilibrium towards the right-hand side of the equation and cause the potash to separate as chloride.

(c) *One salt is least soluble in the cold, but another in the hot, solution.*

"The solubility of salts varies by a difference of temperature; but this does not follow the same progression in all of them. In some it acquires a considerable augmentation by an elevation of heat; in others it remains nearly the same. This condition, which determines the separation of salts, may therefore produce different effects according to the thermometric state; hence it happens, that salts whose solubility is nearly equal at one degree of heat, may, nevertheless, be easily separated, by producing a great change in the temperature, and, by making the effect of the proportions, and that of the difference of solubility, predominate alternately."

"Nitrate of potash and muriate of soda furnish us with a striking example of this effect. Near the freezing-point, nitrate of potash has much less solubility than muriate of soda; but it is considerably increased by heat, and that of muriate of soda very little; so that the solubility of the latter, which was only about half that of the nitrate of potash, comes to a degree at which it is equal, and finally at the boiling point becomes nearly eight times less. By boiling the mixture, therefore, the muriate of soda is made to

crystallise at a high temperature, and then, by cooling, the nitrate of potash, is crystallised : the proportion of each salt is diminished alternately, and by repeated crystallisations they are both entirely separated" (*Chemical Statics*, I. 71–72).

Here the action

$$NaNO_3 + KCl \rightleftharpoons KNO_3 + NaCl$$

can be brought to completion in the direction of the upper arrow by crystallising out, alternately, nitrate of potash at the freezing-point and common salt at the boiling-point. If the common salt were allowed to accumulate, it would, by the law of mass-action, check the formation of potassium nitrate from sodium nitrate and potassium chloride, with the result that one of these salts (potassium chloride) might crystallise out and carry the action backwards in the direction of the lower arrow.

An action of this kind actually occurs when a solution containing sulphate of potash and nitrate of soda is evaporated. The sulphate of potash, which is the least soluble of the four salts,

$$2NaNO_3 + K_2SO_4 \rightleftharpoons 2KNO_3 + Na_2SO_4,$$

crystallises first.

"But when the proportion of the first shall be diminished by the crystallisation, nitrate of potash will also be obtained, because the water remaining at this period is incapable of holding in solution the quantity of this salt which may be formed, and because the sulphate of potash, on its part, is rendered more soluble by the action of the other salt : this result might have been obtained from the commencement of the crystallisation by augmenting the proportion of nitrate of soda" (*Chemical Statics*, I. 70).

Action of acids on insoluble salts.—When a strong acid acts on an insoluble salt of a weak acid, the insolubility of the salt greatly assists the weaker acid in its effort to retain possession of the base.

"In fact, if oxalic acid is added to a salt with base of

lime, a precipitate of oxalate of lime is obtained, much less abundant than if a solution of a neutral oxalate had been used, because the action of the acid allows only part of the oxalate of lime to be formed, but with an oxalate this obstacle would not have existed" (*Chemical Statics*, I. 67).

Here the action

$$H_2C_2O_4 + CaCl_2 \rightleftharpoons \underset{\text{(insoluble)}}{CaC_2O_4} + 2HCl$$

is reversible, since the insolubility of its calcium salt enables the oxalic acid to rob the stronger muriatic acid of part of its lime.

Interesting cases of the same sort are found amongst the sulphides, *e.g.*:

$$CuSO_4 + H_2S \rightarrow \underset{\text{(precipitate)}}{CuS} + H_2SO_4$$

$$ZnSO_4 + H_2S \leftarrow \underset{\text{(dissolves)}}{ZnS} + H_2SO_4.$$

In the former case the insolubility of the sulphide causes it to be precipitated, in opposition to the tendency, which is dominant in the latter case, for the stronger acid to secure possession of the base.

Influence of vaporisation on balanced actions.—In reference to the influence of gases on balanced actions, Berthollet writes:

"When a substance assumes the state of gas, on separating from an intimate combination, it becomes elastic, and can oppose no further resistance to the decomposing action: whence it appears that substances of this nature do not act by their mass. The decomposing substance can then effect a complete decomposition; and it will suffice to employ just as much of it as would have been necessary to form the same combination immediately, or at least a very trifling excess."

"Thus carbonic acid may be disengaged from its combination by another substance, whose affinity for the base of the carbonate might be less; because that other substance can act by its mass, and can therefore overcome the affinity of the carbonic acid, by acting successively: but to expel the

entire of the carbonic acid, the decomposing substance must be used in quantity somewhat greater than that necessary to produce saturation."

"If concentrated sulphuric acid be poured on desiccated muriate of soda, the affinity of the muriatic acid is diminished; and that acid assumes the gaseous state in consequence, and acts no longer by its mass: but if an aqueous solution of muriate of soda be employed, or a diluted acid, whether the sulphuric, or any other, then the muriatic acid may be retained in the water; in which case it can act by its mass" (*Chemical Affinity*, pp. 46–48).

Berthollet shows that a weak fixed acid may displace a stronger volatile acid.—"It is to this effect of elasticity that the decompositions produced by the most fixed acids . . . are to be attributed . . . ; it is thus that sulphuric acid, by means of heat, decomposes the muriates and the nitrates with a fixed base."

"I distilled a mixture of oxalic acid and muriate of soda, and the liquor which passed over contained much muriatic acid" (*Chemical Statics*, I. 192-193).

In the latter case the weak oxalic acid displaced the strong muriatic acid because of its greater fixedness:

$$\underset{\text{(weak fixed acid)}}{H_2C_2O_4} + 2NaCl \rightarrow Na_2C_2O_4 + \underset{\text{(strong volatile acid)}}{2HCl}.$$

Again, phosphoric acid is a very weak acid, since nearly all its salts are decomposed by acetic acid even though insoluble in water; but sulphuric acid, which "expels entirely the muriatic and nitric acids from their combinations, with the assistance of a sufficient degree of heat . . . is itself expelled from its combinations by phosphoric acid, independently of affinities" (*Chemical Affinity*, p. 54).

"Therefore when, by the aid of heat, one body has separated another from its combination, it must not be inferred that its affinity is greater at an ordinary temperature" (*Chemical Affinity*, p. 55).

In fact, if mere fixedness were the real test of affinity, ordinary sand must be regarded as one of the strongest

acids, since in the manufacture of glass it expels the acid from sodium sulphate and converts it into a glassy silicate.

Balanced actions in gases.—Whilst a balanced action in a liquid is often disturbed by the vaporisation of one of the products, this action may be checked by increasing the pressure (and thereby the "active mass") of the gas (*Chemical Statics*, I. 188).

An interesting example of a balanced action in which the gas-concentrations are of dominant importance is shown by the equation

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

The solid iron and its solid oxide have a constant activity, but the action can be influenced strongly by varying the proportions of hydrogen and steam. The strong tendency for the hydrogen to reduce the oxide is shown by the upper arrow; but when, as in Lavoisier's experiment (Ch. VII, p. 118), large quantities of steam are passed over the solid the slight back-action shown by the lower broken arrow becomes important, and condensation of the steam immediately reveals the small quantities of hydrogen that have been produced.

Summary and Supplement.

Mayow, in 1674, showed that nitric acid could be expelled from nitre by oil of vitriol and suggested that this was due to the fact that oil of vitriol was "more concordant" with the alkali than nitric acid.

