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THE GASES OF THE ATMOSPHERE

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THE GASES

OF

THE ATMOSPHERE

THE

HISTORY OF THEIR DISCOVERY

BY

SIR WILLIAM RAMSAY, K.C.B., F.R.S.

OFFICIER DE LA LEGION D'HONNEUR

EMERITUS PROFESSOR OF CHEMISTRY IN UNIVERSITY COLLEGE, LONDON

FOURTH EDITION

WITH PORTRAITS

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"Modern discoveries have not been made by large collections of facts, with subsequent discussion, separation, and resulting deduction of a truth thus rendered perceptible. A few facts have suggested an *hypothesis*, which means a *supposition*, proper to explain them. The necessary results of this supposition are worked out, and then, and not till then, other facts are examined to see if their ulterior results are found in Nature."—DE MORGAN, *A Budget of Paradoxes*, ed. 1872, p. 55.

"*Natura nihil agit frustra* is the only indisputed Axiome in Philosophy. There are no Grotesques in Nature; not anything framed to fill up empty Cantons and unnecessary spaces."—SIR THOMAS BROWNE'S *Religio Medici*.

First Edition, 1896.
Second Edition, 1900.
Third Edition, 1905.
Fourth Edition, 1915.

PREFACE TO THE FOURTH EDITION

SINCE 1905, progress has been made in our knowledge of niton or "radium emanation"; and some light has been thrown on the possible sources of the rare gases of the atmosphere. This has been incorporated at the end of the last chapter.

WILLIAM RAMSAY.

August 1915.

PREFACE TO THE THIRD EDITION

THE radioactive gases, products of the disintegration of the remarkable elements radium and radiothorium, have been recently added to the list of the constituents of the atmosphere. An attempt has been made in an additional chapter to give an account of these; but the reader who is interested in the subject is advised to consult the much

more complete works by Professor Rutherford, Mr. Frederick Soddy, and the Honourable R. J. Strutt, if he wishes to learn more about the nature of the disintegration of the parents of these gases, radium and thorium, and the astonishing changes which they spontaneously undergo. The beginning of the twentieth century has been characterised by a revolution in chemical thought more wonderful than any which has ever been seen, and this has had its influence on our conception of the nature of the atmosphere. But the ground has only been surveyed; future years will certainly bring fuller knowledge.

May 1905.

PREFACE TO THE SECOND EDITION

SINCE the publication of the first edition, atmospheric air has been found to contain other four inactive gases, belonging to the same class of elements as argon. These are helium, discovered by myself in 1895 in certain rare minerals, but first separated from the atmosphere in 1900; and neon, krypton, and xenon, discovered in conjunction with Dr. M. W. Travers in 1898, and separated from argon and from each other during the years 1899 and 1900. An additional chapter has been added, giving an account of these elements. I have also to thank Mr. S. Lupton and Dr. Hartog for some interesting details of the lives of Mayow and of Priestley, which, along with some *errata*, will be found at the end of the book.

December 1900.

PREFACE TO THE FIRST EDITION

THE discovery of a new elementary gas in the atmosphere in 1894 aroused much interest, and public attention has again been directed to the air, which was, for many centuries, a fruitful field for speculation and conjecture. The account of this discovery, communicated to the Royal Society in January 1895, was, however, necessarily couched in scientific language; and many matters of interest to the chemist and physicist were written in an abbreviated style, in the knowledge that the passages describing them would be easily understood by the experts to whom the communication was primarily addressed. But persons without any special scientific training have frequently expressed to me the hope that an account of the discovery would be published, in which the conclusions drawn

from the physical behaviour of argon should be accompanied by a full account of the reasoning on which they are based. An endeavour to fulfil this request is to be found in the following pages. And as the history of the discovery of the better known constituents of the atmosphere is of itself of great interest, and leads up to an acquaintance with the new stranger, who has so long been with us incognito, an effort has here been made to tell the tale of the air in popular language.

January 1896.

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CHAPTER I

THE EXPERIMENTS AND SPECULATIONS OF BOYLE, MAYOW, AND HALES

To tell the story of the development of men's ideas regarding the nature of atmospheric air is in great part to write a history of chemistry and physics. This history is an attractive and varied one: in its early stages it was expressed in the quaint terms of ancient mythology, while in its later developments it illustrates the advantage of careful experimental inquiry. The human mind is apt to reason from insufficient premises; and we meet with many instances of incorrect conclusions, based upon experiment, it is true, but upon experiment inadequate to support their burden. Further research has often proved the reasoning of the Schoolmen to be futile; not indeed from want of logical method, but because important premisses had been overlooked.

Among the errors which misled the older speculators, three stand out conspicuously. These are—

First, *The confusion of one gas with another.*—Since gases are for the most part colourless, and always transparent, they make less impression on the senses than liquids or solids do. It was difficult to believe in the substantiality of bodies which could not be seen, but the existence of which had to be inferred from the testimony of other senses; indeed, in certain instances only by the sense of touch, for many gases possess neither smell nor taste. This peculiarity led, in past ages, to the notion that air possessed a semi-spiritual nature; that its substantiality was less than that of other objects more accessible to our senses. We meet with a relic of this view in words still in common use. Thus the Greek words πνέω, I blow, and πνεῦμα, a spirit or ghost, are closely connected; in Latin we have *spiro*, I breathe, and *spiritus*, the human spirit; in English, the words *ghost* and *gust* are cognate. And the same connection can be traced in similar words in many other languages.

Our sense of smell is affected by extremely minute traces of gases and vapours—traces so small

as to be unrecognisable by any other method of perception, direct or indirect. A piece of musk retains its fragrant odour for years, and the most delicate balance fails to detect any appreciable loss of weight in it. We are capable of smelling gases only: liquids and solids, if introduced into the nostrils, irritate the olfactory nerves, but do not stimulate them so as to incite the sense of smell; yet the admixture of a minute trace of some odorous vapour with air appears entirely to change its properties. The effect of inhaling such air, although sometimes pleasant, is very different from the sensation produced by pure inodorous air, and such admixtures were in olden times naturally taken to be air modified in its properties. But such modifications are obviously almost infinite in number, for varieties of scent are excessively numerous; and it was therefore perhaps deemed useless to attempt to investigate such a substance as air, whose properties could change in so inexplicable and mysterious a manner. Owing, therefore, to its elusive and, as it were, semi-spiritual properties, and to its unexpected changes of character, it was long before its true nature was discovered. It had not escaped observation that "air" obtained by distilling animal

and vegetable matter, or by the action of acids on iron and zinc, differed from ordinary air by being inflammable; but such "airs" were regarded as atmospheric air, modified in some manner, as it is modified when perfumed. And "airs" escaping from fermenting liquids, or produced by the action of acids on carbonates, were neglected. For long no attempt was made to catch them; and the frothing and bubbling were regarded as a species of boiling, as is still seen in the use of our word "fermentation" (*fervere*, to boil).

Second, *Erroneous ideas regarding the phenomena of combustion.*—While it was recognised that a burning candle was extinguished if placed in a confined space, its extinction was attributed not to the absence of air, but to the impossibility of the escape of flame. Indeed, flame was regarded as possessing the same semi-spiritual, semi-material nature as air. Together with earth and water, air and flame or fire formed the four elementary principles of the Ancients; and all substances—stones, metals, animals, and vegetables—were regarded as partaking of the properties of these elements, and often as being constituted of the latter in varying proportions, according as they were cold and dry

(earth), cold and moist (water), hot and moist (air), or hot and dry (fire). It is not within the scope of this book to enter into details regarding such ancient views. Those who are interested in the matter will find them expounded in Kopp's *History of Chemistry*, Rodwell's *Birth of Chemistry*, E. von Meyer's *History of Chemistry*, and in other similar works. But we shall be obliged to consider the later developments of such ideas in the *phlogistic theory*, by means of which all chemical changes connected with combustion were interpreted from the latter part of the seventeenth to the end of the eighteenth century. With erroneous views regarding the nature of combustion, and ignorance as to the part played by the atmosphere in the phenomena of burning, the true nature of air was undiscoverable.

Third, *The lack of attention to gain or loss of weight.*—It was in past times not recognised that nothing could be created and nothing destroyed. In popular language, a candle is destroyed when it is burned, nothing visible being produced from it. The products, we now know, are gaseous and invisible, and possessed of greater weight than the unburnt candle; but for want of careful experiment, it was formerly concluded that the candle, when burnt, was

annihilated. The formation of a cloud in a cloudless sky; the growth of vegetables in earth, from which, apparently, they did not derive their substance; and the reputed growth of metalliferous lodes in mines—these were all adduced as proofs of the creative power of Nature. With such ideas, therefore, the necessity of controlling the gain or loss of material during experiment, by determining gain or loss of weight, did not appear imperative; and hence but few quantitative experiments were made, and little importance was attached to these few. It had, for example, long been noticed that certain metals gained weight when burned and converted into a "calx," or, as we should now say, a metallic oxide, but such gain in weight was not regarded as of any consequence. When considered in relation to the supposed loss of "phlogiston" suffered by a metal on being converted into a calx, it was explained by the hypothesis that phlogiston possessed "levity,"—the antithesis of gravity,—and that the calx weighed more than the metal, owing to its having lost a principle which was repelled instead of being attracted by the earth.

Among the most remarkable early attempts to elucidate the true nature of air, we meet with one

by the Hon. Robert Boyle, who published about the middle of the seventeenth century his *Memoirs for a General History of the Air*. Boyle was one of the most distinguished scientific men of his own, or indeed of any, age, and in his spirit of calm philosophical inquiry he was far in advance of his contemporaries. He was born in the early part of the year 1626, in Ireland, whither his father, Richard Boyle, had emigrated at the age of twenty-two. Boyle's mother, daughter of Sir Geoffrey Fenton, principal Secretary of State for Ireland, died while he was still a child. Yet she must have lived in the recollection of her son Robert, for he wrote: "To be such parents' son, and not their eldest, was a happiness that our Philarethes (himself) would mention with great expressions of gratitude; his birth so suiting his inclinations and designs, that had he been permitted an election, his choice would scarce have altered God's discernment."

In those days of early development, Boyle had finished his school-days at Eton by his twelfth year. He informs us that he devoured books omnivorously, and could hardly be induced to join in games. The next six years of his life he spent on the Continent with his elder brother; and on his

father's death, which happened when he was abroad, he returned to England, and settled at Stalbridge, in Dorsetshire, where he had inherited a manor. Here he passed most of his life in great retirement, with only an occasional visit to London; for though he lived through troublous times, he avoided politics. Indeed, he is known only to have appeared once on a public platform, and that was in defence of the Royal Society, then in its infancy, from attacks made upon it by some too scrupulously loyal Churchmen.

Boyle did not confine his attention exclusively to scientific pursuits: he interested himself deeply in theology, and published numerous tracts on religious subjects. He wrote with equal ease in English, French, and Latin, and his books appeared simultaneously in the first and last of these languages. His researches are remarkable for their wide range and for the boldness of his conceptions. But Boyle, ingenious though he was, was unable to fathom the mystery of atmospheric air. His views regarding it are succinctly stated by him in his *Memoirs for a General History of the Air*, and in the same work he sums up the views of the Ancients. His words are:

"The Schools teach the air to be a warm and moist element, and consequently a simple and homogeneous body. Many modern philosophers have, indeed, justly given up this elementary purity in the air, yet few seem to think it a body so greatly compounded as it really appears to be. The atmosphere, they allow, is not absolutely pure, but with them it differs from true and simple air only as turbid water from clear. Our atmosphere, in my opinion, consists not wholly of purer aether, or subtile matter which is diffused thro' the universe, but in great number of numberless exhalations of the terraqueous globe; and the various materials that go to compose it, with perhaps some substantial emanations from the celestial bodies, make up together, not a bare indetermined feculency, but a confused aggregate of different effluvia. One principal sort of these effluvia in the atmosphere I take to be saline, which float variously among the rest in that vast ocean; for they seem not to be equally mixed therein, but are to be found of different kinds, in different quantities and places, in different seasons. . . . Many men talk much of a volatile nitre in the air, as the only salt wherewith that fluid is impregnated. I must own

the air, in many places, seems to abound in corpuscles of a nitrous nature; but I don't find it proved by experiments to possess a volatile nitre. In all my experiments upon salt-peter, I found it difficult to raise that salt by a gentle heat; and spirits of nitre, which is drawn by means of a vehement one, has quite different properties from crude nitre, or the supposed volatile kind in the air, for 'tis exceeding corrosive." [1]

Boyle then proceeds to collect and comment on the effluvia from volcanoes and from decaying vegetables and animals, and proposes tests for the presence of such ingredients. He even attributes the darkening of silver chloride to its being a reagent for certain salts present in air at one time and not at another, and draws attention to the sulphurous smell produced by "thunder." Farther on (p. 61) he writes:

"The generality of men are so accustomed to judge of things by their senses, that because the air is invisible they ascribe but little to it, and think it but one remove from nothing. And this fluid is even by the Schoolmen considered only as

[1] *Memoirs for a General History of the Air;* Shaw's Abridgment of Boyle's works, edition 1725, vol. iii. p. 26.

a receptacle of visible bodies, without exerting any action on them unless by its manifest qualities, heat and moisture; tho', for my part, I allow it other faculties, and among them, such as are generative, maturative, and corruptive; and that, too, in respect not only of animals and bodies of a light texture, but even of salts and minerals."

In another place (p. 17) he states:

"I conjecture that the atmospherical air consists of three different kinds of corpuscles: the first, those numberless particles which, in the form of vapours or dry exhalations, ascend from the earth,—water, minerals, vegetables, animals, etc.; in a word, whatever substances are elevated by the celestial or subterraneal heat, and thence diffused into the atmosphere. The second may be yet more subtile, and consist of those exceedingly minute atoms—the magnetical effluvia of the earth, with other innumerable particles sent out from the bodies of the celestial luminaries, and causing, by their impulse, the idea of light in us. The third sort is its characteristic and essential property—I mean permanently elastic parts."

Boyle also relates experiments designed to "produce what appears to be air"; and he describes

the production, by the action of oil-of-vitriol on steel filings, of "air" (now known as hydrogen) which possessed the property of elasticity; although he failed to notice its inflammability. He further obtained carbon dioxide by the fermentation of raisins, and probably also hydrogen chloride in the gaseous form by breaking a bulb containing "some good spirit-of-salt" in a vacuous receiver.

The result of shrewd reasoning power, applied, however, to imperfect observations, is well illustrated by the following passages:

"For tho', by reason of its great thinness and of its being, in its usual state, devoid both of tast and smell, air seems wholly unfit to be a menstruum [or solvent]; yet it may have a dissolving, or at least a consuming, power on many bodies, especially such as are peculiarly disposed to admit its operations. For the air has a great advantage by the vast quantity of it that may come to work, in proportion to the bodies exposed thereto. . . . Thus we find a rust on copper that has been long exposed to the air."[1]

Boyle, shortly after, describes the production of "an efflorescence of a vitriolic nature" on mar-

[1] "Suspicions about some hidden qualities of the Air," *ibid.* p. 77.

casite (or sulphide of iron) which has been exposed to the air; and he relates that the "ore of alum, robb'd of its salt, will in tract of time recover it by being exposed to the air, as we are assured by the experienced *Agricola*."

To account for such actions, and for combustion, he proceeds (p. 81):

"The difficulty we find in keeping flame and fire alive, tho' but for a little time, without air, renders it suspicious that there may be dispersed thro' the rest of the atmosphere some odd substance, either of a solar, astral, or other foreign nature; on account whereof the air is so necessary to the subsistance of flame. . . . It also seems by the sudden wasting or spoiling of this fine substance, whatever it be, that the bulk of it is but very small in proportion to the air it impregnates with its vertue; for after the extinction of the flame the air in the receiver was not visibly alter'd; and for ought I could perceive by several ways of judging, the air retained either all, or at least the far greatest part of its elasticity; which I take to be its most genuine and distinguishing property. And this undestroyed springyness of the air, with the necessity of fresh air to the life of hot animals,

suggest a great suspicion of some vital substance, if I may so call it, diffused thro' the air; whether it be a volatile nitre, or rather some anonymous substance, sidereal or subterraneal; tho' not improbably of kin to that which seems so necessary to the maintenance of the other flames."

The experimental part of Boyle's work in this connection relates to the oxidation of cuprous to cupric compounds, with the change of colour from brown to blue or green, either in ammoniacal or in hydrochloric acid solution; and he goes so far as to prove that two ounces of marcasites broken into small lumps, and kept in a room "freely accessible to the air, which was esteemed to be very pure," for somewhat less than seven weeks, gained above twelve grains by oxidation.

In his *Memoirs for a General History of the Air*, Boyle draws up a programme of research, of the carrying out of which, however, there is no record. He proposes (p. 23):

"1. To produce air by fermentation in well clos'd receivers.

"To produce air by fermentation in sealed glasses.

"To separate air from liquors by boiling.

"To separate air from liquors by the air-pump.

"To produce air by corrosion, especially with spirit of vinegar.

"To separate air by animal and sulphureous dissolvants.

"To obtain air in an exhausted receiver by burning-glasses and red-hot irons.

"To produce air out of gunpowder and other nitrous bodies.

"2. To examine the produced aerial substances by their preserving or reviving animals, flame, fire, the light of rotten wood, and of fish.

"To examine it by its elasticity, and the duration thereof.

"To do the same by its weight, and its elevating the fumes of liquors."

We shall all agree that if Boyle had successfully carried out such experiments, our knowledge of the true nature of air would have come quite a century before it did. Some of these experiments were indeed made by John Mayow, his contemporary, whose work and speculations we shall now proceed to consider.

John Mayow was born in the parish of St. Dunstan in the West, London, in 1643. His family was originally Cornish, having come from Bree, in Cornwall. He entered Wadham College, Oxford, on April 3rd, 1658, at the early age of fourteen, and was shortly afterwards made a probationer-fellow of All Souls College. On May 30th, 1665, after nearly seven years of study, he took the degree of B.A.; in 1670, he graduated as Doctor of Laws (LL.D.); but not being attracted by the legal profession, he turned his attention to medicine, and became a medical practitioner at Bath, where he lived during the fashionable season. When not more than twenty-five years of age, he wrote two essays on Respiration, ascribing the inflation of the lungs to the action of the intercostal muscles. These "Tractatus duo" were published in 1668. Some years later he produced the treatise on which his fame rests; it is entitled "Tractatus quinque medico-physici, quorum primus agit de sal-nitro et spiritu nitro-aëreo; secundus, de respiratione; tertius, de respiratione foetus in utero et ovo; quartus, de motu musculari, et spiritibus animalibus; ultimus, de rhachitide; studio Joh. Mayow, LL.D. & Medici, nec

non Coll. Omn. Anim. in Univ. Oxon. Socii. Oxonii e Theatro Sheldoniano, An. Dom. MDCLXXIV." The work was dedicated to Mr. Henry Coventry. It was inserted in an abridged form in the *Philosophical Transactions* of the Royal Society some time after its publication, but received only scant recognition, for the fame of Newton and Boyle overshadowed the labours of less well-known investigators. And Mayow did not live to press his discoveries on the attention of his contemporaries, for he died in October 1679, five years after the publication of his tracts, in his thirty-seventh year. Little is known of Mayow's domestic life, save that he married shortly before his death. His scientific work proves that if he had been granted the usual span of life, his extraordinary genius would have furthered the knowledge of the true explanation of the nature of air, and its function in supporting combustion and respiration, and that his views would have been accepted more than a century before Lavoisier—with fuller knowledge, and with the scientific position which at once gained a hearing—forced precisely similar doctrines upon the attention of the scientific world.

Mayow was a contemporary of Boyle, and fre-

quently made use of Boyle's experiments in support of the theories which he advanced. Curiously enough, while Boyle seems to have read Mayow's work, he does not appear to have been favourably impressed by his conclusions. Boyle, at the age of fifty-two, had doubtless formed his own opinions, and was unwilling that they should be disturbed by the speculations, well founded though they were, of so young a man. And shortly after Mayow's death, the views of Becher, one of his contemporaries, expounded and made definite by Stahl, regarding the nature of combustion, were universally received.

After Lavoisier's theories had overthrown these false views, attention was again directed to Mayow's tracts, first by Blumenbach, in his *Institutiones Physiological*; later by T. Beddoes, in 1790, who wrote a digest of Mayow's work under the title "Chemical Experiments and Opinions extracted from a Work published in the Last Century"; and later by Johann Andreas Scherer, in a work published at Vienna in 1793, and also by Dr. Yeats in 1798. Scherer gives a careful analysis of Mayow's work, somewhat altering the order of his paragraphs, with a paraphrase in German of the Latin text, which he quotes in full. Yeats' treatise is more especially

concerned with the medical aspect of Mayow's work, although it also deals with the purely chemical portion at considerable length.[1] In the following account of Mayow's researches free use has been made of both of these works, as well as of his own "Tracts."

Mayow's contributions to the chemistry of the atmosphere may be classified thus:—

1. The atmosphere consists of particles of two kinds of gas at least: one of these, termed "nitro-aerial particles," is necessary for the support of life and for the combustion of inflammable bodies; while the other, left after this constituent has been removed, is incapable of supporting either life or combustion. The portion which is necessary for life enters, during respiration, into the blood. It is the chief cause of motion in animals and in plants.

2. These "nitro-aerial particles" are also present in saltpetre or nitre, as can be shown by mixing inflammable substances, such as sulphur and charcoal, with nitre to form gunpowder, filling a tube with the powder, and, after setting it on fire, immediately plunging the open end of the tube

[1] An English translation of Mayow's chemical researches has been published by Prof. Crum Brown in the Alembic Club Reprints (James Thin, Edinburgh, 1907).

under water. The sulphur and charcoal will be as completely consumed as if burned in the open air. Such combustion might, however, be ascribed to a "sulphureous" constituent in saltpetre; by "sulphureous" is to be understood combustible, for those substances capable of burning were imagined to contain a "sulphur" which gave them that property. That nitre does not contain such "sulphur" can be shown by exposing it alone to heat, when no change takes place, except fusion. Besides, nitre is compounded of "spirit of nitre" or nitric acid and pure alkali, neither of which contains a combustible sulphur; hence the particles of fire-air must be present in nitre in no small amount. But it is probable that it is the spirit of nitre which contains such fire-air particles, because, as will be shown later, they are not present in the alkali.

One difficulty occurs to Mayow. How is it that so large a quantity of gas as is necessary to support combustion can be contained in a relatively small bulk of saltpetre? He tries whether a solution of saltpetre evolves air-bubbles when placed in a vacuum, and finds that it effervesces less than pure water does. He also prepares

saltpetre by mixing nitric acid and alkali in a vacuum; a brisk effervescence occurs, and the dried-up salt is ordinary saltpetre. Hence saltpetre cannot contain elastic air. Mayow consequently draws a distinction between "air" and "air-particles."

The residue left after the "fire-air," or *spiritus igneo-aerius*, has been removed from ordinary air by breathing or by combustion is proved to be lighter than the fire-air itself; because a mouse dies sooner if kept at the top of air in a confined bell-jar than at the bottom; and a candle goes out sooner. Here the conclusion is right, although the reason given is wrong; for it is the temperature of the respired air which makes it rise, and not the fact that it is specifically lighter than the oxygen.

Metallic antimony gains in weight when it is set on fire by a lens, and burns; if this gain in weight, Mayow remarks, is not due to the absorption of nitro-aerial particles and to the fire, it is difficult to say to what it is due.

The reason why substances burn so violently in nitre compared with air, is because of the proximity of the fire-air particles; and these are

evidently due to the nitric acid, because the residue,—the alkali,—if mixed with sulphur and inflamed, does not produce ignition.

2. All acids contain fire-air particles, for acids have great similarity to each other. This is shown as follows:—Antimony made into a calx by the sun's rays with a burning-glass gives the same calx as when it is evaporated repeatedly with nitric acid and converted into "Bezoar-mineral," *i.e.* oxide of antimony. And iron-rust obtained from sulphide of iron appears to be formed by the union of the fire-air particles with the metallic "sulphur" of the iron.

It has up till now been believed that sulphuric acid is an ingredient of common sulphur. But this is unlikely, for sulphur has a sweetish, and not an acid taste. Moreover, quite a different substance from a vitriol (or sulphate) is obtained by melting together alkali and sulphur; and no effervescence takes place during its preparation. Sulphur, too, is precipitated out of the "liver of sulphur" (potassium persulphide) by the addition of sulphuric acid. Now, were sulphuric acid contained in sulphur, it would hinder the union of the sulphur with the alkali.

It is to be noticed that the volatile sulphuric acid, from the combustion of sulphur, is produced in the following way :—"The flame of the burning sulphur consists, like every other flame, in the violent motion of the sulphur particles with that of the nitro-aerial particles; hence the sulphur particles, at first solid, become sharp and acid, and probably form the ordinary 'spirit of sulphur' (sulphuric acid). If this be not so, I know not in what manner this acid can be produced; for, as has been shown, it is very improbable that it previously existed in the mass of the sulphur before its deflagration. Such a change also, in all probability, takes place in pyrites, when it is converted to green vitriol; because pyrites yields sulphur on distillation; and the green vitriol on distillation gives sulphuric acid, leaving red colcothar (iron oxide) behind."

Similarly, nitre appears to be a triple salt, formed by the union of the fiery part of air with a salt-like substance existing in the earthy material, together forming nitric acid; and this, added to earthy salts (alkali), yields ordinary nitre. "I have tried to show that all acids consist of certain saline particles rendered fluid by the nitro-aerial particles.'

4. Boyle has shown that a flame is extinguished more rapidly in a vacuous space than in a confined space containing air; this is obviously due to absence of nourishment in the air, rather than to its choking by its own vapours; for in the vacuous vessel there is evidently more space for such noxious vapours than in the air-filled vessel, and yet the flame is more rapidly extinguished. Moreover, no combustible matter can be kindled in a vacuum by means of a burning-glass. But it must not be concluded that this fire-air constitutes the whole of ordinary air; because a candle goes out in air confined in a glass while a large quantity of air is still contained in it.

While gunpowder burns owing to the fire-air particles which it contains, and requires no sustenance from external air, the combustion of vegetables is supported partly by the igno-aerial particles which they themselves contain, partly by those of the external air.

Air which has supported combustion loses to some extent its elasticity (*i.e.* diminishes in volume), as shown by the burning of a candle in air confined over water. This is to be ascribed partly to actual loss of elasticity, partly to the

absorption of the fire-air. The loss of volume amounts to about three per cent of the whole quantity of air taken.

All this is exceedingly clear, and in accordance with our modern views, but Mayow's mind is somewhat confused with reference to flame and heat, since he imagined that the diminution of the volume of air in which combustible substances have been burned is due to the escape of heat; and inasmuch as a rise of temperature was known to increase the volume of air, so a loss of heat should, in his opinion, produce the opposite effect. The fire-air particles are apparently regarded as a sort of compound of heat with matter (as indeed in a certain sense they are); and by combustion or by respiration both are removed. The loss of volume is to be explained by the removal of both from the air, and the gain in weight by the union of the matter with the combustible body, such as antimony.

Such is a brief account of Mayow's views on the nature of atmospheric air. But the tale would be incomplete without mention of the fact that he prepared a gas by the action of nitric acid on iron, viz. nitric oxide, which, when introduced into ordinary air confined over water, decreased its volume;

and he found that further admission of nitric oxide produced no further diminution in the volume of the air. A very little more, and he would have recognised in this a means of analysing air, and depriving it wholly of its oxygen. He goes so far as to speculate that a compound is formed between the nitric oxide and the oxygen, but the solubility of gases in water appears not to have struck him as important. He notices, however, that the combination of the two gases is attended by rise of temperature, and is in so far analogous to combustion.

It would lead us too far to consider in detail Mayow's theories of fermentation and of respiration. Suffice it to say that he ascribes the production of animal heat to the consumption of his fire-air particles by the animal, and remarks that the pulse is heightened by respiration. This view was in opposition to that held by his contemporaries, viz. that the purpose of respiration was to cool the blood.

It is impossible to avoid being impressed with the clearness and justice of Mayow's inferential reasoning. All that was wanting was the discovery of oxygen and carbon dioxide, and the identification of the first with his fire-air, and of

the second with one of the products of combustion. But these discoveries were not made until a century after his death. Had he lived, there can be little doubt that, unless discouraged by the want of appreciation with which his ideas were received, he would have continued to labour in the fruitful fields from which he had already reaped so rich a harvest.

Before leaving the seventeenth century, it is perhaps fitting to mention the name of Jean Rey, a French physician, who wrote in 1630 concerning the gain in weight of tin and lead when calcined. While Rey exhibited some leaning towards the modern methods of experimentation, he still lay fettered in the bonds of mediæval scholasticism. In discussing the weight of air and fire, he finds occasion to consider the question whether a vacuum can exist. His words are so quaint that they are worth quoting: "It is quite certain that in the bounds of Nature a vacuum, which is nothing, can find no place. There is no power in nature from which nothing could have made the universe, and none which could reduce the universe to nothing: that requires the same virtue. Now the matter would be otherwise if there could be a vacuum. For if it

could be here, it could also be there; and being here and there, why not elsewhere? and why not everywhere? Thus the universe could reach annihilation by its own forces; but to Him alone who could make it is the glory of being able to compass its destruction." And since air cannot be drawn down by a vacuum, it must descend by virtue of its own weight when it fills a hole. And hence, as air has weight, tin and lead gain in weight when they combine with air. It will be admitted that this is very inferior to the speculations and deductions of Boyle and Mayow.

The next stage in the history of our subject is the consideration of the work of Stephen Hales and of Joseph Priestley. Both of these philosophers were essentially experimentalists. While both discovered gases and prepared them in a more or less pure state, Hales had no theory to guide him, and concluded as the result of his researches that air was possessed of "a chaotic nature"; for he did not recognise his gases as different kinds of matter, but supposed them all to be modified air. Priestley, on the other hand, was an adherent of the theory of phlogiston, and interpreted all his experiments by its help. Hales was a country

clergyman, interested in botany, and undertook researches on air in order to gain knowledge of the growth and development of plants. Priestley was also a divine, who amused himself with experiments during the intervals of composing sermons or writing controversial pamphlets on disputed doctrines. Both possessed the experimental faculty, and both employed it to good purpose.

Hales' chief work is entitled "Statical Essays, containing Vegetable Staticks; or an account of Statical Experiments on the Sap in Vegetables, being an Essay towards a Natural History of Vegetation: of use to those who are curious in the Culture and Improvement of Gardening, etc.: Also, a specimen of an attempt to analyse the air by a great Variety of Chymiostatical Experiments, which were read at several meetings before the Royal Society. By Stephen Hales, D.D., F.R.S., Rector of Farringdon, Hampshire, and Minister of Teddington, Middlesex."

In his "Introduction" Hales reveals his method of research. The determination of weight and volume was at that date especially necessary; for want of numerical data the experimental researches of the time were of a somewhat vague character,

and it often happened that the conclusions drawn from them were incorrect. Hence it is with a feeling of satisfaction that we read (vol. i. p. 2) :—

"And since we are assured that the all-wise Creator has observed the most exact proportions of *number*, *weight*, and *measure* in the make of all things, the most likely way, therefore, to get any insight into the nature of those parts of the creation which come within our observation must in all reason be to number, weigh, and measure. And we have much encouragement to pursue this method of searching into the nature of things, from the great success which has attended any attempts of this kind." For God has "comprehended the dust of the earth in a measure, and weighed the mountains in scales, and the hills in a balance."

From experiments on the rise of sap in plants, many of them very ingenious and well adapted to secure their end, and which are still regarded by botanists as classic, Hales noticed that a quantity of air was inspired by plants. In order to ascertain the composition and amount of this air, the process of distillation was resorted to; for Hales remarks: "That elasticity is no immutable property of air is further evident from these ex-

periments; because it were impossible for such great quantities of it to be confined in the substances of animals and vegetables, in an elastick state, without rending their constituent parts with a vast explosion" (Preface, p. viii). Hence, concluding that the air absorbed by plants and animals could be recovered by their distillation, Hales proceeded to distil a great number of substances of animal and vegetable origin, such as hogs' blood, tallow, a fallow-deer's horn, oyster-shell, oak, wheat, peas, amber, tobacco, camphor, aniseed oil, honey, bees'-wax, sugar, Newcastle coal, earth, chalk, pyrites, a mixture of salt and bone-ash, of nitre and bone-ash, tartar, compound aqua-fortis, and a number of other substances. He collected the "air" in each case over water, and gave numerical data to show what proportion the air bore by weight to the substance from which it had been obtained. He even tried to compare the weight of ordinary air with that of air from distilled tartar; but his experiment led to no positive conclusion, because of the crudeness of his appliances. The compressibility or "elasticity" of the air from tartar, however, was found to be identical with that of common air.

Hales does not appear to have made any special experiments on the properties of his various airs, by trying whether they supported combustion, whether they were themselves combustible, etc. We see from this list that he had under his hands mixtures of hydrocarbons, carbon dioxide, probably sulphur dioxide, hydrochloric acid and ammonia (both, however, dissolving in water as they were formed), oxides of nitrogen, possibly chlorine, and, as minium or red-lead was one of the substances he tried, oxygen in a more or less pure state. It must be remembered that in all cases the gas obtained was mixed with the air originally present in the retort. He next proceeded to produce "air" by the fermentation of grain, of raisins, and of other fruits; this "air" obviously was carbon dioxide more or less pure.

It is curious to note here that he anticipated Lord Kelvin in devising a sounding-lead which should register the depth of the sea by the compression of air, the distance to which the air had receded along the tube being shown by the entry of treacle. He successfully carried out a sounding by means of his apparatus.

The next series of experiments related to the generation of "air" by the action of acids on

metals. *Aqua-regia* and gold, *aqua-regia* and antimony, *aquafortis* and iron, dilute oil-of-vitriol and iron, yielded gases which contracted on standing in contact with water. This, in the case of the oxides of nitrogen, is to be ascribed to their reacting with the oxygen of the air accidentally present in the receiver; but in the last case Hales noticed that the gas absorbed in cold weather was re-evolved on rise of temperature, as one would expect with hydrogen.

These experiments led him to investigate the action of certain mixtures on ordinary air. Thus a mixture of spirits of hartshorn (or ammonia) with iron filings absorbed $1\frac{1}{2}$ cubic inches of air, and one with copper filings twice as much. Further, a mixture of iron filings and brimstone absorbed in two days no less than 19 cubic inches of air.

But it is disappointing to find that, in spite of all the experimental facts which Hales accumulated, he was unable to make use of them. The prejudice in favour of the unity and identity of all these "airs" was too great for him to overcome. True, he sometimes theorises a little, as for example when he remarks (p. 285):—"If fire was a particular kind of body inherent in sulphur (*i.e.* combustible matter of all kinds), as *Mr. Homberg*, *Mr. Lemery*, and

some others imagine, then such sulphureous bodies, when ignited, should rarefy and dilute all the circumambient air; whereas it is found by many of the preceding experiments, that acid sulphureous fuel constantly attracts and condenses a considerable part of the circumambient elastick air: an argument that there is no fire endued with peculiar properties inherent in sulphur; and also that the heat of fire consists principally in the brisk vibrating action and re-action between the elastick repelling air and the strongly attracting acid sulphur, which sulphur in its Analysis is found to contain an inflammable oil, an acid salt, a very fix'd earth, and a little metal."

Enough has now been said to give a fair idea of Stephen Hales' researches. It will suffice if his conclusions be stated in his own words (p. 314):—

"Thus, upon the whole, we see that air abounds in animal, vegetable, and mineral substances; in all which it bears a considerable part; if all the parts of matter were only endued with a strongly attracting power, whole nature would then immediately become one unactive cohering lump; wherefore it was absolutely necessary, in order to the actuating and enlivening this vast mass of attracting

matter, that there should be everywhere intermix'd with it a due proportion of strongly repelling elastick particles, which might enliven the whole mass, by the incessant action between them and the attracting particles; and since these elastick particles are continually in great abundance reduced by the power of the strong attracters, from an elastick to a fixt state, it was therefore necessary that these particles should be endued with a property of resuming their elastick state, whenever they were disengaged from that mass in which they were fixt, that thereby this beautiful frame of things might be maintained in a continual round of the production and dissolution of animal and vegetable bodies.

"The air is very instrumental in the production and growth of animals and vegetables, both by invigorating their several juices while in an elastick active state, and also by greatly contributing in a fix'd state to the union and firm connection of several constituent parts of those bodies, viz. their water, salt, sulphur, and earth. This band of union, in conjunction with the external air, is also a very powerful agent in the dissolution and corruption of the same bodies; for it makes one in every ferment-

ing mixture; the action and re-action of the aerial and sulphureous particles is, in many fermenting mixtures, so great as to excite a burning heat, and in others a sudden flame; and it is, we see, by the like action and re-action of the same principles, in fuel and the ambient air, that common culinary fires are produced and maintained.

"Tho' the force of its elasticity is so great as to be able to bear a prodigious pressure, without losing that elasticity, yet we have, from the foregoing Experiments, evident proof that its elasticity is easily and in great abundance destroyed; and is thereby reduced to a fixt state by the strong attraction of the acid sulphureous particles which arise either from fire or from fermentation; and therefore *elasticity* is not an *essential immutable property of* air-particles; but they are, we see, easily changed from an elastick to a fixt state, by the strong attraction of the acid, sulphureous, and saline particles which abound in air. Whence it is reasonable to conclude that our atmosphere is a *Chaos*, consisting not only of elastick, but also of unelastick air-particles, which in plenty float in it, as well as the sulphureous saline, watry, and earthy particles, which are no ways capable of being thrown off into

a permanently elastick state, like those particles which constitute true permanent air. Since, then, air is found so manifestly to abound in almost all natural bodies; since we find it so operative and active a principle in every chymical operation; since its constituent parts are of so durable a nature, that the most violent action of fire or fermentation cannot induce such an alteration of its texture as thereby to disqualify it from resuming, either by the means of fire or fermentation, its former elastick state: unless in the case of vitrification, when, with the vegetable Salt and Nitre in which it is incorporated, it may, perhaps, some of it, with other chymical principles, be immutably fixt,—since then this is the case, may we not with good reason adopt this now fixt, now volatile *Proteus* among the chymical principles, and that a very active one, as well as acid sulphur; notwithstanding it has hitherto been overlooked and rejected by chymists, as no way entitled to that denomination?"

This quotation shows us how little Mayow's shrewd reasoning and well-devised experiments had impressed the thinkers of his age. While Hales quotes frequently from Boyle's and Newton's works,

his reference to Mayow is meagre; nor does he adopt any one of Mayow's conclusions. One would have thought that, having prepared so many gases by means of apparatus well adapted to their purpose, and having observed that certain substances introduced into air produced contraction, he would have drawn the conclusion that such "airs" were essentially different kinds of matter. But the "Proteus" was too much for him; and he left the subject practically in the same state of "Chaos" in which he found it.

CHAPTER II

"FIXED AIR" AND "MEPHITIC AIR"—THEIR DISCOVERY BY BLACK AND BY RUTHERFORD

BEFORE relating the history of the discoveries of Black, Rutherford, and Priestley, it will be appropriate to give an account of a theory which professed to explain the phenomena of combustion, and with it the conversion of metals into calces, and the reduction of these calces to the reguline or metallic state. Like other theories, it was slow in developing. Its germ is to be traced to the writings of Johann Baptist van Helmont of Brabant, Seigneur of Merode, Royenboch, Oorshot, and Pellines, who was born in Brussels in 1577. He adopted a fantastical creation of Paracelsus, the *archaeus*, a kind of demon which, by means of fermentation, draws together all the particles of matter. Believing that water was the true principle and origin of everything (for he had succeeded in producing

a willow tree, weighing 164 lbs., from water alone, the earth in which it grew having neither gained nor lost appreciably in weight), he conceived that it was acted on by a *ferment* or principle pre-existing in the seed developed by it, and exhaling an odour by which the archaeus was attracted. Water undergoing the action of this ferment developed a vapour, to which van Helmont gave the name of "gas." A "gas" was a substance intermediate between spirit and matter, and the word was probably derived from *Geist*, the common German word for spirit. Another word introduced by him to denote the life-principle of the stars was *Blas*, connected probably with *blasen*, to blow, and our English word *blast*.