Baumé, in 1760, showed that this action could be reversed and that nitre could be precipitated by adding nitric acid to vitriolated tartar (potassium sulphate). The reversal of the action is shown in the equation

$$2KNO_3 + H_2SO_4 \underset{\text{Cold}}{\overset{\text{Hot}}{\rightleftharpoons}} K_2SO_4 + 2HNO_3$$

Bergman (1775), following Geoffroy (1718) and Stahl (1720), drew up tables of "Elective Attractions," showing the order of

affinity of a series of different acids for a given base and conversely. He distinguished between the relative attractions "in the moist way," *i.e.* in solution and "in the dry way," *i.e.* by ignition. Thus, we have :

In the moist way :

$$2NH_3 + PbCl_2 + 2H_2O \rightarrow 2NH_4Cl + Pb(OH)_2.$$

In the dry way :

$$2NH_4Cl + Pb(OH)_2 \rightarrow 2NH_3 + PbCl_2 + 2H_2O.$$

Berthollet, in his "Researches into the Laws of Chemical Affinity" (1801), and in his "Chemical Statics" (1803), recognised the influence of "*mass-action*," and suggested that "Every substance which has a tendency to enter into combination, acts in the ratio of its affinity *and of its quantity*." A weak acid in large quantities may therefore compete with a stronger acid in smaller quantities. The action of the weak acid "in the wet way" is greatly helped if it forms an insoluble salt, *e.g.* :

$$H_2C_2O_4 + 2CaCl_2 \rightleftarrows \underset{\text{(insoluble)}}{CaC_2O_4} + 2HCl.$$

or "in the dry way" if it is less volatile than the stronger acid, *e.g.* :

$$H_2C_2O_4 + 2NaCl \rightleftarrows \underset{\text{(volatile)}}{Na_2C_2O_4} + 2HCl.$$

The influence of mass is seen best, however, in the *balanced actions* between pairs of neutral salts : these differ so little in stability that the interaction is controlled almost entirely by mass-action and solubility. The following cases may be noticed :

(*a*) $$K_2SO_4 + Ca(NO_3)_2 \rightleftarrows \mathbf{CaSO_4} + 2KNO_3,$$

$CaSO_4$ is almost insoluble and is always precipitated first.

(*b*) $$\mathbf{K_2SO_4} + 2NaNO_3 \rightleftarrows Na_2SO_4 + \mathbf{2KNO_3}$$

K_2SO_4 separates first on evaporation, but as $NaNO_3$ accumulates in the solution the action passes from left to right and KNO_3 crystallises.

(*c*) $$\mathbf{2KCl} + Ca(NO_3)_2 \rightleftarrows \mathbf{2KNO_3} + CaCl_2$$

KCl or KNO_3 may crystallise according to the proportions in which the salts are mixed.

(*d*) $$NaNO_3 + KCl \rightleftarrows \mathbf{KNO_3} + \mathbf{NaCl}.$$

At 0° KNO_3 is least soluble, at 100° NaCl; the action may be driven across completely from *L* to *R* by crystallising out these salts alternately at 0° and at 100°.

In *quantitative analysis* these balanced actions are used to secure complete precipitation of Ag or Cl as AgCl, Ba or SO_4 as $BaSO_4$, &c.

In *qualitative analysis* the balance of actions between neutral salts may be used to secure a broad separation of those metals which form

(1) *Insoluble chlorides:* Ag′, Pb″, Hg′

(2) *Insoluble sulphides:*

(*a*) Cu″, Pb″, Hg″, Bi‴ (*c*) [Fe‴], [Cr‴], [Al‴]

(*b*) Sn″, Sn⁗, Sb‴, As‴ (*d*) Zn″, Mn″, Ni″, Co″.

(3) *Insoluble carbonates:* (*a*) Ca″, Sr″, Ba″ (*b*) Mg″

(4) *Insoluble platinichlorides:* K′, NH_4′.

In class (1), since hydrochloric acid is one of the strongest acids, it may be used instead of a neutral chloride; thus in the action

$$AgNO_3 + HCl \rightleftharpoons \mathbf{AgCl} + HNO_3,$$

the nitric acid formed as a second product is not strong enough to redissolve the insoluble chloride or to prevent its precipitation. In class (2), however, the use of sulphuretted hydrogen in place of a neutral sulphide tends to liberate a strong acid; this prevents the separation of the insoluble sulphides of the metals (2*c*) and (2*d*), but those of the metals (2*a*) and (2*b*) are precipitated even in presence of much acid, thus:

$$CuSO_4 + H_2S \rightarrow \underset{\text{(precipitated)}}{\mathbf{CuS}} + H_2SO_4$$

$$ZnSO_4 + H_2S \leftarrow \underset{\text{(dissolves)}}{\mathbf{ZnS}} + H_2SO_4.$$

The further separation of the metals (2*a*) and (2*b*) depends on the fact that the latter dissolve in alkaline sulphides to form soluble sulpho-salts, such as Na_3AsS_4, Na_3SbS_4, &c. The separation of the metals (2*c*) and (2*d*) depends on the fact that the tervalent hydroxides, $Fe(OH)_3$, $Cr(OH)_3$, $Al(OH)_3$, are extremely weak bases, which do not form carbonates or sulphides, and are therefore precipitated in the free state when soluble carbonates or sulphides are added; in qualitative analysis they are separated by the addition of a mixture of ammonia and

ammonium chloride which is not strong enough to precipitate the divalent hydroxides of the metals (2*d*), thus :

$$AlCl_3 + 3NH_4OH \rightarrow \underset{\text{(precipitated)}}{\mathbf{Al(OH)_3}} + 3NH_4Cl$$

but $$ZnCl_2 + 2NH_4OH \leftarrow \underset{\text{(dissolves)}}{\mathbf{Zn(OH)_2}} + 2NH_4Cl.$$

In class (3) a similar method is used to separate magnesium from calcium, strontium, and barium. Like chalk and barium carbonate, magnesium carbonate is insoluble in water ; it is, however, soluble in presence of ammonium salts, thus :

$$MgCl_2 + 2Na_2CO_3 \rightarrow \underset{\text{(precipitated)}[1]}{\mathbf{MgCO_3}} + 2NaCl$$

but $$MgCl_2 + 2(NH_4)_2CO_3 \leftarrow \underset{\text{(dissolves)}}{\mathbf{MgCO_3}} + 2NH_4Cl.$$

In the former case, the tendency of the strong acid (HCl) to combine with the stronger base (NaOH) drives the action in the direction *L* to *R*, already indicated by the insolubility of magnesium carbonate. In the latter case the magnesia is the stronger base and the action from *R* to *L* is assisted further (i) by the mass-action of an excess of ammonium chloride and (ii) by the tendency of this substance to unite with magnesium salts to form compounds, such as $MgCl_2$, NH_4Cl,$6H_2O$, and thereby to weaken the mass-action of the magnesium salt.

[1] Usually as a basic salt.

CHAPTER XX

DISSOCIATION

A. DISSOCIATION AND ASSOCIATION

St. Claire Deville (1857) on dissociation.—The name DISSOCIATION was introduced in 1857 by **H. St. Claire Deville**[1] (*Comptes rendus*, 1857, **45**, 857) to describe the "spontaneous decomposition" of substances by heat, without the intervention of chemical agencies. This definition (which would include thermal decompositions such as the "coking" of coal and the "charring" of sugar) was afterwards limited (*Comptes rendus*, 1863, **56**, 730) so as to include only cases "in which the decomposition takes place partially, and at a temperature inferior to that which corresponds to the *absolute* destruction of the compound," *i.e.* to cases of REVERSIBLE DECOMPOSITION, in which the products recombine when the decomposing forces are removed. These reversible decompositions are very difficult to detect because, after heating and cooling, the original substance reappears unaltered, bearing no trace of the changes which it has undergone.

[1] St. Claire Deville's experiments were summarised in his *Lessons on Dissociation* delivered to the Paris Academy of Sciences in 1864. These were published as a pamphlet, which includes (almost verbatim) the *Comptes rendus* papers of 1864 and 1865, together with the diagrams, which were not reproduced in the *Comptes rendus*.

Grove's experiments on the dissociation of water (1847).—This difficulty was first overcome by **Grove**, who showed in 1847 (Bakerian Lecture, *Phil. Trans.*, 1847, **137**, 1–16) that the combination of hydrogen and oxygen to form water was partially reversed at high temperatures, *e.g.* by heating a platinum wire in steam by an electric current, by passing sparks through steam between platinum points, and by plunging the fused end of a platinum wire under cold water. Under these conditions bubbles of gas were produced, which could be collected and detonated.

In these experiments a small quantity of steam is decomposed into its elements as shown by the equation

$$2H_2O \rightarrow 2H_2 + O_2.$$

As recombination is checked by dilution with a large volume of steam, the mixed gases can be cooled to 100° without recombining; below this temperature the mixture is quite stable, even when the steam is condensed, but detonates in the ordinary way when ignited. The maximum amount of gas collected was about $\frac{1}{2400}$ of the volume of the steam.

The dissociation of water may be represented by the scheme

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

in which the main course of the action is represented by a full arrow, and the slight reversal by a dotted arrow.

Deville's experiments on the dissociation of water (1863) and of carbonic anhydride.—Grove's experiment was repeated on a larger scale in 1863 by Deville (*Comptes rendus*, 1863, **56**, 322), who poured 1 to 2 kilogrammes of fused platinum into water and so secured an abundant liberation of explosive gas.