It is curious to notice how the idea of an *archaeus* survived down to later times under the name of a "life-principle"—a conception that all organic substances must necessarily owe their origin to life itself, and not to the usual chemical and physical transformations.

Van Helmont was acquainted with various kinds of gases, as appears from his treatise "De Flatibus." His *gas sylvestre* was evolved from fermenting liquors, and he knew that it was formed

during the combustion of charcoal, and also that it was present in the Grotto del Cane near Naples. He was likewise acquainted with combustible gases, which he named *gas pingue*, *gas siccum*, or *gas fuliginosum*.

These principles of van Helmont's apparently suggested to his successors, Becher and Stahl, the notion of a principle inherent in every combustible substance, which was lost during combustion. The development of this—the phlogistic—theory is almost wholly due to the latter chemist, and indeed it is difficult to trace Becher's share in it.

George Ernest Stahl was born at Anspach in 1660; he studied and graduated in medicine at Halle, and in 1694 he was appointed second professor of medicine at that University, where he continued to teach for twenty-two years. His most important work was his *Fundamenta chymiae dogmaticae et experimentale*. His theoretical views are contained in the last part of this work. He there treats of *zymotechnia*, or fermentation; *halotechnia*, or the production of salts; and *pyrotechnia*, or the doctrine of combustion. It is the last of these sections which gives an account of the doctrine of *phlogiston*.

The fundamental conception of this doctrine is that all combustible bodies are compounds. During combustion one of these constituents, common to all, was dissipated and escaped, while the other, sometimes an acid, sometimes an earthy powder or calx, remained behind. Thus sulphur and phosphorus, when burnt, give acids; and the metals form *calces*. Non-combustible substances, such as lime, were imagined to be *calces*, and it was supposed that if phlogiston were restored to them, they too would be converted into metals. This combustible principle was thought to be inherent in all combustible bodies whatsoever; it corresponds in kind with the "sulphur" of more ancient writers, but differs from the latter inasmuch as no very precise ideas were entertained of the identity of the "sulphur which conferred on the substances containing it as a constituent, or possessing it as a property, their power of combustion." It was also made more definite by Stahl that substances capable of burning or conversion into calces are compounds containing phlogiston in combination with other substances.

Stahl can hardly be credited with more than the invention of the term "phlogiston," and with

bringing the subject in a clear and definite form before his contemporaries. For Stahl wrote in 1720; and we find Mayow, in 1674, entering into an elaborate argument to prove that sulphuric acid is not contained in sulphur, but that it is produced by the union of the sulphur with his fire-air particles. But Stahl amplified the doctrine which Mayow had controverted, in pointing out that if such substances as phosphorus, sulphur, or metals are heated, they burn, and are changed into phosphoric acid, sulphuric acid, or "calces"; and reciprocally, if phosphoric acid, sulphuric acid, or a calx such as that of tin or lead, is heated with matter rich in phlogiston, such as charcoal, pit-coal, sugar, flour, etc., phlogiston is restored to the burnt substance, and the original material, phosphorus, sulphur, tin, or lead, is reproduced. The idea at once captivated the minds of the chemists of that age, who received it with approbation, and devised experiments designed to extend the applications of the theory and to confirm its truth.

Substances were not supposed always to be completely deprived of phlogiston by combustion. Indeed, if the phlogiston were removed wholly, or nearly so, it was by no means easy to

restore it. Thus the calx of zinc, or of iron, which was regarded as nearly devoid of phlogiston, is difficult to reduce to the metallic state by ignition with substances rich in phlogiston, such as coal or charcoal. The addition of phlogiston alters the appearance of the substance as regards colour or metallic lustre, and these vary according to the proportion of phlogiston present.

There existed no very definite idea regarding the appearance or properties of phlogiston itself. Becher's name for it was *terra pinguis*, and it was represented by Becher and by Stahl as a dry substance of an earthy nature, consisting of very fine particles, which were capable of being set into violent motion; this idea was derived partly from the fact that combustion is usually accompanied by flame, which was supposed to be produced by the motion of the particles of the body, communicated to it by the phlogiston.

It must not be forgotten that at this time it was perfectly well known that metals gain weight on calcination. Jean Rey was quite aware of this, and Boyle relates an experiment to show that tin gains weight when converted into calx; and it will be remembered that Mayow made experiments on

the ignition of antimony by the aid of a burning-glass, and rightly conjectured that the substance produced was the same as that formed by treating it with nitric acid, and subsequent ignition. Boyle's view was that calx of tin was a compound of *tin* and *heat*; Mayow's more correct view was that calx of antimony was a compound of *antimony* and *fire-air*. But in spite of these well-proved facts, the adherents of the theory of phlogiston ignored them, and it does not appear to have occurred to Becher or to Stahl that they were inconsistent with their theories.

When this difficulty was stated, which was not until a much later date, a lame explanation of a metaphysical nature, and in itself contradictory, was all that could be offered. It was that phlogiston is endowed with the contrary of gravity or weight, *i.e.* levity or absolute lightness. This means, of course, that it is repelled by the earth. But if repelled by matter, how comes it that it enters into combination with matter? For it could not remain united if its property were to repel and not to attract. Notwithstanding this, however, the idea satisfied some as to the gain in weight which metals undergo in changing into calces.

It is indeed astonishing that men of such great ability and acumen as Black and Cavendish should have so long lain under the yoke of this absurd theory. It is probable that, in the case of these two great chemists, they stated their results in terms of the theory, partly because they were content to express the facts to which they wished to call attention in this manner, partly because they were not in a position to replace the theory by a more rational one. It is not easy to revolutionise a language, even though its vocabulary be a restricted one. The object of writing is to convey thoughts to others; and it is certainly more convenient to make use of terms understood by others, even if they only imperfectly convey the meaning which it is desired to express, than to attempt a revolution which will probably be unsuccessful, and even if successful, will at all events take time. It is not so difficult to understand Priestley's attitude, which we shall have to consider later; for Priestley was first of all an experimentalist, and was captivated more by the acquisition of a new fact than by assigning to that fact its proper place in the cosmogony of nature.

The influence of the phlogistic theory on the

knowledge of the nature of air was of such a kind as to retard its progress. For how could that knowledge be furthered, when the most active constituent of air was represented by a negation? It may be said that it is easy to be wise after the event—in this case the discovery of oxygen; but here was a theory which was in contradiction to many known facts, which furnished but a lame explanation of phenomena, and which had been anticipated by another theory, subsequently proved to be correct. Its sole support was the authority of its inventors or adapters, and the deeply-ingrained notions of centuries. We may read from it a lesson that it is wiser to seek out facts which test and prove a theory rather than those which support it, and we may learn for the hundredth time the folly of relying on authority, however ancient and associated with famous names it may be. This was happily expressed by Boyle when he wrote:[1] "For I am wont to judge of opinions as of coins: I consider much less in any one that I am to receive, whose inscription it bears, than what metal 'tis made of. 'Tis indifferent enough to me whether 'twas stamped many years or ages since, or came

[1] *A Free Inquiry into the Vulgar Notion of Nature*; Prefatory remarks.

but yesterday from the mint. Nor do I regard how many or how few hands it has passed through, provided I know by the touchstone whether or no it be genuine, and does or does not deserve to have been current. For if, on due proof, it appears to be good, its having been long, and by many, received for such will not tempt me to refuse it. But if I find it counterfeit, neither the prince's image nor superscription, nor the multitude of hands it has passed through, will engage me to receive it. And one disfavouring trial, well made, will much more discredit it with me than all these spurious things I have named can recommend it."

It has been necessary to enter at some length into the nature of the phlogistic theory, because the discoveries of the time were expressed in its language. The *fire-air* or *vital air* of Mayow was termed dephlogisticated air; *i.e.* air wholly deprived of the power of burning, or air more capable of supporting combustion than ordinary air; while airs capable of burning were supposed to be more or less highly charged with phlogiston; indeed, at one time, it was imagined that hydrogen was phlogiston itself.

It is to Joseph Black that the discovery of

carbon dioxide, that constituent of air first to be definitely recognised, if we except Mayow's early work, is generally ascribed. But we must remember that it had been prepared by Becher and by Hales, and had been doubtless obtained in an impure state by many others. It will be seen that Black's work was so complete, and established the identity of this gas in so definite a manner, that his right to be named as its true discoverer can hardly be questioned.

Black was born near Bordeaux in 1728. His father, a wine-merchant, was originally a native of Belfast, being descended from a Scottish family which had been settled there for some time. When twelve years of age, Black returned to Belfast, and received his education in the local grammar-school, afterwards proceeding to the University of Glasgow in 1746, at the age of eighteen. He was a pupil of Dr. Cullen, then Lecturer on Chemistry at the College there, who is mentioned by Professor Thomas Thomson in his *History of Chemistry* as an excellent and instructive lecturer. Black intended to choose the career of medicine, and he indeed practised occasionally as a medical man during the greater part of his life.

He began his medical studies in Edinburgh in the year 1751, and in 1755 he published, as his thesis for the degree of M.D., the work which has rendered his name famous. It appears that as early as 1752 he had been occupied with investigations on quicklime, which was then attracting attention as a remedy for urinary calculi. Opinion was divided regarding its virtue. In a manuscript copy of notes of Black's lectures, which the author is so fortunate as to possess, he mentions that his attention was directed to the subject through the rival views of Drs. Alston and Whytt. It was not long before he proved that, in opposition to the commonly received notion, quicklime had gained nothing from the fire in which it was made, but that the limestone used for its preparation had lost nearly half its weight in becoming caustic. He also attempted successfully to trap the escaping gas, and again placed it in presence of lime, confining it over water. Instead of any escape of material when the lime became mild, "nothing escapes—the cup rises considerably by absorbing air." And in his notes, a few pages farther on, he compares the loss of weight undergone by limestone on being calcined with its loss on being dissolved in muriatic acid. These experi-

ments appear from his journal to have been made before November 1752.

His thesis was not published, however, until 1755. Immediately after, in 1756, he succeeded Dr. Cullen as Professor in Glasgow, where he remained until 1766. During these ten years he began and made great progress with his well-known researches on the heat of fusion of ice, and the heat of vaporisation of water, or, as he termed them, the "latent heats" of water and of steam. In 1766 Dr. Cullen was appointed Professor of Medicine in the University of Edinburgh, and Black again succeeded him as Professor of Chemistry. There he lectured until 1797, when he retired from public life; he died as peacefully as he had lived, in 1799, in the seventy-first year of his age. Thomson, who relates these particulars, was one of his last students; he writes: —"I never listened to any lectures with so much pleasure as to his; and it was the elegant simplicity of his manner, the perfect clearness of his statements, and the vast quantity of information which he contrived in this way to communicate, that delighted me. . . . His illustrations were just sufficient to answer completely the object in view, and no more."

Black's original thesis for his degree was entitled *Experiments upon Magnesia Alba, Quicklime, and other Alkaline Substances.* It was published in 1755, and several times reprinted. It is now to be had in convenient form as one of the "Alembic Club Reprints."

It was the custom in those days to administer alkalies as a remedy for urinary calculi; and about the year 1750 lime-water was tried as a substitute. Opinion was divided as regarded its efficacy; and it was with the view of preparing a better remedy that Black undertook researches on magnesia alba. Black prepared magnesia from "bittern," which remains in the pans after the crystallisation of salt from sea-water, and also from Epsom salts, "which is evidently composed of *magnesia* and the vitriolic acid." The magnesia is thrown down from the sulphate as carbonate, by the addition of pearl ashes, at the temperature of ebullition, the soluble product being "vitriolated tartar," or potassium sulphate. He describes how "magnesia is quickly dissolved with effervescence or explosion of air, by the acids of vitriol, nitre, and of common salt, and by distilled vinegar," and gives an account of the properties of the sulphate, nitrate, chloride, and acetate. He sub-

sequently heated this magnesia, and found that it lost "a remarkable proportion of its weight in the fire," and his "attempts were directed to the investigation of this volatile part." The residue in the retort did not effervesce on the addition of acids; hence the volatile part had been driven away by the heat. "Chemists have often observed, in their distillations, that part of the body has vanished from their senses, notwithstanding the utmost care to retain it; and they have always found, upon further inquiry, that subtile part to be air, which, having been imprisoned in the body, under a solid form, was set free, and rendered fluid and elastic by the fire. We may 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."

Magnesia, thus freed from "air" by ignition, was dissolved in "spirit of vitriol" and thrown down with an alkali. Its weight was nearly equal to that which it possessed before calcination, and it again effervesced with acids. "The air seems to have been furnished by the alkali, from which it was separated by the acid; for Dr. Hales has clearly proved that alkaline salts contain a large quantity

of fixed air, which they emit in great abundance when joined to a pure acid. In the present case the alkali is really joined to an acid, but without any visible emission of air: and yet the air is not retained in it; for the neutral salt, into which it is converted, is the same in quantity, and in every other respect, as if the acid employed had not been previously saturated with magnesia, but offered to the alkali in its pure state, and had driven the air out of it in their conflict. It seems, therefore, evident that the air was forced from the alkali by the acid, and lodged itself in the *magnesia.*"

After an account of some experiments showing that magnesia is not identical with lime or with alumina, he proceeds:—"It is sufficiently clear that the calcareous earths in their native state, and that the alkalis and *magnesia* in their ordinary condition, contain a large quantity of fixed air; and this air certainly adheres to them with considerable force, since a strong fire is necessary to separate it from *magnesia,* and the strongest is not sufficient to expel it entirely from fixed alkalis, or take away their power of effervescing with acid salts.

"These considerations led me to conclude that

the relation between fixed air and alkaline substances was somewhat similar to the relation between these and acids; that as the calcareous earths and alkalis attract acids strongly, and can be saturated with them, so they also attract fixed air, and are, in their ordinary state, saturated with it; and when we mix an acid with an alkali, or with an absorbent earth, that the air is then set at liberty, and breaks out with violence; because the alkaline body attracts it more weakly than it does the acid, and because the acid and air cannot both be joined to the same body at the same time. . . . Crude lime was therefore considered as a peculiar acrid earth, rendered mild by its union with fixed air; and quicklime as the same earth, in which, by having separated the air, we discover that acrimony or attraction for water, for animal, vegetable, and for inflammable substances."

The solubility of slaked lime in water is next discussed. If a solution of lime "be exposed to the open air, the particles of quicklime which are nearest the surface gradually attract the particles of fixed air which float in the atmosphere."

Black next points out that, on mixing *magnesia alba* with lime-water, the air leaves the magnesia

and joins itself to the lime; and as both magnesia and calcium carbonate are insoluble in water, the water is left pure. Similarly quicklime deprives alkalies of their air and renders them caustic. And it follows that if caustic alkali be added to a salt of magnesia or of lime, it will separate the magnesia or the calcareous earth from the acid, in a condition free from "air" but combined with water.

In order to show that the "air" which exists in combination with lime or alkalies is not the air which is contained in solution in water, lime-water was placed under an air-pump, along with an equal quantity of pure water; on making a vacuum, an approximately equal amount of air was evolved from each. "Quicklime, therefore, does not attract air when in its most ordinary form, but is capable of being joined to one particular species only, which is dispersed through the atmosphere, either in the shape of an exceedingly subtile powder, or more probably in that of an elastic fluid. To this I have given the name of *fixed air*, and perhaps very improperly; but I thought it better to use a word already familiar in philosophy than to invent a new name, before we be more fully acquainted with the nature and properties of this

substance, which will probably be the subject of my further inquiry."

The next proceeding was to render "mild alkali" caustic by means of lime, and to determine that nearly the same amount of acid is required to saturate the caustic alkali as to saturate the mild alkali from which the caustic alkali had been prepared. On exposure to air for a fortnight, the caustic alkali again became mild, owing to its absorption of fixed air. Careful experiments were made to prove that such caustic alkali contains no lime, and does not therefore owe its causticity and corrosive properties to the presence of that ingredient. The volatile alkali (ammonium carbonate) was also rendered caustic, and Black "obtained an exceedingly volatile and acrid spirit, which neither effervesced with acids nor altered in the least the transparency of lime-water; and although very strong was lighter than water, and floated upon it like spirit of wine."

After a description of some unsuccessful attempts to render mild alkalies caustic by heat alone (*i.e.* to expel carbon dioxide from potassium carbonate), Black examines the action of the "sedative salt" or boracic acid on mild alkalies, by rubbing

them together in presence of some water. At first there is no effervescence, but on adding successive quantities of boracic acid, brisk effervescence finally takes place, borax being formed. "This phenomenon may be explained by considering the fixed alkalis as not perfectly saturated with air . . . if they expel a small quantity of air from some of the salt, this air is at the same time absorbed by such of the contiguous particles as are destitute of it." And on "exposing a small quantity of a pure vegetable fixed alkali (carbonate of potash) to the air, in a broad and shallow vessel, for the space of two months," crystals were obtained, which possessed a milder taste than that of ordinary salt of tartar, which effervesced with acids more violently than usual, and which could not be mixed with the smallest portion of boracic acid without emitting a sensible quantity of air (hydrogen potassium carbonate). It therefore follows that such alkaline substances have an attraction for fixed air; and this was proved by mixing *magnesia alba* in fine powder with caustic alkali, and shaking for some time. The magnesia was converted into the variety which did not effervesce with acids, and the alkali was rendered mild, like a solution of salt of

tartar. These are the principal results of Black's researches, and he concludes with a table of affinity of acids for fixed alkali, calcareous earth, volatile alkali, and magnesia, contrasting it with the affinity possessed by fixed air for the same bases.

It was the habit of the Scottish students to pass down notes taken during the lectures of their professors from one generation to another. As the lectures were generally read, and not delivered *extempore*, the process resulted in an almost verbatim report of the actual words of the lecturer. One of these copies of lectures, bearing the date 1778, gives an account of the experiments which have been described, in words almost identical with those used in the thesis of 1755. Black appears to have shown his class this air, made, however, according to Hales' plan, by heating magnesium carbonate in a bent gun-barrel, and collected over water in the usual way. He demonstrated its weight by pouring it from one vessel to another, and showed that it extinguished the flame of a candle. He mentions also that in 1752 he discovered that this air is the same as choke-damp, and that it is fatal to animal life. He speaks of the Grotto del Cane, and observes that fixed air

is produced by fermentation, and by the burning of charcoal, and showed to his class experiments in which air from each source is shaken with lime-water, giving a turbidity of carbonate. The well-known experiment of inspiring air through lime-water, which, owing to the small amount of carbonic anhydride it contains, does not produce a turbidity, and expiring through lime-water, showing the formation of carbon dioxide in the lungs, is described and performed. He next describes Cavendish's experiments on the solubility of fixed air and its density, and researches by Dr. Brownrigg and Dr. Gahn of Sweden on its occurrence in mineral waters. He also explains how calcareous petrifactions are produced by the escape of fixed air from water, which then deposits its dissolved calcium carbonate, present in solution as bicarbonate. The deposit of iron from chalybeate waters is ascribed to the same cause, and the explanation is attributed to Mr. Lane.

"Upon the whole," these manuscript notes relate, "this sort of air is quite distinct from common air, though it is commonly mixed with it in small quantity." "With regard to its origin, when treating of inflammable substances and metals

I shall consider this more completely. I shall now only hint that it is a vital air changed by some matter, seemingly the principle of inflammability. This appears from several phenomena when an animal or burning body is enclosed with a certain quantity of this air, until it is changed as much as possible. The air is diminished in volume by the breathing of the animal or by the burning of the candle. And Dr. Priestley has found that 'growing vegetables had the power of restoring this sort of air to common or vital air again, which must be by their taking away some matter which it had received from the burning body or animal.'"

Black's account of fixed air and its properties is the first example we possess of a clear and well-reasoned series of experimental researches, where nothing was taken on trust, but everything was made the subject of careful quantitative measurement. It was not long since Hales had pronounced air to be a chaotic mixture of effluvia. Black showed that common air contains a small amount of fixed air, and that fixed air must be considered as a fluid differing in many of its properties from common air, especially in its being absorbed by quicklime and by alkalies. It must

be remembered that at that time carbon was not recognised as an element; and hence, though Black knew that fixed air was a product of the combustion of charcoal, he did not attribute it to the union of carbon with oxygen, although the sentence quoted above closely approaches to the truth.