Deville also proved the dissociation of water by passing a stream of carbonic anhydride, saturated with water-vapour at 90° to 95° C., through a porcelain tube packed with pieces

of broken porcelain and heated to 1300° C. On absorbing the carbonic anhydride by potash a continuous supply of detonating gas was obtained; at the end of two hours, 25 to 30 cubic centimetres had been collected (*loc. cit.* p. 323).

Dissociation of carbonic anhydride.—When dry carbonic anhydride was passed through the same apparatus, an explosive mixture of carbonic oxide and oxygen was collected at the rate of 20 to 30 cubic centimetres per hour. The combustion of carbonic oxide is therefore a reversible process as shown by the dotted arrow in the equation:

$$2CO + O_2 \rightleftharpoons 2CO_2.$$

Deville's hot-cold tube (1864).—In most cases of dissociation the extent of the decomposition increases very rapidly with the temperature. If a substance be strongly heated and then suddenly chilled it is sometimes possible to fix the products of dissociation in the larger proportions in which they exist at higher temperatures; on the other hand, if the cooling is gradual they recombine and are only retained in the small proportions which are natural at the lower temperature at which recombination ceases. Deville secured this strong heating and rapid cooling in his "hot-cold" tube shown in Fig. 55 (*Lessons on Dissociation*, p. 64). The outer tube of porcelain was heated to whiteness; the inner tube of brass was cooled by a current of water. With this apparatus he demonstrated the decomposition of carbonic oxide, of sulphurous anhydride, and of hydrogen chloride:

$$2CO \rightleftharpoons C + CO_2$$
$$3SO_2 \rightleftharpoons S + 2SO_3$$
$$2HCl \rightleftharpoons Cl_2 + H_2.$$

In the first case, carbon was deposited on the cold tube and carbonic anhydride carried forward (*Comptes rendus*, 1864, **59**, 875); in the second case, sulphide and sulphuric anhydride were both deposited; in the third case, chlorides

of silver and mercury were formed on a cold tube of amalgamated silver and several cubic centimetres of hydrogen were carried forward (*Comptes rendus*, 1865, **60**, 317–325).

Similar changes were produced by sparking. Sulphurous anhydride was condensed completely, $SO_2 \rightarrow S + 2SO_3$, by sparking over sulphuric acid, which absorbed the sulphuric anhydride as fast as it was formed. A mixture of sulphurous anhydride with oxygen was absorbed still more readily:

$$2SO_2 + O_2 \rightarrow 2SO_3.$$

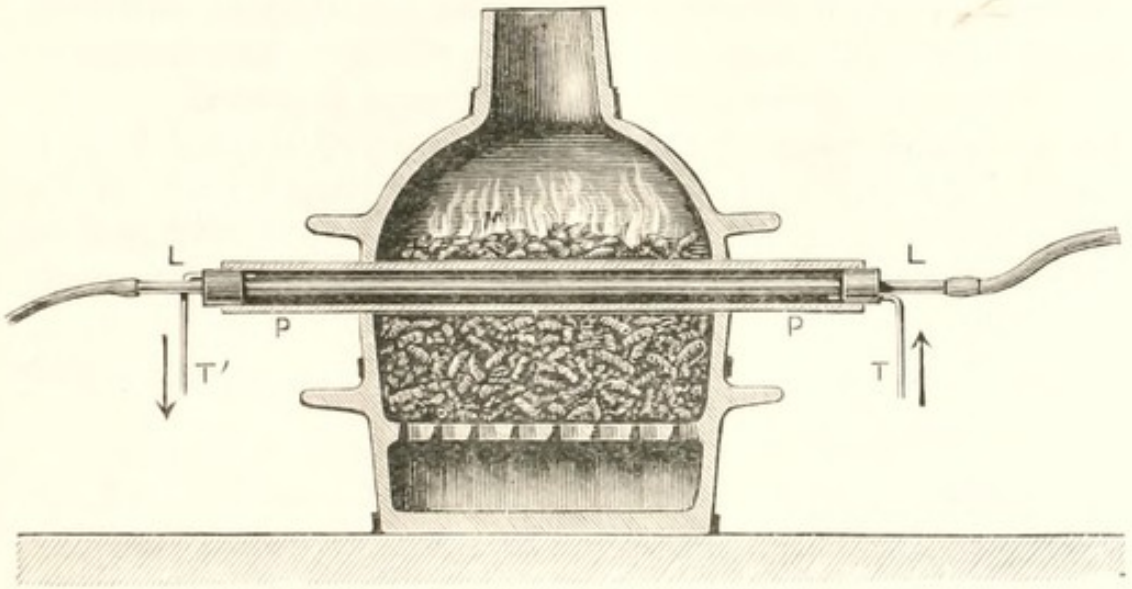


FIG. 55.—DEVILLE'S "HOT-COLD" TUBE.

PP is a hot tube of porcelain. LL is a brass tube cooled with water. The gas to be decomposed passes in at T and out at T'.

Hydrogen chloride, which had been shown by Davy fifty years previously (Ch. XI, p. 224) to give calomel and one-half its volume of hydrogen when sparked over mercruy, was brought into the category of dissociable substances by Deville, who confirmed Davy's earlier observation.

Dissociation of ammonia.—In the course of these experiments Deville discovered that the decomposition of ammonia into nitrogen and hydrogen by sparking as used by Berthollet to establish its composition (p. 262) was a reversible change. By using an acid to absorb the ammonia as fast as it was

formed, Deville was able to recombine the gases completely. Deville wrote:

"If ammonia gas is sparked during several hours, until its volume appears to be exactly doubled, no sensible absorption is observed on introducing drops of water[1] into the eudiometer: the decomposition appears to be complete. But if, instead, one passes in some bubbles of gaseous hydrochloric acid, a slight cloud obviously obscures the mixture of nitrogen and hydrogen into which the ammonia has been transformed. This transformation is then not absolute. This affords an easy explanation of the following experiment. After having decomposed one volume of ammonia as perfectly as possible by sparking, giving two volumes of a mixture of nitrogen and hydrogen, one volume of gaseous hydrochloric acid is introduced into the eudiometer and the sparking is renewed during 8 to 10 hours. At the end of this time the upper part of the apparatus is covered with a layer of sal-ammoniac and the mercury has risen to the platinum wires" (*Comptes rendus*, 1865, **60**, 324).

The decomposition and recomposition of ammonia may be represented by the equations:

$$2NH_3 \rightleftharpoons N_2 + 3H_2. \quad N_2 + 3H_2 + 2HCl \rightarrow 2NH_4Cl.$$

The recombination is now usually demonstrated by sparking over sulphuric acid, a method already used by Deville in combining sulphur dioxide with oxygen.

Bineau (1838) investigates the vapour-densities of ammonium and phosphonium salts.—During the half-century which followed the enunciation of Avogadro's hypothesis, great difficulty was experienced in accepting his view that equal numbers of molecules, under similar physical conditions, always occupied equal volumes. One difficulty arose from the fact that one "equivalent" occupied a different volume in different gases. Thus if 1 volume of oxygen was required to convert a given weight of potassium into its oxide, the quantities of

[1] In *Lessons on Dissociation*, "concentrated sulphuric acid" is used.

gas required to convert the same weight of potassium into chloride were

2 volumes of chlorine gas,
4 volumes of hydrogen chloride gas,
and 8 volumes of sal-ammoniac.

The first three observations can be explained by Avogadro's hypothesis as expressed by the equations:

$$4K + O_2 \ (1\ vol.) = 2K_2O$$
$$4K + 2Cl_2 \ (2\ vols.) = 4KCl$$
$$4K + 4HCl \ (4\ vols.) = 4KCl + 2H_2.$$

But the case of sal-ammoniac is quite anomalous, since Avogadro's hypothesis would indicate that only four volumes of the gas were required, as shown by the equation:

$$4K + 4NH_4Cl \ (4\ vols.) = 4KCl + 4NH_3 + 2H_2.$$

A similar anomaly was observed in the vapour-densities of the ammonium and phosphonium salts examined by **Bineau** in 1838 (*Ann. Chim. Phys.*, 1838, **68**, 416–441).

The following compounds were studied:

$PH_3 + HI = PH_4I$ (phosphonium iodide)
$PH_3 + HBr = PH_4Br$ (phosphonium bromide)
$2NH_3 + CO_2 = (NH_3)_2CO_2$ (ammonium carbamate)[1]
$NH_3 + SH_2 = NH_4HS$ (ammonium hydrosulphide)
$NH_3 + HCN = NH_4CN$ (ammonium cyanide)
$NH_3 + HCl = NH_4Cl$ (ammonium chloride)

In each case an easily crystallised compound was formed, but a study of the *vapour* showed that no contraction in volume had taken place. Thus Bineau found that phosphonium iodide "is formed from equal volumes of phosphoretted hydrogen and hydriodic acid united without condensation, and that its density, in the state of vapour, is the mean of the densities of its components" (*loc. cit.* p. 430.)

[1] The product "sal-volatile" is not a true carbonate, but the ammonium salt of carbamic acid, $NH_2 \cdot CO \cdot OH$; compare p. 430.

Again ammonium carbamate (*loc. cit.* p. 434) "when heated, gives a volume of gas equal to the sum of the volumes of the components of the salt." "The vapour of the salt contains one-third of its volume of carbonic gas and two-thirds of its volume of ammonia gas. The condensation is consequently nil, and the density of the vapour is

$$\frac{1{\cdot}524 + 2 \times 0{\cdot}591}{3} = 0{\cdot}902,"$$

the densities of the components (relatively to air) being 1·524 for carbonic anhydride and 0·591 for ammonia.

The analogous case of nitric oxide, which is formed from its components without condensation, had been discussed by Dalton in 1802, but was explained by Avogadro (Chap. XV, p. 338) on the assumption that the molecules of nitrogen and oxygen were divisible into halves, the "atom" being therefore the half and not the whole molecule:

$$N_2 + O_2 = 2NO.$$

But if a similar method were applied to Bineau's observations it would be necessary to halve again the atomic weight of nitrogen in ammonium chloride, ammonium cyanide, and ammonium hydrosulphide, whilst in the case of the carbamate it must be divided into 3 parts. This further division into 2 and into 3 parts would reduce the atomic weight to one-sixth of Avogadro's figure, namely, $\frac{14}{6} = 2{\cdot}3$, and the formula of nitrogen gas would be N_{12}. The carbon atom would be divided into two parts in the cyanide and three parts in the carbamate, thus reducing its atomic weight to $\frac{12}{6} = 2$. It would also be necessary to divide the atomic weight of oxygen by 3 and to reduce those of chlorine, bromine, iodine and sulphur to one-half of the values generally accepted for these elements.

Such alterations were far too drastic to be justified by the behaviour of a single group of substances, and therefore

served merely to throw discredit upon Avogadro's hypothesis.

Pebal's proof of the dissociation of sal-ammoniac (1862).—Deville's discovery of dissociation suggested a simple explanation of these abnormal vapour-densities. **Kopp,** following Cannizzaro (*Nuovo Cimento*, 1857, **6**, 428), pointed out (*Liebig's Annalen*, 1858, **105**, 390) that the vapour obtained by heating a dissociable substance might

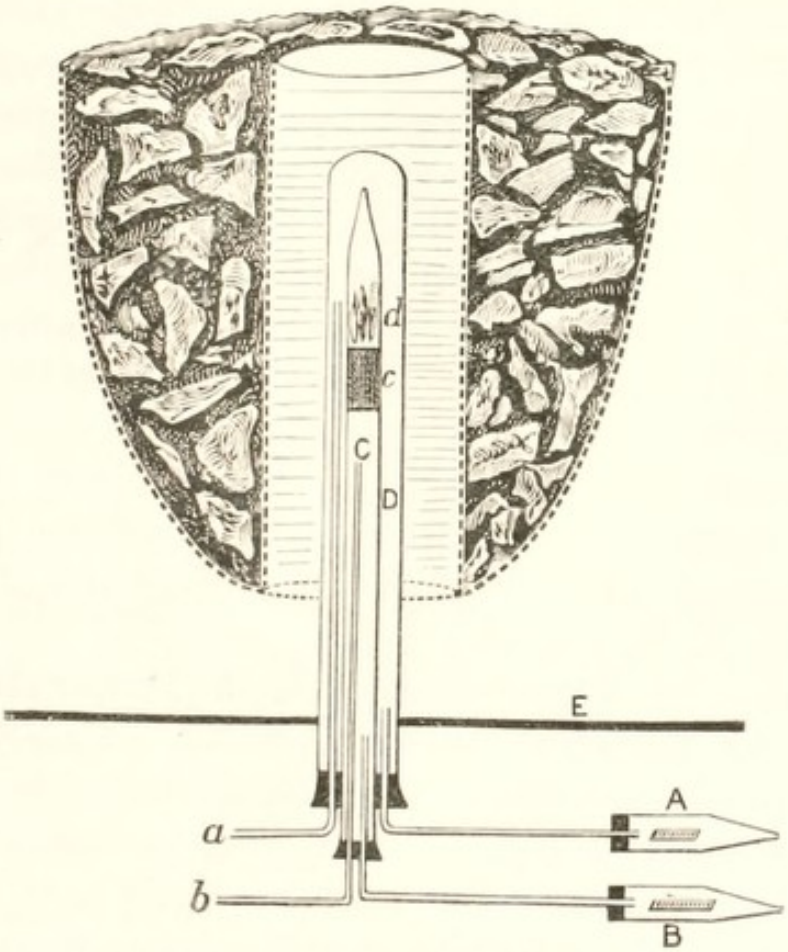


FIG. 56.—PEBAL'S APPARATUS FOR PROVING THE DISSOCIATION OF SAL-AMMONIAC.

be merely a mixture of the decomposition-products, occupying a larger volume and having a much lower density than the undecomposed vapour. This explanation had been suggested tentatively by Bineau in the case of ammonium carbamate, but was first verified in the case of sal-ammoniac, by the experiments of **Pebal** (*Liebig's Annalen*, 1862, **123**, 199–202).

Crystals of sal-ammoniac were heated in a glass tube (Fig. 56), 13 mm. wide, over a plug of asbestos 20 mm. in length; a current of hydrogen was maintained on each side of the asbestos. After the sal-ammoniac had vaporised, the hydrogen *A* from that side of the plug was found to contain free hydrochloric acid and turned blue litmus-paper red, whilst the hydrogen *B* from the other side of the plug contained free ammonia and turned red litmus-paper blue. This separation of ammonia and hydrogen chloride depends on the fact that the ammonia, being a lighter gas than hydrogen chloride, diffuses more quickly through the asbestos, rendering the gas on the other side alkaline and leaving behind a gas containing an excess of acid. Such a separation could not take place, however, if the vapour consisted entirely of undecomposed sal-ammoniac, since this would then diffuse as a whole and would not be resolved into its constituents.

It should be noted that, as ammonia and hydrogen chloride recombine immediately in the cold, the products of dissociation cannot be fixed by the method of sudden chilling, as used by Grove and by Deville.

Variation of vapour-density with temperature discovered by Cahours (1844).—Another anomaly which found a simple explanation in Deville's theory of dissociation is the variation of vapour-density with temperature, discovered by **Cahours** in the cases of acetic acid (*Comptes rendus*, 1844, **19**, 771-773) and phosphorus pentachloride (*Ann. Chim. Phys.*, 1847, [3], **20**, 369–378).

For acetic acid, Cahours found the following values:

Temperature...	145°	152°	219°	231° C.
Density	2·75	2·72	2·17	2·12 (relative to air)

By diluting the vapour with hydrogen **Playfair** and **Wanklyn** (*Journ. Chem. Soc.*, 1862, **15**, 153) were able to measure its density below the normal boiling-point (119°) and found

that the value rose to 4·0 at 60° C. The values required by Avogadro's hypothesis are: for $C_2H_4O_2$ 2·073, for $C_4H_8O_4$ 4·146. The density at 60° C. approximates to that of an acid of the formula $C_4H_8O_4$; at 230° C. it approximates to the value for an acid $C_2H_4O_2$, and is not changed by further heating. Playfair and Wanklyn concluded (*loc. cit.* p. 143) that "in the few cases where any great difference is found between a vapour-density taken at a point near the point of liquefaction, and one taken at a point far removed from the point of liquefaction, there is a chemical and not a merely physical change." The vapour "has sometimes one and sometimes another chemical formula, according as it is more or less heated." In the case of acetic acid the dissociation is expressed by the scheme:

$$C_4H_8O_4 \underset{\text{Low temp.}}{\overset{\text{High temp.}}{\rightleftharpoons}} 2C_2H_4O_2,$$

the action proceeding from left to right with increasing temperature and conversely.