The discovery of nitrogen was next in the order of time. It was made by Daniel Rutherford, a pupil of Black's, and at his instigation, and its description formed a thesis for his degree of Doctor of Medicine.

Daniel Rutherford was born at Edinburgh on November 3rd, 1749. He was the son of a medical man, Dr. John Rutherford, one of the founders of the Medical School in that city. He was educated at Edinburgh University, and after graduating in Arts, became a medical student, taking his degree of M.D. in 1772. His diploma was obtained on 12th September. He then travelled for three years in England, France, and Italy, and in 1775 he returned to his native town, where he practised his profession. In 1786 he succeeded Dr. John Hope in the Chair of Botany in his University, but he did not on that account resign his practice. He was president of the Royal College

of Physicians of Edinburgh from 1796 to 1798. During the greater part of his life he suffered from gout; he died in 1819, at the age of seventy.

Rutherford does not seem to have pursued the study of chemistry further: his duties led him into other fields. His genial, pleasant face, seen in the portrait by Raeburn, shows him to have possessed a happy disposition; and he is said to have maintained until his death his friendship with Black, and his interest in the progress which science was then rapidly making.

The title of Rutherford's dissertation, of which I have been able to find a copy only in the British Museum, is *Dissertatio Inauguralis de aere fixo dicto, aut mephitico.* It was published at Edinburgh in 1772, seventeen years after Black's memorable dissertation on Fixed Air. As will be seen shortly, Priestley had nearly anticipated Rutherford; and, indeed, he speculated on the nature of the residual gas, left after combustion and absorption of the fixed air produced. Evidently Black had noticed that a residue was left after the combustion of carbonaceous bodies in air, and absorption of the fixed air produced by the combustion, and had suggested to Rutherford, then

a student of his, the advantage of further investigating the matter, and ascertaining the properties of the residual gas.

Rutherford begins his essay with an apt quotation from Lucretius :—

> Denique res omnes debent in corpore habere
> Aëra, quandoquidem rara sunt corpora et aër
> Omnibus est rebus circumdatus appositusque.

He next proceeds to define the atmosphere as a pellucid thin fluid, in which clouds float and vapours rise. Its necessity for animal and vegetable life is acknowledged by all. It possesses weight and elasticity. It can be fixed by other bodies; but the air obtained from them by distillation differs from ordinary vital, salubrious air, and is often termed mephitic or poisonous.

After acknowledging his debt to his illustrious preceptor Black, he proceeds to quote from the latter to the effect that mephitic or fixed air is the air which proves fatal to animals and extinguishes fire; which is easily absorbed by quicklime and by alkaline salts; which occurs in the Grotto del Cane, and in mineral waters; and which is produced during exhalation from the lungs, by combustion, and during certain kinds of ferment-

ation. Its density, compared with that of ordinary air, is as $15\frac{1}{2}$ or 16 to 9; hence it can be kept for some time in an open glass, and if a jar of it be inverted over a lighted candle, the candle is extinguished. It has an agreeable taste and smell; and it changes the colour of syrup of violets from blue to purple. It prevents putrefaction, but putrefied bodies are not made fresh by it. It possesses the power of combining with lime, which acquires new properties as the result of its action. Rutherford then recalls Black's experiments on lime and on magnesia, pointing out how these bases absorb fixed air, and how it can be recovered from them and from its compounds with alkalies, sometimes by heat, and always by the action of acids.

Rutherford next describes experiments which show that a mouse, placed in atmospheric air, and left till dead, diminishes the volume of the air by one-tenth; and that the residual air, on treatment with alkali, loses one-eleventh of its volume. The residue extinguishes the flame of a candle; but tinder continues to smoulder in it for a short time. It is thus proved that after the whole of the fixed air has been withdrawn by

alkalies, the residue is still incapable of supporting life and combustion.

Some burning bodies deprive air of its "salubrity" more easily than others. The phosphorus of urine continues to glow in air in which a candle has ceased to burn, or in which charcoal has burned until it is extinguished. Even after the absorption of all fixed air by alkalies, phosphorus burns, emitting clouds of the dry acid of phosphorus, which can be absorbed by lime-water.

"It therefore appears that pure air is not converted into mephitic air by force of combustion, but that this air rather takes its rise or is thrown out from the body thus resolved. And from this it is permissible to draw the conclusion that that unwholesome air is composed of atmospheric air in union with, and, so to say, saturated with, phlogiston. And this conjecture is confirmed by the fact that air which has served for the calcination of metals is similar, and has clearly taken away from them their phlogiston." Such air differs from the air evolved from metals by the action of acids, which is more thoroughly impregnated with phlogiston; and also from that

from decaying flesh, which is a mixture of mephitic air and combustible air.

He proceeds:—"I had intended to add something regarding the composition of mephitic air, and to seek for a reason for its unwholesome effects, but I have not been able to find out anything with certainty. Certain experiments appear to show, however, that it consists of atmospheric air in union with phlogistic material: for it is never produced except from bodies which abound in inflammable parts; the phlogiston ever appears to be taken up by other bodies, and is hence of value in reducing the calces of metals. I say from phlogistic material, because, as already mentioned, pure phlogiston, in combination with common air, can be seen to yield another kind of air [viz. hydrogen]. . . . I have lately heard that Priestley believes that vegetables growing in mephitic air dispel its noxious ingredients, or, as it were, extract them, and restore its original wholesomeness; and that mephitic air, added to air from putrid flesh, partly mitigates its unwholesome character. But I have been unable to try such experiments."

We see, then, that Rutherford's claims to the

discovery of nitrogen amount to this: He removed the oxygen from ordinary air by combustibles such as charcoal, phosphorus, or a candle; and having got rid of the carbon dioxide, in those cases when it was formed, by alkali or lime, he obtained a residue, now known as nitrogen. His view of the nature of this gas, in the phlogistic language of the time, was that the burning bodies had given up some of their "phlogistic material" to the air, which was thus altered. Nitrogen was "phlogisticated air," even though incombustible; hydrogen, too, was phlogisticated air, but air produced by the union of pure phlogiston with atmospheric air. The step taken by Rutherford, under Black's guidance, was an advance, though not a great one, in the development of the theory of the true nature of air; and he may be well credited with the discovery of nitrogen.

CHAPTER III

THE DISCOVERY OF "DEPHLOGISTICATED AIR" BY PRIESTLEY AND BY SCHEELE—THE OVERTHROW OF THE PHLOGISTIC THEORY BY LAVOISIER

We have seen that Stephen Hales must have prepared oxygen, among the numerous gases and mixtures of gases which he extracted from various substances; for, among the many materials which he heated, one was minium, or red-lead. The red-lead of that day, however, must have contained carbonate, because, as we shall see, Priestley always obtained a mixture of oxygen and carbon dioxide from that source. In the account of his researches Hales only incidentally mentions the collection of gas from minium; and he appears to have made no experiments with the object of ascertaining its properties.

The discovery of oxygen was made nearly simultaneously by Priestley and Scheele, though it

appears from the recent publication of Scheele's laboratory notes by Baron Nordenskjöld that Scheele had in reality anticipated Priestley by about two years. His researches, however, were not published until a year after Priestley had given to the world an account of his experiments. Priestley had no theory to defend; his experiments were undertaken in an almost haphazard manner, probably as a relaxation. "For my own part," he says,[1] "I will frankly acknowledge that, at the commencement of the experiments recited in this section, I was so far from having formed any hypothesis that led to the discoveries made in pursuing them, that they would have appeared very improbable to me had I been told of them; and when the decisive facts did at length obtrude themselves upon my notice, it was very slowly, and with great hesitation, that I yielded to the evidence of my senses." On the other hand, Scheele was engaged in forming a theory of the nature of fire. He writes:[2]—"I perceived the necessity of a knowledge of fire, because without this it is impossible to make any experiment; and

[1] *Experiments and Observations on Different Kinds of Air*, vol. ii. By Joseph Priestley, LL.D., F.R.S. Second edition (1776), p. 29.

[2] *Chemical Treatise on Air and Fire* (1777), § 3.

without fire or heat it is impossible to utilise the action of any solvent. I began, therefore, to dismiss from my mind all explanations of fire, and undertook a series of experiments in order to gain as full knowledge as possible of these lovely phenomena. I ere long found, however, that it was not possible to form any correct opinion concerning the appearances which fire exhibits, without a knowledge of the air. After a series of experiments, I saw that air really is concerned in the mixture termed fire, and that it is a constituent of flame and sparks. I learned, moreover, that such a treatise on fire as this could not be compiled with thoroughness without also taking air into consideration."

Scheele's views concerning fire need not be mentioned here; but his researches on air are so methodical and so complete as to command our entire admiration. They remind us of those of Mayow, and had the latter lived a little longer, they would not improbably have been carried out by him. Since, however, Priestley had the advantage of priority of publication, we shall commence with an account of his researches.

Joseph Priestley was born in 1733 at Field-

head, about six miles from Leeds. His father, a maker and dresser of woollen cloth, lost his wife when his son Joseph was about six years of age; and being poor, his sister, Mrs. Keighley, offered to bring up the boy. The early associations of the lad were closely connected with dissent; and after some time spent at a public school in the neighbourhood, he was sent, in 1752, to the Academy at Daventry, in which he was trained for the ministry. There he gained some knowledge of mechanics and metaphysics, and also acquired some acquaintance with Chaldee, Syriac, and Arabic, besides being a competent French and German scholar. After leaving the Academy, he settled at Needham in Suffolk, as assistant in a small meeting-house, where his income was not over £30 a year. His views were, however, too liberal for his hearers; and after some years he moved to Nantwich in Cheshire, where he preached and also taught a school. Here his income was improved, though still miserably small; yet he managed to buy some books, a small air-pump, and an electrical machine. He removed to Warrington in September 1761, being employed there in teaching and in literary work; there he began to pay some attention to

chemistry by attending a course of lectures delivered by Dr. Turner of Liverpool. While at Warrington he wrote a *History of Electricity*, which first brought him into notice, and which procured for him the degree of LL.D. of Edinburgh, thus giving him a right to the title of Doctor, by which he was always afterwards known. At Warrington, too, he married a daughter of Mr. Wilkinson, an ironmaster of Wrexham. We next find him being asked in 1767 to take the pastorship of Mill Hill Chapel at Leeds, a call which he accepted. The house in which he took up his abode before the "minister's house" had been completed was in Meadow Road, next door to the brewery of Jakes and Nell, and this circumstance first induced him to take up the subject of the chemistry of gases, which has made his name famous. Here too he published his *History of Discoveries relative to Light and Colours.* After six years spent at Leeds he became librarian to the Earl of Shelburne (afterwards Marquis of Lansdowne), and travelled with him on the Continent. While with Lord Shelburne he published the first three volumes of *Experiments on Air*, and carried out investigations which were recorded in a fourth volume, published after his removal to Bir-

mingham. After some years spent in this way he was pensioned off, and settled as minister of a meeting-house in Birmingham, where he employed his time partly in theological controversy, and partly in prosecuting researches in chemistry. He published during this period other three volumes giving a description of his experiments on air, and communicated several papers to the *Philosophical Transactions* of the Royal Society, of which he had been made a Fellow. Towards the year 1790 he was so unfortunate as to attack Burke's book on the French Revolution; and this had the effect of rousing popular opinion against him, more especially that of the local clergy, whose political views he had frequently opposed. During the riots which took place at Birmingham in 1791 his house was burned, and he was obliged to escape to London under an assumed name. After some years spent in the charge of a meeting-house at Hackney, he left England for America. His opinions, though by no means uncommon at the present day, were so antagonistic to those of his English contemporaries that he was cut by his Fellows of the Royal Society, and he therefore resigned his Fellowship. And this feeling was in no way lessened by the action of the

French Government of the time, which made him a Citizen of the Republic, and even chose him as a member of their Legislative Assembly. Arriving in America in 1795, he was well received, and settled at Northumberland, not far from Philadelphia. There he died in 1804.

In Priestley's work on gases he employed the form of apparatus which had been used by Mayow a century before. Such apparatus is indeed generally used now: the flasks with bent delivery-tubes, the Woulfe's bottles with two necks, and the pneumatic trough filled with water or mercury were his chief utensils. By means of such apparatus, gases can be collected in a state of comparative purity: they can be easily transferred from one vessel to another, and substances which it is desired to submit to their action can be readily introduced. Scheele, on the other hand, employed less convenient methods: his gases were generally collected in bladders, and their transference to bottles must have been attended with the introduction of atmospheric air. Scheele's method was to allow a certain amount of gas to escape from the generating flask in order to expel air; an empty bladder was then tied over the neck, and the gas entered the

bladder. When he wished to transfer the gas to a bottle, the bladder was tied at some distance from the neck, and its loose open end was secured by a string round the neck of a bottle full of water. The string confining the gas was then untied, and the bottle was inverted; the water ran into the bladder and was replaced by gas. A cork was also enclosed in the bladder, and it was possible to push this cork into the neck of the bottle and re-tie the string which confined the gas; and then, by loosing the string which secured the bottle to the bladder, the full bottle could be conveyed away. This process is obviously a clumsy one, although in Scheele's hands it yielded splendid results; and the methods which Priestley had borrowed from Mayow have attested their superiority by their survival.

The earliest date at which Priestley began to experiment with gases was the beginning of the year 1766, led, no doubt, by the lectures he had heard at Warrington. In 1767, at Leeds, he had made some experiments on the conductivity of "airs" for electricity, using for this purpose common, inflammable, and fixed airs. He appears to have abandoned the study of gases in 1768, and to have

resumed it in 1772. The first gas which he then investigated was "nitrous gas," or, as it is now named, nitric oxide. It had previously been prepared by Mayow (see p. 25) by the action of nitric acid on iron; and Mayow had made the important observation that when it was introduced into ordinary air confined over water, the volume of the air was decreased, and a rise of temperature occurred. But Mayow did not apply his discovery to the analysis of air, though he rightly conjectured that the reason of the decrease in volume of the latter was due to combination between the nitric oxide and his "fire-air particles." It was left for Priestley to rediscover this fact, and to apply it to the analysis of air, or, as he expressed it, to the determination of its "goodness."

Priestley's use of a mercurial trough enabled him to collect and investigate various kinds of airs,—among others "marine acid air" or gaseous hydrogen chloride, a gas differing entirely in properties from ordinary air. This made his mind familiar with the thought that different kinds of air exist, not necessarily modifications of atmospheric air. He had previously from his experiments come to the conclusion that "atmospheric air is

not an unalterable thing, for that the phlogiston with which it becomes loaded from bodies burning in it, and animals breathing it, and various other chemical processes, so far alters and depraves it as to render it altogether unfit for inflammation, respiration, and other purposes to which it is subservient; and I had discovered that agitation in water, the process of vegetation, and probably other natural processes, by taking out the superfluous phlogiston, restore it to its natural purity. But I own I had no idea of the possibility of going any further in this way, and thereby procuring air purer than the best common air."

On the 1st of August 1774, Priestley heated by means of a burning-glass red oxide of mercury. This was produced by heating mercury until it oxidised, and therefore had been untouched by acids, or by any substance which could have "imparted phlogiston" to atmospheric air. The resulting air was insoluble in water, and supported combustion better than common air, for a candle burned more brightly, and a piece of red-hot wood sparkled in it. This air he also produced from "red precipitate," the product of heating nitrate of mercury; and at the same time from red-lead, or minium.

It differed from "modified nitrous air," in which a candle also burns brightly, inasmuch as shaking with water the gases produced after a candle had burned for some time in it did not deprive it of its power of supporting combustion; nor did it diminish the bulk of common air, as the nitrous air does in some degree. Priestley here refers to a mixture obtained by distilling nitrates, which is essentially a mixture of nitric peroxide with oxygen. A candle burns in such a mixture, depriving the nitric peroxide of part of its oxygen, and converting it into nitric oxide mixed with nitrogen. Nitric oxide, deprived of the excess of peroxide by shaking with water, with which the peroxide reacts and is absorbed, is no longer capable of supporting the combustion of a candle; and when added to ordinary air it combines with its oxygen, again forming nitric peroxide, which in its turn is absorbed by water.

Priestley's experiments were performed at intervals from August 1774 till March 1779, and at that date it occurred to him to mix with his dephlogisticated air some nitric oxide over water; absorption took place, and he concluded that he might assume his new air to be respirable. And

what surprised him especially was, that even after addition of nitric oxide and agitation with water, the residue still supported the combustion of a candle. A mouse, too, lived half an hour in the new air, and revived after being removed; whereas similar experiments with an equal volume of common air had shown that, after respiring it for a quarter of an hour, a mouse was indisputably dead. Even after the mouse had breathed it for so long a time, it was still capable of supporting the combustion of a candle; and this induced him to add more nitric oxide to the respired air, when he found that a further contraction occurred. He reintroduced the same unfortunate mouse into the remainder of the air—a portion to which nitric oxide had not been added—when it lived for another half-hour, and was quite vigorous when withdrawn.

Subsequent experiments with nitric oxide showed that air from red precipitate or from "*mercurius calcinatus*" (red oxide of mercury in each case, although prepared in different ways) was "between four and five times as good as common air." He proceeds:[1]—"Being now satisfied with respect to the *nature* of this new species of air, viz.

[1] *Loc. cit.* p. 46.

that being capable of taking more phlogiston from nitrous air, it therefore originally contains less of this principle, my next inquiry was, by what means it comes to be so pure, or, philosophically speaking, to be so much *dephlogisticated.*" He therefore went on to heat the various oxides of lead, but without any special results worth chronicling. On moistening red-lead with nitric acid, however, and distilling the mixture, he obtained, in successive operations, air which was "five times as good" as common air. This process formed lead nitrate, which on distillation yielded nitric peroxide and oxygen; the gas was, of course, collected over water, which absorbed the peroxide, allowing pure oxygen to pass. He found that red-lead was not the only "earth" which produced this effect; but that "flowers of zinc" (zinc oxide), chalk, slaked lime, and other substances also gave a gas, when distilled with nitric acid, which was "better" than common air. In some cases he broke up nitric acid by heat into water, nitric peroxide, and oxygen; in others he heated nitrates. His conclusion is: "*Atmospherical air*, or the thing we breathe, *consists of the nitrous acid and earth*, with so much phlogiston as is necessary to its elasticity; and likewise so much

more as is required to bring it from its state of perfect purity to the mean condition in which we find it."[1]

When such experiments were made by heating nitrates in a gun-barrel, "phlogisticated air" was obtained. This was nitrogen, for the iron had reduced the oxides of the latter, and combining with their oxygen, had formed nitrogen; moreover, it had absorbed to a greater or less extent the oxygen simultaneously produced.

Having concluded that respirable air was a compound of nitrous acid, phlogiston, and earth, Priestley endeavoured to ascertain what was the nature of this earth. He concludes "that the *metallic earths*, if free from phlogiston, are the most proper, and next to them the *calcareous earths*."

"Dephlogisticated air may be procured from any kind of earth with which the spirit or nitre will unite." A few quantitative experiments would surely have refuted this erroneous conclusion. Those which he attempted to make were very crude. A bladder (of which he does not give the capacity) was filled with

[1] *Loc. cit.* p. 55.

Phlogisticated air, and weighed			7	dwts.	15	grs.
Nitrous air	„	„	7	„	16	„
Common air	„	„	7	„	17	„
Dephlogisticated air	„	„	7	„	19	„

He concludes (taking into consideration that inflammable air is very light) "that the less phlogiston any kind of air contains, the heavier it is; and the more phlogiston it contains, the lighter it is."[1] Strange that this should not have led to the rejection of the phlogistic hypothesis!