The dissociation of phosphorus pentachloride.—For phosphorus pentachloride vapour, Cahours found (*Ann. Chim. Phys.*, 1847, [3], **20**, 373):

Temp.....	182°	200°	250°	300°	336° C.
Density	5·078	4·851	3·991	3·654	3·656

By diluting with air, Wurtz was able to measure the density of the vapour at 129° C. under a partial pressure of 175 mm., and found that the value increased to 6·4 (*Comptes rendus*, 1873, **76**, 603), thus approaching the value 7·217 required by the formula PCl_5. The lower values observed at temperatures above 129° C. were obviously due to dissociation, as shown by the equation:

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2,$$

the dissociation being substantially complete above 300°C.

If the low vapour-densities were actually due to dissociation, they should be raised by adding one of the products since this would tend to accelerate their recombination. Wurtz found (*loc. cit.* p. 608) that when the pentachloride was vaporised at 160 to 176° C. into an atmosphere of phosphorus trichloride, it had the vapour density 7·226, agreeing closely with the value of 7·217 calculated for the formula PCl_5.

The dissociation of sulphur vapour.—The decrease of vapour density with rising temperature is shown in a still more marked degree by sulphur, the vapour-density of which falls from 6·57 at 524°C. (Dumas, *Ann. Chim. Phys.*, 1832, **50**, 175) to 2·23 at 860°C. and 1040°C. (Deville and Troost, *Ann. Chim. Phys.*, 1860, **58**, 287 and 298). The latter value corresponds with the formula S_2; the former approximates to that required by the formula S_6; later measurements at lower temperatures and reduced pressures have given values approximating to that required for the formula S_8.[1] It is probable that the vapour contains molecules of two types, as shown by the equation:

$$S_8 \rightleftarrows 4S_2,$$

but intermediate forms such as S_6 and S_4 are by no means excluded.

The dissociation of nitrogen peroxide discovered by Playfair and Wanklyn (1862).—Playfair and Wanklyn discovered in 1862 (*loc. cit.* p. 156) that the vapour-density of nitrogen peroxide (diluted with nitrogen) decreases with rising temperature as follows:

Temp.....	4·2°	11·3°	24·5°	97·5° C.
Density	2·588	2·645	2·520	1·783

[1] Bleier and Kohn (*Ber.*, 1900, **33**, 51) found $S_{7.85}$ at 193° C. and 2·1 mm. pressure. Biltz (*Ber.*, 1901, **34**, 2493) obtained an average value $S_{7·96}$ in ten readings at the normal boiling-point, under pressures ranging from 200 to 540 mm.

Deville and Troost found (*Comptes rendus*, 1867, **64**, 237–243) for the pure vapour :

Temp. ...	26·7°	49·6°	60·2°	80·6°	100·1°	121·5°	135°	154° C.
Density...	2·65	2·27	2·08	1·80	1·68	1·62	1·60	1·58

The values calculated by Playfair and Wanklyn were 3·179 for N_2O_4, 1·589 for NO_2. The percentage composition of the vapour is therefore :

	$N_2O_4 \rightleftarrows 2NO_2$	
At 26·7° C.	80%	20%
At 49·6°	60	40
At 100·1°	11	89

the dissociation being complete from 154° C. upwards.

Playfair and Wanklyn concluded "that peroxide of nitrogen exists in two states ; that there are two bodies having the same percentage composition as peroxide of nitrogen, but which are polymeric." The change of molecular state was associated by them with "the wonderful deepening of colour which peroxide of nitrogen undergoes on being heated," and which had been noted by Priestley ninety years before (p. 76).

The two changes are undoubtedly due to a common cause, namely, the dissociation of a dense colourless tetroxide, N_2O_4, into a deeply-coloured dioxide, NO_2, of lower density. The liquid, boiling at 22° C., which Gay-Lussac prepared in 1816 by heating lead nitrate and cooling the vapours by means of ice and salt (*Ann. Chim. Phys.*, 1816, **1**, 405), is pale yellow ; it probably consists of N_2O_4 with only a trace of NO_2. The solid, melting at −10° C., is a colourless ice (Deville and Troost, *Comptes rendus*, 1867, **64**, 238, footnote), and must be regarded as the pure tetroxide, free from all traces of dioxide.

The dissociation of nitrogen peroxide,

$$N_2O_4 \rightleftarrows 2NO_2,$$

cannot be proved by chilling the brown dioxide, which loses

its colour immediately when cooled ; nor can Pebal's method of diffusion be applied to a substance which gives only one product of decomposition. But the dissociation, indicated by the changing vapour-densities and made visible by changes of colour, is revealed in a striking way by the large absorption of heat which accompanies it. To raise the temperature of 92 grams of the gas through 1° C. requires (Berthelot and Ogier, *Ann. Chim. Phys.*, 1883 [v], **30**, 392)

Between 27	and 67° C.	74·7	calories
,, 67	,, 103°	57·0	,,
,, 103	,, 150°	27·0	,,
,, 150	,, 198°	9·1	,,

As the heat-capacity of a gas usually increases with rising temperature, the remarkable absorption of heat in the lower ranges must be due to a chemical change : a direct comparison has shown that the heat-capacity is greatest just when the degree of dissociation (as calculated from the vapour-densities) is increasing most rapidly and that the two changes run parallel throughout ; thus the percentage of dissociation occurring over three consecutive ranges of temperature were calculated to be as follows (Berthelot and Ogier, *loc. cit.* p. 398) :

From vapour density.		From heat capacity.	
27–70° C.	35·6%	27–67° C.	40·0%
70–100°	23·6%	67–103°	26·3%
100–136°	9·5%	103–150°	13·2%

Deville (1867) does not accept the dissociation of sal-ammoniac, acetic acid, phosphorus pentachloride, and nitrogen peroxide.—It is remarkable that Deville found himself unable to accept the view that sal-ammoniac vapour contained free ammonia and free hydrogen chloride : these, he held, were formed from the undecomposed vapour by the process of diffusion. Further, he did not consider that dissociation was responsible for the change of vapour-density with temperature, and concluded that :

"For all vapours condensible above zero, what is called the vapour-density is a mathematical fiction, to which it is impossible to give a physical meaning. Its interpretation is only possible when the vapour, at a point sufficiently above the boiling-point, obeys the law of Mariotte, and possesses the constant coefficient of expansion, 0·00367, of the perfect gases" (*Comptes rendus*, 1867, **64**, 242).

The association of water.—In the case of water-vapour, the vapour-density agrees almost down to the boiling-point with that calculated for the formula H_2O. But Bose (*Zeit. Elektrochem.*, 1908, **14**, 271) has recently found evidence of polymerisation in the neighbourhood of 100°, the increase of density corresponding with the formation of about 9% of H_4O_2. Liquid water at 100° appears to be polymerised to such an extent that the *average* size of the molecules is approximately that shown by the formula H_4O_2 (Guye, *Trans. Faraday Soc.*, 1910, **6**, 78). The formation of unstable complex molecules during the condensation of a vapour is usually described as ASSOCIATION. The phenomenon does not differ essentially from those cases of dissociation ($S_8 \rightleftarrows 4S_2$, $N_2O_4 \rightleftarrows 2NO_2$), in which only a single product is formed. The term is, however, usually applied to cases in which the vapour has a normal density and the polymerisation is, for the most part, confined to the liquid and solid states.

The evidence of association in liquid water is particularly strong. Röntgen pointed out in 1891 that the anomalous contraction between 0° and 4° might be explained by a gradual dissociation of "ice-molecules" into denser "water-molecules." Sutherland suggested that these might be formulated as follows:

"steam-molecules" H_2O = "hydrol"
"water-molecules" H_4O_2 = "dihydrol"
"ice-molecules" H_6O_3 = "trihydrol."