Priestley had the curiosity to breathe his "good" air. He says: "My reader will not wonder that, after having ascertained the superior goodness of dephlogisticated air by mice living in it, and the other tests above mentioned, I should have the curiosity to taste it myself. I have gratified that curiosity by breathing it, drawing it through a glass syphon, and by this means I reduced a large jar full of it to the standard of common air. The feeling of it to my lungs was not sensibly different from that of common air, but I fancied that my breast felt peculiarly light and easy for some time afterwards. Who can tell but that in time this pure air may become a fashionable article

[1] *Loc. cit.* p. 94.

in luxury? Hitherto only two mice and myself have had the privilege of breathing it."[1]

It will be seen from this account that Priestley's work was to some extent that of an amateur. He performed experiments, often without any definite object; and he was not always successful in devising theories. As before remarked, his chemical pursuits were to him a recreation, and were undertaken during the intervals of his necessary work. His mind was therefore not given over to them alone; and this is to be seen from the character of his writings. His style is a delightfully familiar one: he exposes his inmost thoughts with perfect frankness, and his writings are therefore very readable.—We have now to compare his work with that of his contemporary, Scheele, whose mission in life was that of a chemist; and the reader will be interested in noting the different points of view which these two eminent discoverers adopted.

Carl Wilhelm Scheele was born on the 9th of December 1742 in Stralsund, the capital of Swedish Pomerania, where his father was a merchant and a burgess. He was the seventh of eleven children.

[1] *Loc. cit.* p. 102.

After receiving his education, partly in a private school, partly in the public school (*gymnasium*) at Stralsund, he was apprenticed at the age of fourteen to the apothecary Bauch in Gothenburg. In those days an apothecary was in large measure a manufacturer as well as a retailer of drugs. He had to prepare his medicines in a pure state from very impure materials, as well as to mix them in order to carry out prescriptions; and indeed he himself often, as sometimes happens still, ventured to prescribe in mild cases. Scheele's master taught him such methods, and in addition instructed him in the use of the chemical symbols in vogue at that date; these he afterwards freely employed in his manuscripts, and this renders them exceedingly difficult to decipher. There still exists a catalogue of the drugs his master kept; many of them are of a fantastic nature, such as "ointment of vipers," "human brain prepared without heat," etc.; but among them were many of the well-known salts of metals, and the commoner acids, besides phosphorus, sulphur, rock-crystal, some ores, and some carbon compounds; for example, benzoic acid and camphor. There was a fair chemical library, which included the works of Boerhaave and Lemery, and his master

devoted much pains to his instruction. In a letter to Scheele's father, however, he expressed a fear that too great devotion to study and experimental work would undermine the health of a growing lad.

In 1765 the business was sold, and Scheele obtained a situation in Malmö with an apothecary named Kjellström. His master testified that he had extraordinary application and ability, and related that he was in the habit of criticising all that he read, saying of one statement, "This may be the case"; of another, "This is wrong"; of a third, "I shall look into this." His memory was prodigious: he is said never to have forgotten anything which he had read relating to his favourite subject. He took little interest in anything else, and both his employers appear to have encouraged him to the utmost in his favourite pursuit. In 1768 he left Malmö for Stockholm; but here the exigencies of his duties interfered with his leisure for experimentation. While there, in conjunction with his friend Retzius, he discovered tartaric acid, which up till then had never been separated from tartar, its potassium salt. Here too he made investigations on the acid of fluor-spar (hydrofluoric acid); but finding his time too greatly occupied with routine work, he

took a situation at Upsala, the seat of the largest university of Sweden, in 1770. At that time Bergman was Professor of Chemistry there, and Linnaeus occupied the Chair of Botany; both had then achieved a wide reputation. With Bergman he soon established close relations, and Retzius wrote that it was difficult to say which was pupil and which teacher. While at Upsala he wrote his great work on *Fire and Air*, which we shall shortly have to consider. From his laboratory notes it appears that before 1773 he had obtained oxygen by the ignition of silver carbonate, red mercuric oxide, nitre, magnesium nitrate, and from a mixture of arsenic acid and manganese dioxide. Here too he discovered chlorine, and made researches on manganese, arsenic, and baryta. In 1775 he was elected a member of the Royal Swedish Academy of Sciences, an honour which much improved his social status. In the same year he became manager of a business at Köping, where he passed the rest of his days, in spite of urgent appeals to engage in more remunerative work; indeed, he was strongly pressed to go to Berlin, and also, it is said, to London, for his publications had led to his recognition as one of the greatest chemists of the age. His book on *Fire*

and Air was not published for some years after the manuscript had been in the printer's hands. We learn from his letters that he was much afraid of being anticipated in his discoveries, as indeed events showed that he had reason to be.

From his letters and from the verdict of his contemporaries, Scheele is depicted as an amiable and honourable man, singularly free from vanity and selfishness. His last memoir on the action of sunlight on nitric acid was published in 1786; he died suddenly at the early age of forty-three in May of that year, two days after his marriage to Sara Margaretha Pohl. His devotion to science had told on his health, and his death was caused by a complication of diseases. Yet he was during his life, as after his death, regarded as one of the greatest of chemists: his great knowledge, extraordinary aptitude in experimenting, and high intellectual powers place him among the foremost men of science of his day.

Near the beginning of his *Treatise on Air and Fire*,[1] Scheele defines air. It is that fluid invisible substance which we continually breathe; which

[1] The accurate translation of Scheele's *Treatise* published by the Alembic Club (William F. Clay, 1894) has been made use of here.

surrounds the whole surface of the earth, is very elastic, and possesses weight. "It is always filled with an astonishing quantity of all kinds of exhalations, which are so finely divided in it that they are scarcely visible, even in the sun's rays."[1] It also contains another elastic substance resembling air, termed aerial acid by Bergman (identical with Black's fixed air). Since atmospheric air has not been completely converted into fixed air by admixture of foreign materials, "I hope I do not err if I assume as many kinds of air as experiment reveals to me. For when I have collected an elastic fluid, and observe concerning it that its expansive power is increased by heat and diminished by cold, while it still uniformly retains its elastic fluidity, but also discover in it properties and behaviour different from those of common air, then I consider myself justified in believing that this is a peculiar kind of air. I say that air thus collected must retain its elasticity even in the greatest cold, because otherwise an innumerable multitude of varieties of air would have to be assumed, since it is very probable that all substances can be converted by excessive heat into a vapour resembling air."[2]

[1] § 4. [2] § 5.

After defining the properties characteristic of air, namely, its power of supporting combustion, its diminution by one third or one quarter during the combustion of any substance which does not produce any fluid resembling air, its insolubility in water, its power of supporting life, and the fact of its being favourable to the growth of plants, Scheele demonstrates that air must consist of at least two elastic fluids. This he proves by exposing it to "liver of sulphur" (polysulphide of potassium), when six parts out of twenty were absorbed. He obtained the same result by employing a solution of sulphur in caustic potash, and also by polysulphide of calcium, prepared by boiling lime-water with sulphur, and by means of yellow sulphide of ammonium. Nitric oxide, "the nitrous air which arises on the dissolution of metals in nitrous acid," produces a similar contraction, and so also do oil of turpentine and "drying oils" in general. Dippel's animal oil, obtained by distilling bones, and ferrous hydroxide, produced from "vitriol of iron" and "caustic ley," or ferrous sulphate and caustic potash, may also be used as absorbents; as may also iron filings moistened with water, a solution of iron in vinegar, and a solution of cuprous

chloride. "In none of the foregoing kinds of air can a candle burn or the smallest spark glow."

He accounts for these results by the theory that all such absorbents contain phlogiston, which is attracted by the air, and, combining with it, diminishes its bulk. The alkalies and lime attract the vitriolic acid of the sulphides used, and the air attracts the phlogiston. "But whether the phlogiston which was lost by the substances was still present in the air left behind in the bottle, or whether the air which was lost had united and fixed itself with the materials, such as liver of sulphur, oils, etc., are questions of importance."[1] The conclusion that such air, which had received phlogiston and had contracted in volume, ought to be specifically heavier than common air was, however, rudely dissipated by experiment. The air must therefore contain two fluids, one of which does not manifest the least attraction for phlogiston, while the other is peculiarly disposed to such attraction. "But where this latter kind of air has gone to, after it has united with the inflammable substance, is a question which must be decided by further experiments, and not by conjectures."[2]

[1] § 16. [2] § 16.

To decide this question, Scheele burned in air substances such as phosphorus, which do not produce by their combustion any kind of "air." The result was that the air lost 9 volumes out of an original 30, or about one-third of its bulk. A flame of hydrogen burning in air caused it to lose one-fifth of its volume. On burning a candle, some spirits of wine, or some charcoal, in a confined quantity of air, very little, if any, diminution of volume was noticed; but on shaking the air with milk of lime, contraction ensued, but not to the same extent as when phosphorus was burnt in it. This greatly puzzled Scheele; we now know that such combustibles are not able to remove all the oxygen, but that they are extinguished when only a portion of each has entered into combination. Here, again, however, his memory comes to his help, for he says, "It is known that one part of aerial acid mixed with ten parts of ordinary air extinguishes fire; and there are here in addition, expanded by the heat of the flame and surrounding the latter, the watery vapours produced by the destruction of those oily substances. It is these two elastic fluids, separating themselves from such a flame, which present no

small hindrance to the fire which would otherwise burn much longer, especially since there is here no current of air by means of which they can be driven away from the flame. When the aerial acid is separated from this air by milk of lime, then a candle can burn in it again, though only for a very short time."[1] Thus the question was correctly solved. Scheele's acumen led him at once to make experiments admirably adapted to discover the true reason; he was not turned aside by any imaginary difficulties, but went straight to the point. He next burned sulphur in confined air, and found little alteration of volume, but on shaking with clear lime-water, absorption took place, and one-sixth of the air was removed. "The lime-water was not in the least precipitated in this case, an indication that sulphur gives out no aerial acid during its combustion, but another substance resembling air; this is the volatile acid of sulphur, which occupies again the empty space produced by the union of the inflammable substance with air."[2]

The next set of experiments were devised "to prove that ordinary air, consisting of two kinds of elastic fluids, can be compounded again, after these

[1] § 22. [2] § 23.

have been separated from one another by means of phlogiston."

"I have already stated that I was not able to find again the lost air. One might indeed object that the lost air remains in the residual air which can no more unite with phlogiston; for, since I have found that it is lighter than ordinary air, it might be believed that the phlogiston, united with this air, makes it lighter, as appears to be known already from other experiments. But since phlogiston is a substance, which always presupposes some weight, I much doubt whether such hypothesis has any foundation."[1] He had formerly conjectured that hydrogen, the "air" obtained by the action of vitriol on zinc, might be phlogiston; "still, other experiments are contrary to this."

Scheele next directs attention to acid of nitre, and points out that when prepared in absence of organic material, it is nearly colourless; but that if phlogiston be given to it, it becomes red. At the end of a distillation of pure nitre with pure sulphuric acid, however, red fumes are produced: "Where does the acid now obtain its phlogiston? There is the difficulty."

[1] § 24.

He collected some of this "red air" in a bladder containing milk of lime, to prevent its corrosive action; and having tried whether the resulting gas, which was now no longer red, would support combustion, "the candle began to burn with a large flame, whereby it gave out such a bright light that it was sufficient to dazzle the eyes. I mixed one part of this air with three parts of that air in which fire would not burn; I had here an air which was like the ordinary air in every respect. Since this air is necessarily required for the origination of fire, and makes up about the third part of our common air, I shall call it after this, for the sake of shortness, Fire-air; but the other air, which is not in the least serviceable for the fiery phenomena, I shall designate after this with the name already known, Vitiated air."[1] How history repeats itself! Here is Scheele, in 1772, reproducing Mayow's name "fire-air particles" for the same substance of which Mayow had inferred the existence a century before, and which he had pointed out as being present in the acid of nitre as well as in common air.

This air is not a "dry acid of nitre converted

[1] § 29.

into elastic vapours," for it does not produce nitre with alkalies; moreover, it can be prepared from substances which have nothing in common with nitre, no compound of nitre having been used during their preparation. Scheele next describes experiments proving that "fire-air" is produced by the distillation of black oxide of manganese with concentrated oil of vitriol, or with the "phosphorus acid of urine" (phosphoric acid), by distilling nitrate of magnesium, made by dissolving the "white magnesia employed in medicine" (magnesium carbonate) in *aquafortis* (nitric acid), or by distilling "mercurial nitre" (mercuric nitrate). The cheapest and the best method of producing "fire-air" is to distil purified nitre in a glass retort. But Scheele also obtained it from "calx of silver" (silver carbonate) prepared from silver nitrate and "alkali of tartar" (potassium carbonate); during this process he got aerial acid, which had been present originally in the alkali of tartar; but it was easily removed by means of milk of lime. Similarly, "calx of gold," obtained from a solution of gold with "alkali of tartar," gave "fire-air" when heated; but no aerial acid, for that air escapes during the precipitation of the "calx."

The brown-red precipitate obtained by adding "alkali of tartar" to "corrosive sublimate" (potassium carbonate to mercuric chloride, giving a basic carbonate of mercury and potassium chloride) yielded a mixture of fire-air and aerial acid when heated. But if the "calx of mercury" had been prepared by means of the "acid of nitre," or in modern language by heating mercuric nitrate, a pure "fire-air," unmixed with "aerial acid," was the product. And lastly, arsenic acid, when heated gave ordinary white arsenic together with "fire-air."

This fire-air was completely absorbed by "liver of sulphur" (a polysulphide of potassium, formed by heating together potassium carbonate and sulphur); and a mixture of four parts of "fire-air" with fourteen parts of "vitiated air" lost the whole of its fire-air on standing for fourteen days in contact with liver of sulphur. Dippel's animal oil, and burning phosphorus, charcoal, and sulphur, all absorbed "fire-air"—completely if it was pure, incompletely if it was mixed with "vitiated air"; in short, the identity of "fire-air" prepared from calces, etc., with that in ordinary air was completely established.

As "vitiated air" is lighter than ordinary air,

it follows that "fire-air" must be heavier; and experiment proved this to be the case.

To completely disprove the possible contention that nitre was necessary for the production of "fire-air," some "calx of mercury" (or red oxide), which had been prepared by boiling mercury for a long time in contact with air, was heated. The products were metallic mercury and "fire-air." "This is a remarkable circumstance, that the fire-air which had previously removed from the mercury its phlogiston in a slow calcination, gives the same phlogiston up to it again, when the calx is simply made red-hot."[1] Is it not remarkable that the true explanation should not have forced itself upon Scheele's mind, which was so acute, and so capable of forming true deductions?

The next set of experiments dealt with the phenomena of respiration. A rat, confined in air until it died, polluted the air with one-thirtieth of aerial acid. Respiration from Scheele's own lungs had the same effect. A few flies, bees, and caterpillars also polluted the air in the same way. Peas, roots, herbs, and flowers all converted about one-fourth part of ordinary air into "aerial acid."

[1] § 80.

"These are accordingly strange circumstances, that the air is not noticeably absorbed by animals endowed with lungs, contains in it very little aerial acid, and yet extinguishes fire. On the other hand, insects and plants alter the air in exactly the same way, but still they convert the fourth part of it into aerial acid."[1] And so he makes experiments which prove that it is the fire-air which is converted into "aerial acid" by peas; and that "fire-air" is absorbed by fresh blood, and acquires no aerial acid from it. And, further, he was able to breathe fire-air for a long time, especially if a "handful of potashes" was put into the bladder. A couple of large bees, confined in "fire-air," along with milk of lime, consumed practically the whole of the air in eight days. But plants, confined in fire-air," along with milk of lime, would not grow; however, they yielded a little aerial acid. Scheele is again puzzled here by the circumstance that the blood and the lungs have not the same action on air as insects and plants, inasmuch as the former convert it into vitiated air, and the latter into aerial acid. We now know that air will not support life of warm-blooded animals when

[1] § 87.

the oxygen falls below a certain not very small amount, while insects appear to be capable of exhausting the oxygen to a great extent; and it is probable that the plants, under the unnatural circumstances in which they were placed, gave off a considerable amount of carbon dioxide. Scheele's explanation in terms of phlogiston is not successful. He wrote:—"I am inclined to believe that fire-air consists of a subtle acid substance united with phlogiston, and it is probable that all acids derive their origin from fire-air. Now if this air penetrates into plants, these must attract the phlogiston, and consequently the acid, which manifests itself as aerial acid, must be produced."[1] This is reversing what may be termed the true explanation on the basis of the phlogistic theory. For Scheele supposes that oxygen contains phlogiston, and by losing it, yields carbon dioxide. On the other hand, the consistent explanation would be that carbon is carbonic acid plus phlogiston, and that when it burns it loses phlogiston and becomes carbonic acid again. We see how confused the phlogistic ideas became after the discovery of oxygen, and how ripe the time was for Lavoisier

[1] § 93.

to formulate views which are now universally accepted.

In the concluding sections of his treatise Scheele describes experiments which prove the solubility of "fire-air" in water; he mentions a convenient test for free oxygen in solution, viz. a mixture of ferrous sulphate and lime, which turns dark green, and finally rust-coloured, when added to water containing oxygen; and he shows that water is deprived of oxygen by the presence of a leech, kept in it for two days.

It is impossible not to recognise in Scheele one of the most acute intellects and able experimenters whom the world has ever seen. And although we cannot but feel surprise that his discoveries did not lead him to take the step of renouncing the hypothesis of phlogiston, it must be borne in mind that the doctrine was surrounded with the halo of old age, and sanctioned by many names of great repute in their time. We shall see later that Cavendish, one of the greatest of English chemists, on weighing the rival theories, decided in favour of the phlogistic hypothesis. The actual escape of flame, a visible entity, from a burning substance, may have had much to do with this decision; and the uncer-

tainty concerning the nature of heat, and the doubt whether it was not a form of imponderable matter, may have led both Scheele and Cavendish to retain the older views. It was Lavoisier who first dared to throw off the shackles of tradition; and this he did before oxygen had been discovered, as early as 1772.

Antoine Auguste Lavoisier was born in Paris on the 26th of August 1743. His father was wealthy, and spared no expense on his education. In his twenty-first year he obtained a gold medal from the Academy of Sciences for an essay on the best method of lighting the streets of Paris, but it was some years before he made definite choice of his subject. He published memoirs relating to geology and to mathematics, before the fame of Black's and Priestley's discoveries reached him and induced him to turn his attention to scientific chemistry. Lavoisier's life was divided between his researches and the performance of public duties. In his twenty-fifth year he was elected a Member of the French Academy of Sciences, and, somewhat later, became its treasurer. He drew up numerous reports for the Government on questions on the borderland of Science and Technology; for example, on the

preparation of paper for bills, which would not admit of forgery; on experimental agriculture; and on the manufacture of gunpowder. In 1771 he married Marie Anna Pierette Paulze, the daughter of a "fermier-général," or collector of Government revenue; and after his death she became the wife of Count Rumford, another distinguished scientific man. Made a "fermier général" himself, it was during his tenure of this office that Lavoisier was accused—along with others holding similar positions—of misappropriating revenue moneys, with the result that, under the dictatorship of the infamous Robespierre, he and twenty-eight of those who held like office were guillotined publicly, on the 8th of May 1794. It is stated that Lavoisier's last plea, presented by Hallé—for permission to finish a research—was refused by Coffinhal, with the brutal phrase, "La Republique n'a pas besoin de savants; il faut que la justice suive son cours." Within twenty-four hours the execution took place.

Lavoisier was a tall, handsome man, with a remarkably pleasing face. He possessed great influence, and used it all for good.

The first account which we possess of Lavoisier's revolutionary ideas, for revolutionary they were

then deemed, was in a sealed note, placed in the hands of the Secretary of the Academy on the 1st of November 1772. It is to the following effect:—

"About eight days ago I discovered that sulphur, when burned, instead of losing weight, gains weight; that is to say, from one pound of sulphur much more than one pound of vitriolic acid is produced, not counting the moisture gained from the air. Phosphorus presents the same phenomenon. This increase of weight is due to a great quantity of air which becomes fixed during the combustion, and which combines with the vapours. This discovery, which I confirmed by experiments which I regard as decisive, led me to think that what is observed in the combustion of sulphur and phosphorus might likewise take place with respect to all the bodies which augment in weight by combustion and calcination; and I was persuaded that the gain of weight in calces of metals proceeded from the same cause. Experiment fully confirmed my conjectures. I effected the reduction of litharge in closed vessels with Hales' apparatus, and I observed that at the moment of the passage of the calx into the metallic state, there was a

disengagement of air in considerable quantity, and that this air formed a volume at least a thousand times greater than that of the litharge employed. As this discovery appears to me to be one of the most interesting which has been made since the time of Stahl, I thought it expedient to secure to myself the property, by depositing the present note in the hands of the Secretary of the Academy, to remain secret till the period when I shall publish my experiments. LAVOISIER.