Following the analogy of nitrogen peroxide, it may be

supposed that steam above (say) 150° C. consists entirely of hydrol, but that small quantities of dihydrol are formed as the boiling-point is approached. Liquid water is obviously a mixture consisting mainly of "water-molecules"; but at high temperatures "steam-molecules" are present in large proportions, whilst "ice-molecules" become important as the freezing-point is approached. Ordinary ice, like solid nitrogen peroxide, is probably a homogeneous material, consisting entirely of "ice-molecules," H_6O_3. But Tammann by compressing to 2,500 atmospheres and cooling to −22°C. has frozen out a dense ice, which sinks instead of floating in liquid air, but swells up and reverts to ordinary light ice when warmed up to −130° C.; this dense ice is probably composed of the denser "water-molecules," and may be regarded as pure dihydrol, H_4O_2. There are, however, four or five varieties of dense ice and two or more of light ice known (Tammann, *Annual Reports*, 1910, 1912, 1913; Bridgman, *Proc. Amer. Acad.*, 1912, **47**, 441).

B. The Conditions of Chemical Change.

H. B. Baker (1894) on the influence of moisture on the dissociation of sal-ammoniac.—In his earlier papers Deville described dissociation as a "spontaneous decomposition" by heat without the intervention of any chemical agency. The later work of H. B. Baker and others has rendered it doubtful whether dissociation can ever occur under such conditions. In his experiments on the "Influence of Moisture on Chemical Change" (*Trans. Chem. Soc.*, 1894, **65**, 611–624), **H. B. Baker** found that dry ammonium chloride could be vaporised *without decomposition* into the dried bulb of a Victor Meyer's vapour-density apparatus, specially constructed of hard glass and heated to 350° C. Six experiments gave an average vapour-density 27·8, relatively to hydrogen, as compared with 26·75 calculated

for the formula NH_4Cl. A similar value, 28·8, was obtained (*Trans. Chem. Soc.*, 1898, **73**, 426) by Dumas' method, the dried salt being vaporised into a dried bulb protected from the moisture of the atmosphere by a long tube of phosphoric anhydride.

Baker also found that ammonia and hydrogen chloride, after being dried during a week by contact with purified phosphoric anhydride,[1] did not contract on mixing and gave no fumes of ammonium chloride. But "If a trace of moisture be admitted to the mixture of dried gases, dense white fumes are at once produced, and the mercury rushes up into the tube" (*Trans. Chem. Soc.*, 1894, **65**, 615).

Carefully-prepared quicklime and ammonium chloride, after drying during 17 days, gave no ammonia when mixed and heated, the ammonium chloride subliming unchanged from the lime. But when the rest of the ammonium chloride was mixed with lime, after allowing moist air to enter the tube, ammonia was evolved freely on heating the mixture.

From such experiments it appears that moisture is necessary both for the production of sal-ammoniac from ammonia and hydrogen chloride and for its decomposition by heat or by the action of quicklime.

Influence of moisture on the dissociation of calomel.—In 1900 (*Trans. Chem. Soc.*, 1900, **77**, 646) Baker showed that calomel or mercurous chloride, dried by sulphuric acid and vaporised in a Victor Meyer apparatus containing nitrogen and heated to 444° C., gave a vapour-density 118·4 (hydrogen = 1); similar material, dried during three weeks in presence of phosphoric anhydride, gave in five experiments the average value 217·4, approaching the value 235 required for the formula Hg_2Cl_2. Calomel vapour dried by phosphoric anhydride did not amalgamate gold

[1] If the phosphoric anhydride is pure it does not absorb ammonia that has been dried by potash.

leaf, but the moist vapour at once attacked it owing to the liberation of mercury in the dissociation :

$$Hg_2Cl_2 \rightleftharpoons Hg + HgCl_2.$$

Alexander Smith has recently shown (*Zeit. physikal. Chem.*, 1911, **76**, 713) that calomel, heated at 115° C. during $5\frac{1}{2}$ months in a sealed bulb containing phosphoric anhydride, became so thoroughly dried that it would not vaporise at all at 352° C. (usual vapour pressure 347 mm.).

Baker's work on the oxides of nitrogen (1894–1912).— Baker found in 1894 (*loc. cit.* p. 613) that oxygen and nitric oxide if carefully prepared and dried by phosphoric anhydride during 10 days did not combine when mixed ; no contraction took place over mercury and no darkening of the gas could be seen. But "when a small quantity of water was introduced, dense brown fumes of the peroxide were immediately produced."

The dissociation of the gaseous peroxide,

$$N_2O_4 \rightleftharpoons 2NO_2,$$

did not appear to be affected by drying the gas ; but later experiments showed that the boiling-point of the liquid was raised from + 22° to over + 69° C. by drying during more than a year (*Trans. Chem. Soc.*, 1912, **101**, 2341).

The trioxide, N_2O_3, or nitrous anhydride, forms blue crystals melting at − 111° C., but dissociates completely when vaporised at atmospheric temperatures :

$$N_2O_3 \rightarrow NO_2 + NO \text{ or } 2N_2O_3 \rightarrow N_2O_4 + 2NO.$$

The dried liquid, when evaporated, gave vapour-densities ranging from 38·1 to 62·2 (hydrogen = 1). As N_2O_3 requires V.D. 38 only, the vapour was not merely undissociated, but actually associated, consisting largely of complex molecules, *e.g.* N_4O_6, analogous to those present in the vapour of phosphorous anhydride, P_4O_6 (*Trans. Chem. Soc.*, 1907, **91**, 1862). After 3 years' drying the boiling-point of the liquid was raised from − 2° to + 43° C. :

"The vapour of the very dry trioxide was red, and on cooling to + 10° C. it condensed to a green liquid, which on further cooling turned bright blue, showing that it was still nitrogen trioxide. On allowing some nitrogen, dried by passage through a long column of phosphoric oxide, to enter the tube, the small amount of moisture it contained caused rapid dissociation, and the resulting sudden increase blew out the stopper of the tube."

Five years' drying gave a liquid which, instead of becoming olive-green above – 20° C., was permanently blue at ordinary temperatures and perhaps consisted of undecomposed N_4O_6 (*Trans. Chem. Soc.*, 1912, **101**, 2341).

Influence of moisture on combustion.—Baker's work on dissociation formed part of an investigation initiated by H. B. Dixon, on the influence of moisture on chemical change and especially on combustion. The following actions are checked, or altogether arrested, by careful drying :

$$2CO + O_2 \rightarrow 2CO_2$$
$$C + O_2 \rightarrow CO_2$$
$$S + O_2 \rightarrow SO_2$$
$$P_4 + 5O_2 \rightarrow P_4O_{10}$$
$$2H_2 + O_2 \rightarrow 2H_2O$$

A dried mixture of carbonic oxide and oxygen was sparked without exploding (H. B. Dixon, *Phil. Trans.*, 1884, **175**, 630). Both sulphur and phosphorus were distilled to and fro in sealed tubes containing dried oxygen without taking fire, whilst purified carbon was only partially burned by prolonged heating in oxygen (H. B. Baker, *Phil. Trans.*, 1888, **179**, 571). Hydrogen and oxygen were found to be almost incapable of exploding when pure and dry (Baker, *Trans. Chem. Soc.*, 1902, **81**, 400).

The mixed gases, prepared by the electrolysis of purified baryta, were passed through a column of phosphoric anhydride and collected in cleaned vacuous tubes of hard glass,

each containing a small tube filled with purified phosphoric anhydride. The mixture was sealed in by a plug of fusible metal and put aside to dry (Fig. 57).

"Comparative tubes were made at the same time from the same length of tubing and treated in precisely the same way, except that no phosphoric oxide was sealed up in them. After 10 days' drying, two such tubes were heated side by side in the same Bunsen burner flame. In twelve experiments, the wet tube exploded and the dry tube did not. In only one experiment has a dry tube exploded, but in this case the tube had been carried for some miles by hand, and most probably some of the phosphoric oxide had been shaken into the part of the tube which was heated. In two experiments, where only 2 days' drying had been allowed, water was slowly formed in the dried tube, but although visible moisture was present, no explosive combination took place, and a slow combination only occurred."

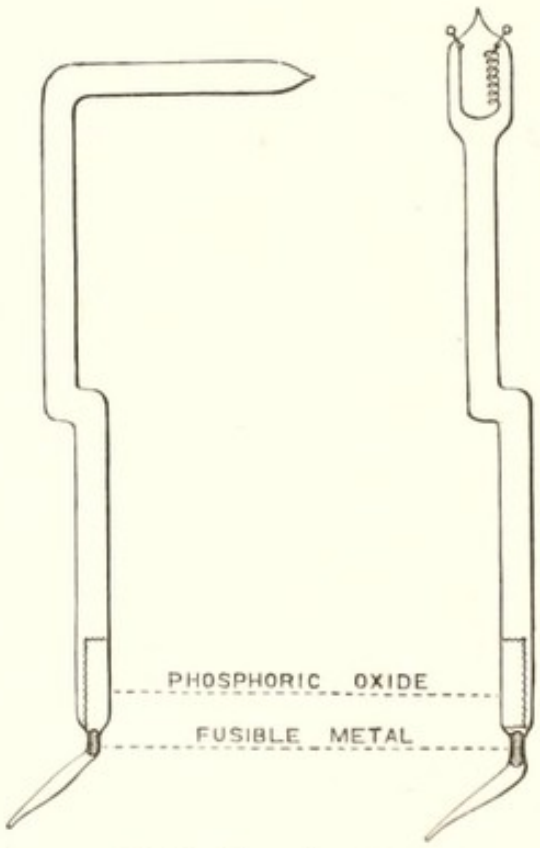


FIG. 57.—H. B. BAKER'S APPARATUS FOR HEATING DRIED MIXTURES OF HYDROGEN AND OXYGEN (1) by means of a burner, (2) by a silver wire heated to fusion.

Silver was melted in the dried gas, and small sparks were passed through it without producing an explosion: but the melting of platinum and the passage of larger sparks always detonated the mixture.

Conditions under which chemical change takes place.—The experiments described in the preceding paragraphs show that chemical changes frequently involve factors which

are not shown in the ordinary equations. The metals potassium, sodium, magnesium, zinc, cadmium and iron do not dissolve in liquefied hydrogen chloride, nor does it act at all on quicklime or marble (Gore, *Proc. Roy. Soc.*, 1865, **14**, 204–213). Dry chlorine does not act upon sodium either at the ordinary temperature or when fused (Wanklyn, *Chem. News*, 1869, **20**, 271), and has but little action on silver, zinc, magnesium and potassium (Cowper, *Trans. Chem. Soc.*, 1883, **43**, 153–155). Nitric acid, which has been freed from water and from lower oxides of nitrogen, has no action upon purified copper, silver, cadmium or mercury, nor upon commercial magnesium at ordinary temperatures; even when boiling it does not attack iron or tin, nor dissolve Iceland spar or marble (Veley, *Phil. Trans.*, 1898, A. **191**, 388). Copper does not dissolve readily even in diluted nitric acid if freed from lower oxides of nitrogen, but as soon as it begins to dissolve these are produced in increasing quantities and the action is rapidly accelerated (Veley, *Proc. Roy. Soc.*, 1889, **46**, 216–222). Highly purified zinc, redistilled in a vacuum, is "nearly unacted on by sulphuric or hydrochloric acid" (Reynolds and Ramsay, *Trans. Chem. Soc.*, 1887, **51**, 857), but it is rendered soluble by contact with the less active metals, such as lead, copper and platinum. Metals do not combine with dried chlorine, nor sodium and potassium with dried oxygen; dry lime does not combine with carbonic anhydride (Veley, *Trans. Chem. Soc.*, 1893, **63**, 821), nor does sulphuric anhydride combine with dry quicklime or with the dry oxide of copper (Baker, *Trans. Chem. Soc.*, 1894, **65**, 622). Pure iron does not rust, does not dissolve in cold dilute sulphuric or nitric acid, and has no action on aqueous copper sulphate or copper nitrate (Lambert, *Trans. Chem. Soc.*, 1912, **101**, 2069).

In the case of metals dissolving in acids, the conditions for dissolution are clearly identical with those for the production of a battery, namely, two electrodes (*e.g.* zinc and

copper) and an electrolyte (*e.g.* dilute sulphuric acid). The pure anhydrous acids do not conduct and do not therefore provide a proper electrolyte. Pure zinc, on the other hand, fails to dissolve in dilute acids because, in the absence of impurities, such as lead, arsenic and carbon, there is only one electrode provided for the passage of the current.

Armstrong (1885) regards chemical change as reversed electrolysis.—H. E. Armstrong, in 1885 (*B.A. Report, Aberdeen*, 945–964), applied these ideas boldly to chemical changes of every type. In electrolysis, an electrolyte is decomposed by energy supplied from an external source: in a battery, decomposition of the electrolyte is itself a source of energy. The decomposition of the electrolyte taking place in the single fluid cell results in the conversion of

$$Zn + SO_4|H_2 + Cu$$

into

$$ZnSO_4 + H_2 + Cu.$$

In the Daniell cell two electrolytes are decomposed in series, the system

$$Zn + SO_4|H_2 + SO_4|Cu + Cu$$

changing to

$$ZnSO_4 + H_2SO_4 + Cu + Cu.$$

In the Grove cell the change is from

$$Zn + SO_4|H_2 + ONO_2H + Pt$$

to

$$ZnSO_4 + H_2O + NO_2H + Pt\ ;$$

dilute sulphuric acid is electrolysed, but the concentrated nitric acid in the cell is reduced, rather than electrolysed, and may be regarded as constituting the second of the two electrodes between which the electrolysis of the sulphuric acid takes place.

Armstrong, adopting a hint given by Faraday, suggested, in 1885 that all chemical changes are electrolytic in character and take place under the same conditions that prevail in a cell, namely, by the co-operation of three distinct substances, at least one of which must be an electrolyte. In the union

of hydrogen and oxygen these two substances would function as "depolarising" electrodes for a trace of water acting as electrolyte:

$$2H_2 + 2O|H_2 + O_2$$

giving $$2H_2O + 2H_2O.$$

Seventeen years before Baker's experiments were carried to a successful conclusion, Armstrong acting on this belief, ventured to affirm, "that some day it would be ascertained that a mixture of pure oxygen with pure hydrogen was not explosive" (*Proc. Chem. Soc.*, 1885, **1**, 39). He added, however, that "Water not being an electrolyte, . . . it was difficult to understand that the presence of water pure and simple should be of influence in the case of a mixture of oxygen and hydrogen" (*loc. cit.* p. 40); to be effective the water must be sufficiently impure to render it conducting.

The startling verification of these two daring predictions by Baker's experiments in 1902 affords the strongest evidence of the correctness of the views on which they were based.

Summary and Supplement.

A. Dissociation and Association.

Grove, in 1847, discovered that steam could be decomposed by hot platinum, bubbles of detonating gas to the amount of $\frac{1}{2400}$ being formed when the steam condensed. The decomposition actually amounts to

0·0078% at 1124° C.	1·18% at 1882° C.
0·0189% at 1207°	1·77% at 1984°
0·034% at 1288°	

(Nernst, Wartenburg, *Zeit. physikal. Chem.*, 1906, **56**, 533, 541). If the steam were cooled slowly, the hydrogen and oxygen would recombine as shown by the lower arrow in the equation

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

but by cooling quickly to a temperature below that at which the gases recombine it is possible to fix the decomposition products as they are formed at higher temperatures.

St. Claire Deville, in 1857, described the "spontaneous decomposition" of substances by heat as *dissociation*, but in 1863 limited the term to *reversible decompositions*. By using a "hot-cold tube" he was able in 1865 to prove the dissociation of :

(1) *Water* $2H_2O \rightleftarrows 2H_2+O_2$
(2) *Carbon dioxide* $2CO_2 \rightleftarrows 2CO+O_2$
(3) *Carbonic oxide* $2CO \rightleftarrows C+CO_2$
(4) *Sulphur dioxide* $3SO_2 \rightleftarrows S+2SO_3$
(5) *Hydrogen chloride* $2HCl \rightleftarrows Cl_2+H_2$ (the chlorine being fixed in the form of metallic chlorides on the cold tube).

He brought about similar decompositions by sparking, but showed that sulphur dioxide and oxygen could be recombined by sparking over sulphuric acid and hydrogen and nitrogen by sparking in presence of hydrogen chloride :

$$2SO_2+O_2 \rightleftarrows 2SO_3 \rightarrow \text{(fixed as } H_2S_2O_7)$$
$$3H_2+N_2 \rightleftarrows 2NH_3 \rightarrow \text{(fixed as } NH_4Cl).$$

Pebal, in 1862, separated by diffusion the products of dissociation of ammonium chloride :

$$NH_4Cl \underset{\text{Low temp.}}{\overset{\text{High temp.}}{\rightleftarrows}} NH_3+HCl,$$

He thus proved the correctness of the view suggested by **Cannizzaro** (1857) and by **Kopp** (1858) that the abnormalities detected by **Bineau** (1838) in the vapour densities of the ammonium and phosphonium salts were due to the dissociation of the salts. Deville, however, rejected all cases of dissociation in which the products could not be fixed by suddenly chilling the vapour.