"PARIS, 11*th November* 1772."

There is no account in Hales' work of his reducing litharge in closed vessels. It is to be presumed that Lavoisier heated in a retort a mixture of litharge and charcoal, and that the air which he speaks of was a mixture of oxides of carbon. This account does not inform us of Lavoisier's views on combustion, but merely shows the date at which he had first obtained what he supposed were results new to science. We recognise that Mayow had anticipated him in this.[1]

[1] The following passage in a letter from Magellan to Madame Lavoisier makes it probable that Lavoisier had been told of Mayow's work :— "Quand, après les découvertes de Lavoisier, on lui opposa Mayow, dont il n'avoit jamais entendu parler, il chargea son ami Magellan, qui habitait Londres, de lui procurer les œuvres du savant anglais. Magellan s'adressa

It was not until Priestley, when dining with him in the autumn of 1774 (being in Paris with Lord Shelburne at the time), had informed Lavoisier of his discovery of "dephlogisticated" air, that the ideas of the latter upon the subject became precise. Priestley's own words are:—"Having made the discovery some time before I was in Paris, in the year 1774, I mentioned it at the table of Mr. Lavoisier, when most of the philosophical people of the city were present, saying that it was a kind of air in which a candle burned much better than in common air, but I had not then given it any name. At this all the company, and Mr. and Mrs. Lavoisier as much as any, expressed great surprise. I told them I had gotten it from *precipitate per se*, and also from *red-lead*. Speaking French very imperfectly, and being little acquainted with the terms of chemistry, I said *plombe rouge*, which was not understood till Mr. Macquer said I must mean *minium*."

Shortly after this Lavoisier repeated Priestley's experiments and confirmed their truth; and this led to the true explanation of experiments of

en vain à tous les libraires de Londres; il lui fut impossible de trouver une exemplaire des œuvres de Mayow." Yet this work was in the catalogue of the Royal Society's library at that date.

which an account is given in the *Memoirs* of the French Academy for 1774, and which were fundamental in their character. They referred to the calcination of tin in hermetically-sealed retorts. The tin was placed in a retort which was heated on a sand-bath until the metal had melted. The beak of the retort, previously drawn out into a capillary, was then sealed, the air expelled having been collected and its weight noted. The retort was then cooled and weighed. It was again heated, and the temperature was maintained until the calcination of the tin stopped. With a large retort the calcination was more complete than when a smaller one was employed, this implying that the degree to which the calcination proceeded was dependent upon the amount of air present. After cooling the retort a second time, it was again weighed, when it was found to have undergone no change of weight. The beak was then broken, and air entered with a hissing noise. The gain in weight was now about 10 grains with a large retort. The tin and its calx were next weighed, and it was found that the gain in weight of the tin was always equal to the loss of weight of the air in the retort, measured by the quantity of air which entered on breaking the

beak of the retort, less the air driven out of the retort before hermetically sealing it. From this Lavoisier concluded that calx of tin is a compound of tin and air.

Lavoisier's next research, communicated to the Academy in 1775, and published in 1778, was entitled "On the Nature of the Principle which combines with Metals during their Calcination, and which increases their Weight." In this he describes experiments showing that when metallic calces are converted into metals by heating with charcoal, a quantity of fixed air is expelled; and here for the first time he points out that *fixed air is a compound of carbon with the elastic fluid contained in the calx.* He then describes the preparation of oxygen by Priestley's process of heating red oxide of mercury (*mercurius precipitatus per se*), and shows that the red oxide, when heated with charcoal, manifests the properties of a true calx, inasmuch as metallic mercury is formed, and a large quantity of fixed air is produced.

His next paper, which appeared in 1777 in the *Mémoires* of the Academy, deals with the combustion of phosphorus; and here he recapitulates Ruther-

ford's experiments, and shows that one-fifth of the air disappears, and that the residue, to which he gave the name "mouffette atmosphérique," is incapable of supporting combustion. It will be remembered that Rutherford named this residue "phlogisticated air," inasmuch as he imagined it to have absorbed phlogiston from the burning phosphorus; Scheele, too, had made a similar experiment with a similar result. From these observations, Lavoisier concluded that air consists of a mixture or compound of two gases, one capable of absorption by burning bodies, the other incapable of supporting combustion.

This paper was immediately followed by another, also published in 1777. Its title is, "On the Combustion of Candles in Atmospheric Air, and in Air eminently respirable." In this memoir he distinguishes between four kinds of air:— 1. Atmospheric air, in which we live and which we breathe. 2. Pure air, alone fit for breathing, constituting about one-fourth of atmospheric air, and termed by Priestley "dephlogisticated air." 3. Azotic gas, identical with Rutherford's "mephitic air," and of which the properties were then unknown. 4. Fixed air, which he proposed to call

"acide crayeux," or acid of chalk, discovered twenty-five years previously by Black.

By this time his theory was well developed. He accounted for the phenomena of combustion without having recourse to the phlogistic hypothesis: the calx was produced by the union of the metal with the active constituent of air; and when carbonaceous material burned, the carbon united with this same constituent, producing fixed air. But there were still difficulties in his way: it was known that in dissolving metals in dilute vitriol or muriatic acid, a combustible and very light air was evolved; and that the metals were thereby converted into calces in combination with the respective acids. This fact was not explained even by the supporters of the phlogistic theory, but it had the effect of preventing them from accepting Lavoisier's views. Some considered that hydrogen and phlogiston were identical, and that on dissolving a metal the calx was formed by the escape of the phlogiston; while others had a hazy idea that hydrogen was a compound of water and phlogiston; but of this more hereafter.

Lavoisier's objection to such a theory was that the calx was *heavier than the metal*, and that

hydrogen, though light, still possessed weight.[1] Moreover, he had ascertained that the calces of mercury, tin, and lead are compounds of these metals with active air, and that as fixed air is produced by heating such calces with carbon, fixed air must be a compound of carbon and vital air, or, as he named it, the "oxygine principle," inasmuch as its combination with phosphorus, sulphur, and carbon resulted in the formation of acids (ὀξύς, an acid).

In 1777 he read another memoir, "On the Solution of Mercury in Vitriolic Acid, and on the Resolution of that Acid into Aeriform Sulphurous Acid, and into Air eminently respirable." Priestley had already shown that this process yielded sulphur dioxide; Lavoisier carried the temperature higher, and, decomposing the sulphate of mercury, produced

[1] This, as previously remarked, had already been noticed. In Maquer's *Élémens de Chymie-pratique*, published in 1752, a work which ran through many editions, we read (p. 307): "There happens during all these calcinations, and especially in that of lead, a very strange phenomenon for which it is very difficult to assign a reason. It is that those bodies, which lose no small proportion of their substance, whether by the dissipation of phlogiston, or because part of the metal is exhaled as vapour, yield *calces* increased in weight after calcination; and this increase is by no means inconsiderable. . . . Physicists and chemists have devised many ingenious systems to account for this phenomenon, but no one of them is absolutely satisfactory. As no well-established theory has been devised, we shall not undertake to attempt an explanation of this singular fact."

metallic mercury, sulphur dioxide, and oxygen. It appeared therefore that sulphurous differed from sulphuric acid in containing a smaller proportion of oxygen.

He also experimented with iron pyrites, and his experiments recall those of Boyle. Boyle found that "marcasite," a disulphide of iron, on exposure to air, gained in weight, while vitriol of iron was formed. Lavoisier performed the same experiment, not "in a very pure air," as Boyle did when he left the pyrites exposed in a quiet dust-free room, but in a confined quantity of ordinary air; and he found that the air was rendered incapable of supporting combustion, or, in other words, its oxygen was removed.

In the same volume of the *Memoirs* of the Academy for 1778, another of Lavoisier's papers—"On Combustion in General"—is to be found. In this he showed that oxygen gas is the only substance which supports combustion; that during the burning of combustible substances in air a portion of the oxygen disappears, and converts the burning substance into one of two kinds of compounds: either an acid, such as sulphuric acid from sulphur, phosphoric acid from phosphorus, or carbonic acid

from carbon (for in those days the term "acid" was applied to what we now term an anhydride); or in the case of metals a calx, or compound of oxygen with the metal. The processes are analogous, but differ in the rate at which they take place; for the calcination of metals is a much slower operation than the combustion of sulphur or phosphorus. It is the rapidity of the action which leads to actual inflammation. He next examined and attacked the theory of phlogiston, and maintained that the existence of phlogiston is purely hypothetical, and quite unnecessary for the explanation of the phenomena. But his papers were received with doubt. The change demanded was too great; the trammels of custom were too firmly bound. He gained no converts.

Until the true nature of hydrogen had been explained, the attack on the phlogistic theory could not be said to be complete. This combination of hydrogen and oxygen to form water was first proved by Cavendish. And as soon as Sir Charles Blagden, in 1781, had communicated Cavendish's results to Lavoisier, the latter at once saw their bearing on the new theory which he was endeavouring to uphold, and perceived how they

would give a final blow to the adherents of the theory of phlogiston. For it had been frequently adduced as an objection to his new views, that they were incapable of explaining why hydrogen should be evolved during the solution of metals in acids, or why it should be absorbed during the reduction of calces to the metallic state. Lavoisier at once repeated Cavendish's experiments on a large scale, and was assisted on that occasion by Laplace, Sir Charles Blagden also being present. A considerable quantity of water was produced, and the volumes of the combining gases were found to be 1 of oxygen to 1·91 of hydrogen. Shortly after, in conjunction with Meunier, he performed the converse operation, in decomposing steam by passing it over iron wire heated to redness in a porcelain tube. The iron withdrew the oxygen from the water, while the hydrogen passed on and was collected in the gasholder.

The explanation of the solution of metals in acids was now easy: it depended on the decomposition of water. While the oxygen united with the metal to form a calx, the hydrogen was evolved; the calx dissolved in the acid, forming a salt of the metal. And the operation of producing hydrogen

by the action of steam on red-hot iron met with an equally simple explanation: the oxygen and iron united to form an oxide,—the ancient *ethiops martial*,—while the hydrogen escaped. The converse took place during the reduction of a calx to the metallic state by hydrogen. Here the hydrogen seized on the oxygen of the calx, removed it in the form of water, and the metal was left. These experiments were due to Cavendish; all that Lavoisier did was to show the true nature of the phenomena. The opponents of the new doctrines —Priestley chief among them—did their best to disprove the view that water was a compound of oxygen and hydrogen. But in vain. Many of Lavoisier's opponents had to admit the justice of his views; and in 1787 De Morveau, Berthollet, and Fourcroy joined Lavoisier in reconstructing the nomenclature of chemistry on a new basis, which is substantially that in use at the present day. Black, too, was a convert, but Priestley and Cavendish remained true to their old faith, and one of Priestley's last acts was to publish a defence of the phlogistic theory. We shall see later how Cavendish carefully considered the rival theories, and what reasons induced him to cast his vote for the older one.

Among the numerous memoirs which Lavoisier communicated to the Academy during the ten years between 1772 and 1782, one still remains to be mentioned. It was published as early as 1777, but it must be remembered that many of these memoirs were antedated. It referred to the respiration of animals; and Lavoisier concluded, on the ground that the phenomena of respiration are essentially similar to those of combustion and calcination, that the only portion of the air which supports animal life is the oxygen. The azote or nitrogen is inhaled along with the oxygen, but is exhaled unaltered. The oxygen, however, is gradually converted into carbonic acid; and when a certain amount, but by no means the whole, has been thus changed, the air becomes unfit for respiration. If the carbonic acid is withdrawn by means of lime-water or caustic alkali, the residue is air poor in oxygen, and the azote is the same as that left after the calcination of metals, or the burning of a candle, in air.

At the time of his impeachment Lavoisier was engaged in experiments on perspiration, along with Séguin. He had nearly finished his experimental work, but had drawn up no account of it. His

request that his life might be prolonged until he had compiled a statement of his results was refused; but Séguin, who was fortunately spared, undertook the task. The facts collected do not, however, bear directly on our subject, and shall not be further alluded to here.

This account of Lavoisier's researches would be incomplete without a reference to his text-book of chemistry, *Traité élémentaire de Chimie*, in which his views are stated in order, and with great clearness. The nomenclature current at the time was so cumbrous that it was almost, if not quite, impossible for the supporters of the new theory to express their meaning in an intelligible manner. De Morveau had suggested a nomenclature for salts; Black, too, had invented one; but neither of these systems was adapted to represent the new views. It was partly with the object of avoiding such embarrassment that Lavoisier wrote his *Treatise*.

He begins with a clear statement of what is generally termed "the states of matter"—solid liquid, and gaseous — and points out that solids and liquids are almost all capable of change into the aeriform state by the addition of "caloric." Proceeding next to the consideration of the

nature of air, he shows that it must necessarily contain all those gases capable of existence at the ordinary temperature; and he explains how water-vapour must be one of them, seeing that even though water is a liquid at the ordinary temperature, it is capable, like many other liquids, of existing as vapour, when mixed with other gases. He next treats of the analysis of air, and describes his classical experiment of heating four ounces of mercury for twelve days in a retort communicating with a bell-shaped receiver, standing in a mercury trough. Having marked the initial height of the air in the jar by means of a piece of gummed paper, he found that, after twelve days' heating close to the boiling-point, the air had diminished in volume by about one-sixth, and that the mercury had become covered with a red deposit of *mercurius calcinatus per se*, which, when collected, weighed 45 grains. The residual air in the retort and in the jar was incapable of supporting life or combustion; but the *red precipitate*, when heated, lost $3\frac{1}{2}$ grains of its weight, yielding $41\frac{1}{2}$ grains of metallic mercury, while it evolved 7 or 8 cubic inches of oxygen, capable of supporting the combustion of a candle

vividly, and of causing charcoal to burn with a crackling noise, throwing out sparks. Oxygen was thus successfully separated from air, and obtained from it in a pure condition for the first time, in a single series of operations.

In Lavoisier we see a master mind, not only capable of devising and executing beautiful experiments, but of assimilating those of others, and deducing from them their true meaning. Although his additions to the known chemical compounds were few in number, and cannot be compared with those of Scheele or of Priestley, yet his reasoning in disproof of the phlogistic theory was so accurate and so exact that it rapidly secured conviction. With the exceptions already mentioned, almost all the eminent chemists of the day accepted his conclusions; and one—Kirwan—who had written a formal treatise in defence of the phlogistic theory, was so fair-minded that after his work had been translated into French and published with comments, he acknowledged that the old theory was dead, and that truth had conquered.

It will be interesting now to trace Cavendish's part in developing the history of the discovery

of the constituents of air, and to note his arguments in favour of the phlogistic theory. Although Cavendish never publicly acknowledged its insufficiency, yet he had ceased to occupy himself with chemical problems at the time when its adoption was universal, and his true opinions have never been recorded.

CHAPTER IV

"PHLOGISTICATED AIR" INVESTIGATED BY CAVENDISH—HIS DISCOVERY OF THE COMPOSITION OF WATER

WHILE Lavoisier was engaged in experiments on oxygen, Cavendish, too, was devoting his attention to the constituents of air, but in a somewhat different manner. His early experiments led him to the discovery of the composition of water; and it has already been pointed out how necessary a knowledge of the true nature of hydrogen is to the understanding of the phenomena of combustion. His second paper deals with the inactive constituent of air—the mephitic portion, now known as nitrogen or azote. But before considering these, a sketch of his life will prove of interest.

The Honourable Henry Cavendish was a very singular man, retiring and uncommunicative to a degree; hence little is known of his early life.

He was the elder son of Lord Charles Cavendish, who was the third son of the second Duke of Devonshire. His only brother, Frederick, was also an eccentric, but a very benevolent man, and the two brothers, though they seldom met, lived on excellent terms with each other. Henry Cavendish was born at Nice in October 1731. His mother died when he was two years old. Nothing is known of his childhood and youth, save that he attended Hackney School from 1742 to 1749, and that he went to Cambridge in the end of 1749, and remained till 1753 without taking a degree. After leaving Cambridge it is supposed that he lived in London for ten years. It is known that his allowance from his father amounted to £500 a year, and that his rooms were a set of stables fitted up for his accommodation. It is probable that this was his own choice, and that he made use of them chiefly as a laboratory and a workshop. Although at his father's death and by the legacy of an aunt he acquired a large fortune, he never spent more than a fraction of it. He left more than a million sterling to his relative, Lord George Cavendish; but they saw each other only once a year, and the interview seldom lasted

more than ten minutes. The writer of his obituary notice, M. Biot, epigrammatically said:—"Il était le plus riche de tous les savans, et le plus savant de tous les riches."

He was a regular attendant at the meetings of the Royal Society, of which he was made a Fellow in 1760, and was a constant diner at the Royal Society Club. It is said that he used to talk to his neighbour at table so long as others did not join in the conversation; but if the conversation took a general turn, he was silent.

His death took place in February 1810, and was as solitary as his life. It is related by his servant that Cavendish, on feeling his end approaching, dismissed him from the room, telling him to come back in half an hour. He disobeyed instructions, and, being anxious, found some pretext to enter the room. Cavendish ordered him away in a voice of displeasure, and on returning the man found his master dead.

Such a life demands our pity; yet, if an object of human life is to give pleasure to its possessor, we can hardly say that Cavendish's was a failure. Ordinary mortals have a craving for the sympathy of their fellows; Cavendish appears to have been devoid

of any such sensation. Indeed, his experiments were in many cases not published until long after they had been made. He appears to have carried on his work for his own information, and to have been indifferent to the impression which his labours made on his fellow-men. Yet his inquiries cover a more extensive field than those of almost any other man of science. They begin with experiments on arsenic, by which he endeavoured to determine the difference between the element arsenic and its two oxides. He held that arsenic acid was more thoroughly "deprived of phlogiston" than arsenious acid (*i.e.* more highly oxidised); and on the same occasion he studied the effect of the addition of air to nitric oxide, produced by the action of nitric acid on the element arsenic and on arsenious oxide. His next experiments related to heat; and had he published them, he would doubtless have anticipated Black in his discovery of latent heat. His paper on "Factitious Airs," published in the *Philosophical Transactions* for 1766, deals with the properties of hydrogen, carbon dioxide, and the gases produced by the destructive distillation of organic substances. As we shall see later, he supposed that hydrogen, generated by the action of acids

on metals, came out of the metal, and was an unknown principle in combination with phlogiston, if indeed it was not phlogiston itself; and this idea is not absurd, for many metals, and indeed a very large number of minerals, evolve hydrogen when heated, the gas having been "occluded" in their pores.

In 1772 he communicated privately to Dr. Priestley the results of a series of experiments dealing with nitrogen. To prepare it he passed air repeatedly over red-hot charcoal, and absorbed the resulting carbon dioxide in potash. The residue was nitrogen. His description of it is—"The specific gravity of this air was found to differ very little from that of common air; of the two it seemed rather lighter. It extinguished flame, and rendered common air unfit for making bodies burn in the same manner as fixed air, but in a less degree, as a candle which burned about 80 seconds in pure common air, and which went out immediately in common air mixed with $\frac{6}{55}$ths of fixed air, burned about 26 seconds in common air mixed with the same proportion of this burnt air."[1] He named it, as usual, "mephitic air," and it is certain that, although Cavendish did not publish his results, his

[1] *Brit. Assoc. Report*, 1839, p. 64.

discovery was not later in date than Rutherford's. Dealing next with the phenomena observed when that curious fish, the torpedo, produces shocks, he ascribed them to the discharge of electricity, and he was the first to distinguish between intensity, or potential, and quantity of electricity,—a distinction now familiar to all.

It was in 1777 that he commenced his beautiful "Experiments on Air," the first account of which was published in 1783. They led to the discovery of the constant quantitative composition of the atmosphere, of the compound nature of water, and of the composition of nitric acid, and pointed the way to the recent discovery of argon.

In determining the composition of the atmosphere Cavendish made use of nitric oxide in presence of water, as a means of removing oxygen. This process, originally devised by Mayow, was rediscovered by Priestley, who employed it to ascertain the "goodness" of various samples of air; in Cavendish's hands it became an accurate quantitative method. The title of his paper, published in the *Philosophical Transactions* for 1783, is "Of a new Eudiometer." The term "eudiometer," signifiying "measurer of goodness," was

devised when it was supposed that ordinary air presented considerable variations in its power of supporting respiration and combustion, according to the seasons, and according to the place from which it was collected. Dr. Ingenhousz had found a greater absorption when air from near the sea-coast was tested by Priestley's method with nitric oxide, than when town-air was employed; and he ascribed the salubrious nature of sea-air to its being richer in "vital air." The Abbé Fontana, too, had made similar experiments, and had come to similar conclusions. Cavendish modified Fontana's apparatus, rendering it capable of giving more accurate results; and during the last half of the year 1781 he analysed the air collected on sixty days, some fine, some wet, and some foggy. He also collected air from different localities, sometimes at Marlborough Street, sometimes at Kensington, which was then a country village. The results of his analyses establish as the composition of air, freed from carbon dioxide by potash:

79·16 per cent of phlogisticated air (nitrogen).
20·84 per cent of dephlogisticated air (oxygen).

This result does not differ materially from those

obtained by the best modern analyses, which give, within very small variations:

79·04 per cent of nitrogen, argon, etc.,
20·96 per cent of oxygen,

after absorption of carbon dioxide, ammonia, and water-vapour.

In the following year, 1784, Cavendish published the first of his great memoirs, entitled *Experiments on Air*. His experiments were made principally "with a view to find out the cause of the diminution which common air is well known to suffer by all the various ways in which it is phlogisticated, and to discover what becomes of the air thus lost or condensed."

Cavendish chose processes for "phlogisticating" air in the course of which no fixed air should be produced. He therefore avoided the use of animal and vegetable materials, and confined himself to combustibles, such as sulphur or phosphorus, to the calcination of metals, the explosion of inflammable air, and the admixture of nitrous air. He adds as a suggestion, "Perhaps it may be supposed that I ought to add to these the electric spark; but I think it much more likely that the phlogistication of the air, and production of fixed air, in this

process is owing to the burning of some inflammable matter in the apparatus." We shall see later what magnificent results arose from this last mode of "phlogisticating" air.

He begins with an account of a repetition of an experiment of Mr. Warltire's, related by Priestley, in which a mixture of hydrogen and air was exploded in a copper vessel, with the result that they observed a loss of a few grains in weight; it is also stated by Warltire that if the explosion took place in a glass vessel, it became dewy, "which confirmed an opinion he had long entertained, that common air deposits its moisture by phlogistication." But Cavendish, using a glass vessel of much greater capacity than Warltire's, could remark no change of weight; and he concluded that 423 measures of hydrogen, or "inflammable air" as he named it, are "nearly sufficient to completely phlogisticate 1000 of common air, and that the bulk of the air remaining after the explosion is then very little more than $\frac{4}{5}$ths of the common air employed; so that, as common air cannot be reduced to a much less bulk than that, by any method of phlogistication, we may safely conclude that, when they are mixed in this proportion and exploded, almost all the in-

flammable air, and about $\frac{1}{5}$th part of the common air, lose their elasticity, and are condensed into the dew which lines the glass.

"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 8 feet long and about $\frac{3}{4}$ of an inch in diameter, in order to deposit the dew." "By this means upwards of 135 grains of water were condensed in the cylinder, which had no taste or 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." "And by this experiment it appears that this dew is plain water, and consequently that almost all the inflammable and about $\frac{1}{5}$th of the common air are turned into pure water."

But on firing little by little a mixture of "dephlogisticated air" or oxygen, obtained from red precipitate (that is, mercuric oxide prepared by heating the nitrate), with twice its volume of "inflammable air" or hydrogen, the resulting water was acid to the taste, and on evaporation with

alkali gave a small quantity—about 2 grains—of nitre. Cavendish suspected that the acid came from the nitrate of mercury in his red precipitate, and, to test this, procured his oxygen from other sources—from red-lead and sulphuric acid, and from the leaves of plants—but still with the same result: nitric acid was formed. Repeating the experiment so as to have present an excess of hydrogen, he found that no acid was produced.

"From the foregoing experiments it appears that when a mixture of inflammable and dephlogisticated air is exploded in such proportion that the burnt air is not much phlogisticated, the condensed liquor contains a little acid, which is always of the nitrous kind, whatever substance the dephlogisticated air is procured from; but if the proportion be such that the burnt air is almost entirely phlogisticated, the condensed liquor is not at all acid, but seems pure water, without any addition whatever; and as, when they are mixed in that proportion, very little air remains after the explosion, almost the whole being condensed, it follows that almost the whole of the inflammable and dephlogisticated air is converted into pure water." The quantity of uncombined gas was so

small that it must be regarded as an impurity. "There can be little doubt that it proceeds only from the impurities mixed with the dephlogisticated and inflammable air, and consequently that if those airs could be obtained perfectly pure, the whole would be condensed."

The next paragraph is interesting. "During the last summer also [of 1781] a friend of mine [Sir Charles Blagden; see p. 112] gave some account of them [these experiments] to Mr. Lavoisier, as well as of the conclusion drawn from them, that dephlogisticated air is only water deprived of phlogiston; but at that time, so far was Mr. Lavoisier from thinking any such opinion warranted, that, till he was prevailed upon to repeat the experiment himself, he found some difficulty in believing that nearly the whole of the two airs could be converted into water."

And next comes an important deduction. "Phlogisticated air appears to be nothing else than the nitrous acid united to phlogiston; for when nitre is deflagrated with charcoal, the acid is almost entirely converted into this kind of air." This is the first statement of the true relation between nitrogen and nitric acid; we should now state the

matter by the expression, "Nitrogen is nothing else than nitric acid deprived of oxygen." And the further deduction is made that "it is well known that nitrous acid is also converted by phlogistication into nitrous air, in which respect there seems a considerable analogy between that and the vitriolic acid; for this acid, when united to a smaller proportion of phlogiston, forms the volatile sulphurous acid and vitriolic acid air, both of which, by exposure to the atmosphere, lose their phlogiston, though not very fast, and are turned back into the vitriolic acid; but when united to a greater proportion of phlogiston, it forms sulphur, which shows no signs of acidity." "In like manner the nitrous acid, united to a certain quantity of phlogiston, forms nitrous acid and nitrous air, which readily quit their phlogiston to common air; but when united to a different, in all probability a larger quantity, it forms phlogisticated air, which shows no signs of acidity, and is still less disposed to part with its phlogiston than sulphur."

But the origin of the acid in water made from inflammable and dephlogisticated air was still unexplained. To settle this point Cavendish added to an explosive mixture of oxygen and hydrogen a

tenth of its volume of nitrogen, and found that the water was much more strongly acid; and if hydrogen was much in excess, a still greater amount of nitric acid was produced. After relating these experiments he proceeds:—

"From what has been said there seems the utmost reason to think that dephlogisticated air is only water deprived of its phlogiston, and that inflammable air, as was before said, is either phlogisticated water or else pure phlogiston, but in all probability the former." In a footnote he gives his reason for the choice, viz. that it requires a red-heat to cause hydrogen and oxygen to combine, while nitrous air combines with oxygen at the ordinary temperature; now, if hydrogen were pure phlogiston, one would expect it to combine more readily than nitrous gas, which has been shown to be a compound of nitric acid with phlogiston. It seems inexplicable that dephlogisticated air should refuse to unite at the ordinary temperature with pure phlogiston, when it is able to extract it from substances with which it has an affinity. Hence it is unlikely that hydrogen is phlogiston itself.

And a few paragraphs farther on Cavendish very nearly discards the phlogistic theory by this

statement: "Instead of saying air is phlogisticated or dephlogisticated by any means, it would be more strictly just to say, it is deprived of, or receives, an addition of dephlogisticated air; but as the other expression is convenient, and can scarcely be considered as improper, I shall still frequently make use of it in the remainder of this paper."

And now we come to the consideration of Lavoisier's new theory, and its rejection in favour of the old one of phlogiston. It is curious to follow the reasoning which made such an exceptionally acute thinker as Cavendish deliberately reject the true explanation. Cavendish first states his results in Lavoisier's terms:—

"According to this hypothesis, we must suppose that water consists of inflammable air united to dephlogisticated air; that nitrous air, vitriolic acid air (sulphur dioxide), and the phosphoric acid are also combinations of phlogisticated air, sulphur, and phosphorus with dephlogisticated air; and that the two former, by a further addition of the same substance, are reduced to the common nitrous and vitriolic acids; that the metallic calces consist of the metals themselves united to the same substance,—commonly, however, with a mixture of

fixed air; that on exposing the calces of the perfect metals to sufficient heat, all the dephlogisticated air is driven off, and the calces are restored to their metallic form; but as the calces of the imperfect metals are vitrified by heat, instead of recovering the metallic form, it should seem as if all the dephlogisticated air could not be recovered from them by heat alone. In like manner, according to this hypothesis, the rationale of the production of dephlogisticated air from red precipitate is, that during the solution of the quicksilver in the acid and the subsequent calcination, the acid is decompounded, and quits part of its dephlogisticated air to the quicksilver, whence it comes over in the form of nitrous air, and leaves the quicksilver behind united to dephlogisticated air, which, by a further increase of heat, is driven off, while the quicksilver resumes its metallic form. In procuring dephlogisticated air from nitre, the acid is also decompounded; but with this difference, that it suffers some of its dephlogisticated air to escape, while it remains united to the alkali itself in the form of phlogisticated nitrous acid. As to the production of dephlogisticated air from plants, it may be said that vegetable substances

consist chiefly of three different bases, one of which [hydrogen], when united to dephlogisticated air, forms water; another [carbon] fixed air; and the third phlogisticated air [nitrogen]; and that, by means of vegetation, each of these substances are decomposed, and yield their dephlogisticated air; and that, in burning, they again acquire dephlogisticated air, and are restored to their pristine form.

"It seems, therefore, from what has been said, as if the phenomena of nature might be explained very well on this principle, without the help of phlogiston; and indeed, as adding dephlogisticated air to a body comes to the same thing as depriving it of its phlogiston and adding water to it, and as there are perhaps no bodies destitute of water, and as I know no way by which phlogiston may be transferred from one body to another, without leaving it uncertain whether water is not at the same time transferred, it will be very difficult to determine by experiment which of these opinions is the truest; but as the commonly-received principle of phlogiston explains all phenomena, at least as well as Mr. Lavoisier's, I have adhered to that."

"Another thing which Mr. Lavoisier endeavours to prove is that dephlogisticated air is the acidifying principle. From what has been explained, it appears that this is no more than saying that acids lose their acidity by uniting to phlogiston, which, with regard to the nitrous, vitriolic, phosphoric, and arsenical acids, is certainly true." "But as to the marine acid and acid of tartar, it does not appear that they are capable of loosing their acidity by any union with phlogiston."

Here Cavendish does not consider the question of gain of weight on loss of phlogiston, or if he does, he must ascribe it to simultaneous entry of water. And experimental research at that time was not far enough advanced to enable him to decide finally as to the truth of this hypothesis.

In his next memoir, read before the Royal Society on June 2nd, 1785, Cavendish relates experiments on the passage of electric sparks through air, the experiment having first been tried by Priestley. Priestley says:[1]—"Lastly, the same effect [*i.e.* the diminution of the volume of common air], I find, is produced by the *electric*

[1] *Experiments and Observations on Different Kinds of Air*, vol. i. p. 181, and vol. ii. p. 238. Second edition, 1776.

spark, though I had no expectation of this event when I made the experiment." And again :—"At the time of my former publication, I had found that taking the *electric spark* in given quantities of several kinds of air had a very remarkable effect on them ; that it diminished common air and made it noxious, making it deposit its fixed air exactly like any phlogistic process ; from whence I concluded that the electric matter either is or contains phlogiston."

Cavendish had mentioned this process casually as one of the methods of phlogisticating air ; in beginning his second paper he says :—"I now find that though I was right in supposing the phlogistication of the air does not proceed from phlogiston communicated to it by the electric spark, and that no part of the air is converted into fixed air, yet that the real cause of the diminution is very different from what I suspected, and depends upon the conversion of phlogisticated air into nitrous acid." The apparatus he used was very simple. It consisted of a glass siphon filled with mercury, each leg dipping into a glass likewise containing mercury ; the air was admitted by a gas-pipette into the bend of the siphon, and on con-

necting the mercury in one of the glasses with a ball placed near the prime conductor of an electric machine, and the other with earth, sparks could be made to pass from the mercury in one limb to that in the other.

The product obtained by passing sparks through air in this manner turned litmus red, and gave rise to no cloud in lime-water, while the air was reduced to two-thirds of its original volume; nor did the lime-water give a precipitate on introducing some fixed air, thus showing that it had been saturated by an acid. It was found, too, that "soap-lees," or solution of caustic potash, if present, diminished the volume more rapidly than did lime-water; and repeated trials proved that "when five parts of pure dephlogisticated air were mixed with three parts of common air, almost the whole of the air was made to disappear." The nitrate of potassium thus produced caused paper soaked in it and dried to deflagrate; and it contained no suphuric acid, "There is no reason to think that any other acid entered into it except the nitrous." But it gave a precipitate with silver nitrate; and Cavendish, suspecting that this was silver nitrite, prepared some potassium nitrite by heating the nitrate; on comparing the white

precipitate which this solution gave with silver nitrate with that obtained from his "soap-lees," he found them identical. There was therefore no "muriatic acid" present, which would have yielded chloride of silver, of appearance somewhat similar to the nitrite.

As it had previously been shown to be probable that phlogisticated air is nitrous air united with phlogiston, and that nitrous air is nitric acid united with phlogiston, "we may safely conclude that in the present experiments the phlogisticated air was enabled, by means of the electric spark, to unite to, or form a chemical combination with, the dephlogisticated air, and was thereby reduced to nitrous acid, which united to the soap-lees and formed a solution of nitre; for in these experiments the two airs actually disappeared, and nitrous acid was actually formed in their room." "A further confirmation of the above-mentioned opinion is that, as far as I can perceive, no diminution of air is produced when the electric spark is passed either through pure dephlogisticated air or through perfectly phlogisticated air, which indicates a necessity of a combination of these two airs to produce the acid. Moreover, it was found in the

last experiment that the quantity of nitre procured was the same that the soap-lees would have produced if saturated with nitrous acid; which shows that the production of the nitre was not owing to any decomposition of the soap-lees."

Nothing more clearly shows the care with which Cavendish reasoned than these last quotations. No loophole is left unstopped; every precaution is taken to make the proof as faultless as it is possible for a proof to be.

But this was not enough. It was necessary for Cavendish to show that, so far as he could ascertain it experimentally, *all* the phlogisticated air was capable of combining with dephlogisticated air to form nitre. This he next proceeded to do.

"As far as the experiments hitherto published extend, we scarcely know more of the phlogisticated part of our atmosphere than that it is not diminished by lime-water, caustic alkalies, 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; so that though the nitrous acid, by being united to phlogiston, is converted into air possessed of these properties, and consequently, though it was reason-

able to suppose that part at least of the phlogisticated air of the atmosphere consists of this acid united to phlogiston, 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. 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 nitrous acid, or whether there was not a part of a different nature from the rest, which would refuse to undergo that change. The foregoing experiments, indeed, in some measure decided this point, as much the greatest part of the air let up into the tube lost its elasticity; yet, as some remained unabsorbed, it did not appear for certain whether that was of the same nature as the rest or not. For this purpose I diminished a similar mixture of dephlogisticated and common air in the same manner as before, till it was reduced to a small part of its original bulk. I then, in order to decompound as much as I could of the phlogisticated air which remained in the tube, added some dephlogisticated air to it, and continued the spark until no further diminution took place. Having

by these means condensed as much as I could of the phlogisticated air, I let up some solution of liver of sulphur to absorb the dephlogisticated air; after which only a small bubble of air remained unabsorbed, which certainly was not more than $\frac{1}{120}$th of the bulk of the phlogisticated air let up into the tube; so that, if there is any part of the phlogisticated air of our atmosphere which differs from the rest, and cannot be reduced to nitrous acid, we may safely conclude that it is not more than $\frac{1}{120}$th part of the whole." We shall afterwards see that this is a marvellously close estimate. There is actually $\frac{1}{84}$th part of the supposed nitrogen of the air which will not combine with oxygen when sparked with it in presence of potash.

But there still remained, in Cavendish's opinion, one point unproved. It was still conceivable that the potash might contain some "inflammable matter" which would diminish the air on sparking, and therefore oxygen nearly pure was sparked in presence of potash; but only a very small diminution of volume occurred, owing probably to some nitrogen present as an impurity in the oxygen. Water was substituted for potash with the same result; but if litmus was added to the water the colour was dis-

charged, and lime-water introduced into the tube gave a cloud, showing that "the litmus, if not burnt, was at least decompounded, so as to lose entirely its purple colour and to yield fixed air; so that, though soap-lees cannot be decompounded by the process, yet the solution of litmus can, and so very likely might the solutions of many other combustible substances."

Such are the chemical researches of Cavendish. Of all experimenters on the subject he was undoubtedly the greatest, though Mayow and Scheele were near rivals. But his researches were so complete that it is scarcely possible to criticise. He was not content with partial results: every point was proved and re-proved, and every possibility of erroneous conclusion was allowed for. It is curious that he did not employ the balance to check his results. Had he done so he could not have remained an adherent of the phlogistic theory. Although, as we have seen, he was perfectly acquainted with the method in which his results were interpreted by Lavoisier, he chose the old well-trodden path leading to the wilderness of distorted facts. Lavoisier tried to repeat Cavendish's experiments, but without success; but an account

is to be found in the last part of his *Experiments on Air*, published in 1788, of the successful repetition by a Committee of the Royal Society of the conversion of nitrogen into nitric acid by the electric spark in presence of oxygen and potash.

His remaining papers deal with meteorological and astronomical subjects. One, published in 1790, refers to the height of a remarkable aurora seen in 1784; another to the civil year of the Hindoos; and another to a method for reducing lunar distances. And in 1798 his famous memoir on the density of the earth appeared. It would be quite beyond the province of this book to enter into any detail regarding it; but it may be remarked in passing that the method consisted in measuring, by means of a torsion balance, the attraction of one leaden ball for another, and that recent experiments, made with the utmost refinement, have barely altered the number which he obtained, 5·4, to 5·527.

His last paper, on an improvement in a machine for dividing astronomical instruments, was published in 1809, the year before his death.

Nothing has been said as yet regarding the rival claims of Watt to the discovery of the composition

of water, and little need be said. The discovery was made by both in 1784, yet Cavendish visited Watt at Birmingham, in 1785, and was apparently on the best of terms with him; and Watt, as proved by Cavendish's diary, showed him many of his devices connected with the steam-engine. There can be no doubt that Watt had also discovered that when hydrogen and oxygen are exploded together water is the sole product, but he coupled the phenomenon with views involving the material nature of heat, or caloric, as it was then called, which Cavendish repudiated.

Cavendish's later work was carried out in a villa at Clapham, which was fitted as a laboratory, workshop, and observatory, but he had a town-house near the British Museum, at the corner of Gower Street and Montague Place. He had also a library in Dean Street, Soho, which was available for any scientific man who chose to present himself. So singular were Cavendish's habits that when he wished a book he went to this house and borrowed it as from a public library, giving a receipt for it.

Of all men, Cavendish was probably the most singular, but there can be no question of his extraordinary genius.

CHAPTER V

THE DISCOVERY OF ARGON

WITH the advent of Lavoisier's system of representing the phenomena of combustion, and the expression in his terms of the various changes resulting in air when metals are oxidised, and when carbonaceous substances burn, the investigation of air was abandoned. It was no longer regarded as a mysterious element, possessed of "chaotic" properties, but was held to be a mixture of oxygen, nitrogen, and small quantities of carbon dioxide and water vapour, together with a trace of ammonia. More exact determinations of the proportion between its oxygen and so-called nitrogen than Cavendish had made by the nitric-oxide method were carried out in 1804 by Gay-Lussac and Humboldt, by explosion with measured quantities of hydrogen, according to the method suggested by Volta; and they concluded, from a large number of analyses

made on specimens collected in all weathers and from various localities, that 100 volumes of air contained 21 volumes of oxygen and 79 volumes of nitrogen. These experiments, too, led Gay-Lussac to the conviction that oxygen and hydrogen unite to form water in the exact proportion of one volume of the former to two volumes of the latter; and he published, some years later, accounts of numerous experiments of the same kind, as the result of which he found that, when two gases combine or react with each other, they do so in some simple number of volumes; for example, one to one, one to two, or one to three.