Cahours, in 1844 and 1847, discovered that the vapour-densities of acetic acid and of phosphorus pentachloride diminished as the temperature rose. **Playfair** and **Wanklyn**, in 1862, observed a similar phenomenon in nitrogen peroxide and attributed it to dissociation :

$$C_4H_8O_4 \rightleftarrows 2C_2H_4O_2$$
$$PCl_5 \rightleftarrows PCl_3+Cl_2$$
$$N_2O_4 \rightleftarrows 2NO_2.$$

Above 150° C. nitrogen peroxide consists entirely of the brown gas NO_2; at 100° C. there is $\frac{1}{9}$ of N_2O_4 by weight, at 50° C. $\frac{3}{5}$, and at 27° C. $\frac{4}{5}$. The liquid (b.p. 22° C.) consists almost entirely of N_2O_4, which finally freezes out at − 10° C. as a colourless ice. The dissociation of the colourless tetroxide is accompanied by an absorption of heat, and produces a remarkable increase in the heat-capacity of the gas.

Similar phenomena occur in the case of water. The vapour at 100° C. consists of "steam-molecules," H_2O, mixed with about 9% of "water-molecules," H_4O_2. The liquid is probably a similar mixture, but consisting mainly of "water-molecules," H_4O_2, in which at lower temperatures "ice-molecules" (perhaps H_6O_3) of lower density are formed in increasing proportions, giving rise finally to an expansion of volume between 4° and 0° C. Ordinary *light ice* is evidently composed of the same "ice-molecules" in the crystalline state, but the *dense ice*, which freezes out under pressures above 2,300 atmospheres (Tammann), may be composed of the denser "water-molecules." There are probably 4 or 5 varieties of dense ice, one of which melts at 78°C. under 20,000 atmospheres pressure (Bridgman): it is also possible that light ice exists in several forms (Tammann).

B. The Conditions of Chemical Change

Wanklyn, in 1869, showed that dry chlorine did not act on solid or on molten sodium; this observation was confirmed, and extended to other metals, by **Cowper** in 1883.

H. B. Dixon, in 1884, found that a dried mixture of *carbonic oxide* and oxygen was not explosive.

H. B. Baker, in 1888, showed that *sulphur* and *phosphorus* could be distilled and that purified *carbon* could be heated to redness in dry oxygen without ignition. In 1894 he showed that dry *ammonium chloride* could be vaporised without dissociating and that it sublimed unchanged from quicklime; conversely, dry ammonia and dry hydrogen chloride did not combine when mixed. *Sulphur trioxide* did not combine with quicklime or with cupric oxide. Dry *nitric oxide* did not combine with oxygen. In 1900, he showed that dry calomel could be vaporised, as Hg_2Cl_2, without decomposition and that the vapour did not amalgamate gold-leaf: the later work of A. Smith has

shown that further drying prevents the calomel from vaporising at 352° C. In 1902, Baker showed that pure dry *hydrogen* and *oxygen* did not inflame at a red heat, nor when a silver wire was melted in the gas; when dried less perfectly, a slow combustion took place, but there was no explosion even when visible moisture was present in the tube. In 1907, he showed that *nitrous anhydride*, which dissociates completely at ordinary temperatures ($N_2O_3 \rightarrow NO_2 + NO$), can be vaporised as a mixture of N_2O_3 and N_4O_6 if carefully dried. In 1912 he showed that longer drying raised the boiling-point of the anhydride from −2° to +43° C. and that the boiling-point of *nitrogen peroxide* was raised from +22° to +69° C.

The experiments of **Gore, Veley, Reynolds and Ramsay, Lambert** and others have shown that purified acids do not act on commercial metals, and that purified metals are not acted on by commercial acids. The conditions for interaction are the same as in a battery, which consists of three essential parts, namely, two electrodes and an electrolyte. **Armstrong**, in 1885, suggested that all chemical action was *reversed electrolysis*, a view that is supported by the whole of Baker's work.

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1779–1792. *Physical and Chemical Essays* (Opuscula Physica et Chemica, Six Volumes[1]; the earlier essays, tr. E. Cullen, Two Volumes, 1784). Amongst these Essays are the following :
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(*b*) 1778. "Of the Analysis of Waters." Hardness produced by acids or by salts with an earthy, metallic base, 107
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BERTHOLLET, CLAUDE LOUIS, *b.* 1748, Annecy, in Savoy ; *d.* 1822, Arcueil, nr. Paris. After the revolution, Berthollet took the place of Lavoisier as the recognised leader of French science. He assisted Napoleon in organising the expedition to Egypt, and read his paper on "Chemical Affinity" at Cairo. The Société d'Arcueil, which met at his house at Arcueil, near Paris, included Berthollet (father and son), La Place, Biot, Gay-Lussac, Humboldt, Thenard, De Candolle, and Decostils. Three volumes of Memoirs, published in 1807, 1809, and 1817, contain some of the most important papers of this period of chemistry

[1] Vol. IV. (1787). "Meditationes de Systemate Fossilum Naturale," translated from a Swedish paper dated 1784, appears to contain the earliest use of the word "ammonia" (*loc. cit.*, p. 293) ; Kopp, however, gives the date 1782 for the first use of this word.

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From 1822 to 1848 Berzelius wrote a series of *Annual Reports* on the Progress of Physical Science. The German translations by Gmelin and by Wöhler are familiar under the name of Berzelius's *Jahresberichte*, and are quoted in several places in the text. Another important publication is his *Textbook of Chemistry*, First Edition, 3 Vols. (in Swedish), 1808–1818 ; Fifth Edition, 5 Vols. (in German), 1843–1848 ; quoted on p. 398

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BLACK, JOSEPH, *b.* 1728 near Bordeaux; *d.* 1799, Edinburgh. Professor of Anatomy and Chemistry at Glasgow; then Professor of Chemistry at Edinburgh

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DAVY, Sir HUMPHRY, *b.*, 1778, Truro ; *d.*, 1829, Geneva. Professor of Chemistry at the Royal Institution ; President of the Royal Society.

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(*a*) 1831. "Induction of Electric Currents."
(*b*) 1833. "Identity of Electricities of Different Sources."
(*c*) 1833–4. "Electro-chemical Decomposition."
(*d*) 1846. "On the Magnetisation of Light."
The 1834 paper (repr. *Experimental Researches in Electricity*, Vol. I. pp. 195–258), includes the definitions of electrode, anode, and cathode (p. 196), electrolytes (p. 197), ions, anions, and cations (p. 198), and Faraday's two laws of electrolysis, stated as follows : "*That the chemical power of a current of electricity is in direct proportion to the absolute quantity of electricity which passes*" (p. 241), and that the "*electro-chemical equivalents* [*of the ions*] *are the same as their ordinary chemical equivalents.*"

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GAY-LUSSAC, LOUIS JOSEPH, *b.* 1778, Limousin; *d.* 1850, Paris. Professor of Chemistry at the École Polytechnique and of Physics at the Sorbonne; Professor of Chemistry at the Jardin des Plantes.
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PRIESTLEY, JOSEPH, *b.* 1773, near Leeds ; *d.* 1804, Northumberland, U.S.A. Priestley's papers, many of which appeared first in the *Philosophical Transactions* of the Royal Society, were published in six volumes as follows : *Experiments and Observations on different kinds of Air*, Vol. I. (1774), Vol. II. (1775),

Vol. III. (1777). *Experiments and Observations Relating to Various Branches of Natural Philosophy, with a Continuation of the Observations on Air* (1777); ditto, Vol. II. (1781), with an index to both the Volumes, and a "Summary View of all the most remarkable facts in this and the four preceding volumes"; Vol. III. (1786). In the text, following the method adopted in Priestley's Summary, the six volumes are quoted by consecutive numbers I. to VI. The experiments on the "Discovery of Oxygen" are quoted from *A.C.R.* VII.

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