The almost constant relation between the volumes of oxygen and nitrogen in air made it appear not unlikely, in the opinion of some, that air was a compound, and not a mixture; for the law of combination in definite proportions had by this time been enunciated by Professor Thomas Thomson, Dalton's intimate friend. But between the numbers 21 and 79 there exists no such simple ratio; and, moreover, on artificially producing air by mixing oxygen and nitrogen, there are none of the usual phenomena which characterise the formation of a compound: there is no rise or fall of temperature,

nor does the product differ in any way in properties from the constituents. And in 1846 Bunsen showed that the proportion between oxygen and nitrogen is not a constant one, but that the oxygen varies between 20·97 and 20·84 ; the experimental error did not exceed 0·03 volume, while the difference found amounted to 0·13 volume. Regnault, Angus Smith, A. R. Leeds, and von Jolly confirmed these results at later dates, from analyses of air collected from all parts of the world.

That air contains ammonia was first observed by Scheele. He found that the stopper of a bottle containing muriatic acid, when exposed to air, became covered with a film or deposit which he recognised to be sal ammoniac, or ammonium chloride.

The amount of ammonia in atmospheric air is, however, exceedingly small, and it is best detected in rain-water, which dissolves it; thus the air is considerably poorer in ammonia after a shower. The ammonia, small though its proportion is, plays a great part, although not an exclusive one, in yielding to plants their supply of nitrogen. The rain, percolating through the soil, leaves the ammonia behind, in some form of combination; and

it is then attacked by the nitrifying ferments and converted into nitrates, from which the plants derive the nitrogen which forms part of their substance, in combination with carbon, oxygen, and hydrogen.

There are also traces of nitric and nitrous acids in air, which are apparently in combination with ammonia. While the ammonia has been found to vary between 0·1 and 100 volumes per million volumes of air—the latter number refers to Manchester streets—nitrous and nitric acids are present in still smaller amounts; and in spite of the widespread opinion that ozone is contained in air, its occurrence is still a matter of dispute. That some powerful oxidising agent such as ozone or hydrogen peroxide is present appears certain; but the characteristic test for ozone—the formation of peroxide of silver on exposure of metallic silver to its influence—has never been successful. On the other hand, a small quantity of hydrogen dioxide—also, like water, a compound of oxygen and hydrogen, but one containing more oxygen than water—appears to be almost constantly present in air. Its amount is also extremely minute: it does not exceed one part per million. Its presence in air was dis-

covered by Schönbein. The atmosphere further contains dust, some of which appears to consist largely of metallic iron, which is conjectured to be of extraterrestrial origin—minute meteorites in fact—and also the spores of micro-organisms; but these spores, however important from a biological or a sanitary point of view, hardly come within the scope of the chemical composition of air. They serve to emphasise the conjectures of Boyle and of Scheele that air may contain "corpuscles" of all sorts, some in the form of dry exhalations, while other innumerable particles may be sent out from the celestial luminaries. But it has been found that air contains corpuscles of another nature, the consideration of which will come later.

Up to within the last few years it was supposed that the constituents of air had all been discovered. But Lord Rayleigh and Sir William Ramsay found that the supposed nitrogen of the air is in reality a mixture of nitrogen with a new gaseous element, to which they give the name "argon," on account of its chemical inactivity (ἄργον, idle, inactive).

In his presidental address to Section A of the British Association at Southampton in 1882, Lord Rayleigh alluded to an investigation which he had

begun on the densities of hydrogen and oxygen, relatively to each other. The object of the research was to discover whether the atomic weights of these gases, determinable from their densities and from the proportions by volume in which they combine, was actually as 1 to 16, or whether some fractional number was necessary to express the weight of an atom of oxygen relatively to that of hydrogen. In 1888 his first account of the determination was published in the *Proceedings* of the Royal Society. In 1889 he published a continuation of his first paper, and in 1892 he gave his final results; the number obtained was 15·882 for the atomic weight of oxygen, calculated from its density, hydrogen being taken as 1. In 1893 further experiments on densities were published,[1] those of oxygen and nitrogen being specially considered with reference to the density of air. He found the weights of one litre of oxygen, nitrogen, and air, at normal temperature and pressure to be—

Oxygen	1·42952 grams
"Nitrogen"	1·25718 „
Air	1·29327 „

[1] *Proc. Roy. Soc.* vol. liii. p. 134.

A simple calculation leads to the composition of purified air. The percentage of oxygen must be 20·941, and that of "nitrogen" 79·059, in order to give a mixture of which the weight of a litre is 1·29327. Now this corresponds with the results of the best analyses, quoted on p. 128. And the accuracy of these determinations of density is confirmed by this means, as well as by results of other experiments made by Leduc, von Jolly, and Morley.

But Lord Rayleigh was not content to prepare his gases by one process only. The oxygen, of which the mean value of the weight of a litre is given above, was prepared in three different ways: by the electrolysis of water, by heating chlorates, and by heating potassium permanganate. The results showed that the only difference which could be detected, and that an extremely minute one, must be attributed to experimental error. The actual weights of the contents of his globe were—

Electrolysis, May 1892 . . .	2·6272 grams
„ „ „ . . .	2·6271 „
Heating chlorates, May 1892 . .	2·6269 „
„ „ June „ . .	2·6269 „
Heating permanganate, January 1893	2·6271 „

These numbers are subject to a deduction of

0·00056, due to the fact that when the globe was empty of air, its capacity was somewhat reduced, owing to the external pressure of the atmosphere.

It was next deemed necessary to test whether nitrogen was homogeneous by preparing it too by several different methods. In the same paper Lord Rayleigh (p. 146) mentions that nitrogen, prepared from ammonia, its compound with hydrogen, is somewhat lighter than "atmospheric nitrogen," the deficiency in weight amounting to about 1 part in 200. Now it is evident from inspection of the numbers quoted above that the accuracy of the density determination may be trusted to within 1 part in 10,000, and that the balance would detect a discrepancy one-fiftieth of that observed in the densities of "atmospheric" and "chemical" nitrogen. In a letter to *Nature*, Lord Rayleigh asked for suggestions from chemists as to the reason of this curious anomaly, but his letter went without reply. He himself was inclined to believe that the difference was due to the decomposition of some of the ordinary molecules of nitrogen, usually believed to consist of two atoms in union with each other, in molecules consisting of one atom and as it is held that equal numbers of molecules

inhabit the same volume, temperature and pressure being equal, if the total number of molecules in his globe were increased by the splitting of some double atom molecules into single-atom molecules, the effect would be that, owing to an admixture of some lighter molecules, the density would be somewhat reduced.

But two other suppositions were entertained as possible. The oxygen might have been imperfectly removed from the nitrogen derived from the atmosphere; or, on the other hand, the nitrogen from ammonia might conceivably have retained traces of hydrogen. In the former case the nitrogen would have an increased weight owing to admixture of some heavier oxygen; in the latter, a diminished weight, due to the presence of the lighter hydrogen. The first of these suppositions is out of the question, inasmuch as it would have required that the nitrogen should contain one-thirtieth of its volume of oxygen, or one-sixth of that present in air, in order that its density should be raised by one two-hundredth; for the densities of oxygen and nitrogen are not so very different. The second supposition was negatived by introducing hydrogen purposely, and removing it by passing the gas over red-hot copper oxide, which

oxidises the hydrogen to water. This yielded nitrogen of the same density as that which had not undergone that treatment.

One other possibility was considered: the atmospheric nitrogen might contain some molecules of greater complexity than two-atom molecules, say N_3-molecules. Now it is known that when oxygen is electrified by the passage of a rain of small sparks through it, it acquires new properties: it possesses an odour, it attacks metallic mercury and silver, and its density is increased. And this product, ozone, has been shown to consist of three-atom molecules of oxygen, by various experiments of which an account cannot be given here; their presence accounts for the increased density of oxygen thus treated.

It was not inconceivable that if such a "silent electric discharge" were to be passed through "atmospheric" nitrogen, it might increase the number of such three-atom molecules, and might render the gas still denser; or if passed through "chemical" nitrogen, it might increase its density so as to make it equal to that of "atmospheric" nitrogen. Lord Rayleigh made such experiments, but without changing the density in the least: the

nitrogen from ammonia or from oxides of nitrogen, which has been termed "chemical" nitrogen, still remained too light by about one two-hundredth, and the atmospheric nitrogen still remained too heavy by the same amount.

At this stage Professsr Ramsay asked and received permission to make some experiments on the nitrogen of the atmosphere, with the view of explaining its anomalous behaviour. He had several years before made experiments on the possibility of causing nitrogen and hydrogen to combine directly, by passing the mixture over heated metals; among these was magnesium, and although no direct combination to any great extent was observed, still it was noticed that magnesium was a good absorbent for nitrogen, when that gas was passed over the red-hot filings of the metal. This process was therefore applied to the absorption of "atmospheric" nitrogen, in order to find out whether any portion of it was different from the rest. The plan adopted was to heat turnings of magnesium, which can be made very thin and loose, to redness in a tube of hard glass, in contact with the nitrogen of the atmosphere, carefully purified from oxygen, which would otherwise have

also combined with the metallic magnesium. As absorption proceeded, more nitrogen was admitted from a reservoir, and after a certain quantity had been absorbed, the residual gas was extracted from the tube by a mercury pump, and weighed.

The amount weighed was very small,—smaller perhaps than had up till then been thought possible, if accurate results were to be obtained. But here large differences were to be looked for. Only 40 cubic centimetres—the twenty-fifth part of a litre —was weighed; and its weight was only 0·050 gram. But with careful weighing the error should not exceed one five-hundredth of the amount weighed; and if there were to be any increase in density, that increase should be expected greatly to exceed this small fraction.

The first weighing—in May 1894—showed that the nitrogen had increased in density by reason of the operations, and instead of being fourteen times as heavy as hydrogen, it was nearly fifteen times as heavy.

The result was encouraging, and led to the probability of the nitrogen being altered in some way, or of the presence of some new component of the atmosphere. An experiment was therefore begun

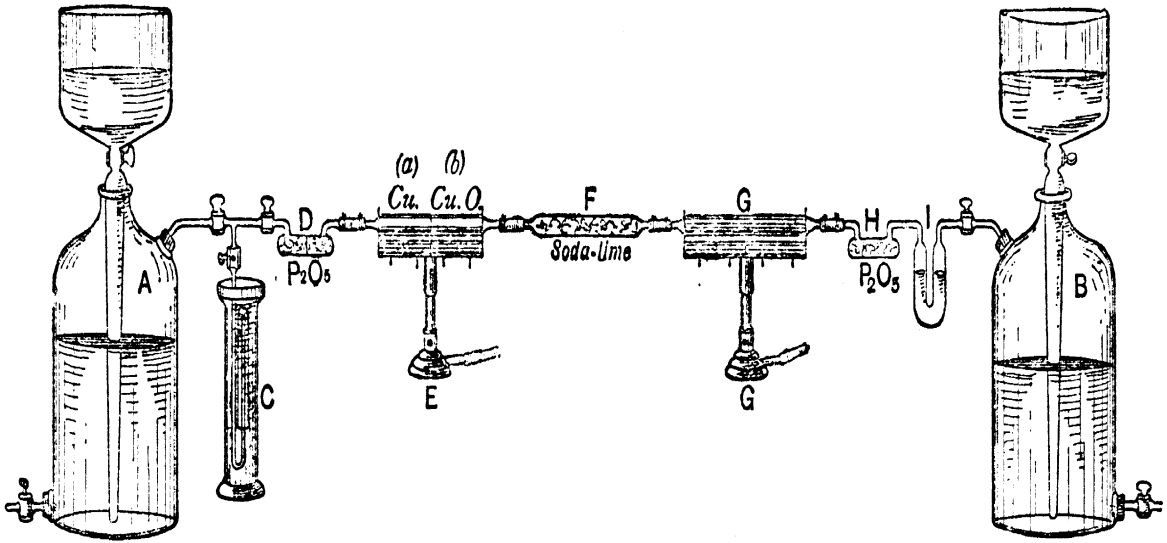


FIG. 1.

on a larger scale, the atmospheric nitrogen being passed backwards and forwards from one large glass gasholder A to another B, through a tube G filled with magnesium heated to redness, to absorb nitrogen; over red-hot copper oxide (*a*) (*b*), so that any carbonaceous matter such as dust should be oxidised to carbon dioxide and water; and these, if produced, were absorbed by placing in the train of tubes, one filled with a mixture of soda and lime F and I, to absorb any carbon dioxide which might possibly be formed, and two filled with pentoxide of phosphorus D and H, to dry the gas, so that water-vapour, carried along with the gas from the gasholders (which contained water) might be removed before the gas passed over the red-hot magnesium; for water acts on hot magnesium, forming oxide of magnesium and hydrogen, and the gas would have become contaminated with the latter had this precaution not been taken.

The process was continued for ten days, by which time most of the nitrogen had been absorbed. The apparatus was then somewhat altered, so as to make it possible to work with a smaller quantity of gas; but the tubes destined to absorb nitrogen, hydrogen, etc., were filled with the

same materials as before. In a few days more the volume was reduced to one-seventh of what it had been when the transference to the smaller apparatus was made, or about one-eightieth of the original volume of the atmospheric nitrogen taken.

The gas was then weighed, this time in a larger bulb, the weight being 0·2190 gram; and such is the possibility of precision in weighing on a good balance, that a difference of one two-thousandth of the whole weight was detectable. The density of the gas was now found to be 16·1. At this stage it was still believed that the new gas was an ozone-like modification of nitrogen, difficult to attack by magnesium. It was supposed that just as oxygen, when exposed to an electric discharge, undergoes a cleavage of its molecules, two-atom molecules becoming one-atom molecules for an instant, which then unite to form three-atom molecules, so the action of the magnesium on the nitrogen might be to withdraw one atom of nitrogen from the two-atom molecule, leaving a single uncombined atom, which might not improbably find two partners, each of its own kind, to form with them a three-atom molecule—a sort of nitrogen-ozone, in fact. Hence it was resolved to continue the absorption with fresh magnesium for a

still longer time, in the hope of its being possible to isolate the three-atom nitrogen molecules. But it became apparent that the bright metallic magnesium was now not much attacked; and on estimating the total amount of nitrogen absorbed, by treating the compound of nitrogen and magnesium with water, and liberating the nitrogen as ammonia, it appeared that only a small quantity of magnesium nitride had been formed. The density of this further purified gas was again determined, when it was found that a litre now weighed 1·7054 gram, corresponding to a density of 19·086.

A portion of this gas was mixed with oxygen and exposed to a rain of electric sparks in presence of caustic soda; in fact, Cavendish's old plan of causing nitrogen to combine was now resorted to. Contraction occurred, and on removing the excess of oxygen, the diminution of volume was found to amount to 15·4 per cent of the original volume taken. Making the supposition that the gas of density 19 still contained nitrogen, and allowing for its influencing the density, it followed that the pure gas should be twenty times as heavy as hydrogen.

A tube such as is usually employed in examin-

ing the spectra of gases at low pressures was next filled with the gas of density 19. Such a tube, called a Plücker's tube, after its inventor, contains wires of platinum sealed through at each end, where it is about half an inch in width; the middle portion of the tube is about 3 inches long, and its bore is a fine capillary. When the platinum wires are connected with the secondary

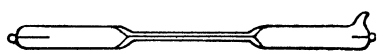


FIG. 2.

terminals of a Ruhmkorff's coil, and the tube is partially exhausted, a brilliant glow appears in the capillary portion. If viewed through a glass prism, different gases show different sets of coloured lines crossing the usual gradation of colours of the spectrum. Thus hydrogen exhibits three striking lines, one bright red, one peacock-blue, and one violet; nitrogen shows a large number of somewhat hazy bands, red, orange, yellow, and yellow-green in colour, besides a number of bands of a violet colour; but the new gas, while exhibiting the bands characteristic of nitrogen, showed in addition certain groups of red

and green lines which did not appear to belong to the spectrum of any known gas.

While these experiments were in progress, Lord Rayleigh was occupied in preparing nitrogen from other sources, and in determining its density; and in every case it was evident that nitrogen from all sources except the atmosphere weighed somewhat less than atmospheric nitrogen. He therefore proceeded to repeat Cavendish's experiment, and like Cavendish, he obtained a small residue of gas which would not disappear on sparking with oxygen, in presence of caustic soda. The sparks, as they passed, could be observed through a spectroscope (which consists of an arrangement of prisms and lenses so designed as to examine the components of the light emitted by the sparks), and he, too, was struck with the unusual character of the spectrum. His experiments proved, besides, that the amount of residue was roughly proportional to the amount of air taken; thus, beginning with 50 cubic centimetres of air, the residue was 0·32 cubic centimetre; and from 5 cubic centimetres of air, only 0·06 cubic centimetre of gas was obtained.

These small amounts are not proportional to

the quantities of air taken; but, as will afterwards be seen, the discrepancy is owing to the solubility of the new gas in water. Still they served to show that from a comparatively large amount of air, more of the new gas could be obtained than from a smaller amount.

At this stage the two discoverers joined forces, and letters passed almost daily between them, describing the results of experiments which one or other had made. And just prior to the meeting of the British Association at Oxford in August 1894, it was decided that the proof of the existence of a new constituent gas in air was sufficiently clear to render it advisable to make to the Association a short announcement of the discovery. The statement was received with surprise and interest; chemists were naturally somewhat incredulous that air, a substance of which the composition had been so long and so carefully studied, should yield anything new. One of the audience inquired whether the name of this new substance had been discovered; as a matter of fact it was then under consideration.

But it was still conceivable, although improbable, that the new gas was being produced by the very

processes designed for its separation, and attention was first turned to devising a complete proof of its actual presence in air. Now it is known that the rates of diffusion of gases through a narrow opening, or through a number of minute holes, such as exist in a pipe of porous clay, *e.g.* a tobacco-pipe stem, are in inverse proportion to the square roots of the densities of the gases. Oxygen is, in round numbers, sixteen times as dense as hydrogen; the square roots of 16 and 1 being 4 and 1, it was found by Graham, who first carefully investigated this subject, that four times as much hydrogen would pass through a porous diaphragm in a given time, as oxygen. The *compound* of hydrogen and oxygen, however, in the state of gas, *viz.* steam, is not separated by such a process into its constituents; it diffuses as such, and since it is nine times as dense as hydrogen, the relative rates of diffusion of steam and hydrogen are as 1 : $\sqrt{9}$, or as 1 to 3; that is, for every 3 parts of hydrogen passing through such a septum, 1 part of steam would pass in the same time.

An experiment was therefore devised, in which a large quantity of air was made to stream slowly through a long train of stems of churchwarden

tobacco-pipes, placed inside a glass tube, the latter being closed at each end, except for the entrance and exit tubes of the tobacco-pipes; in the encasing glass tube a vacuum was maintained, and the gases, passing through the walls of the pipe-stems, were pumped off and discharged. According to what has just been said, these should be the lighter gases, nitrogen and oxygen, which ought to pass through the porous stems more quickly than the supposed heavier constituent of air; while the air issuing from the end of the train of pipes should contain relatively more of the heavier constituent, and should in consequence have a greater weight than an equal volume of air. But it was obviously convenient to remove the oxygen before weighing this sample of altered air, and this was done in the usual way by passing the mixed gases over red-hot copper. It was found that such nitrogen was even heavier than ordinary atmospheric nitrogen; not much, it is true, but still consistently heavier. The denser constituent could, in fact, be concentrated by this means. The proof was therefore indubitable that the new gas existed in air as such.

There is another method of proof, however, which was not left untried. Experiment showed

that the solubility of the new gas in water is considerably greater than that of nitrogen, although less than that of oxygen. In 100 volumes of water at the ordinary temperature, about 1·5 volumes of nitrogen will dissolve, about 4·5 volumes of oxygen, and about 4 volumes of the new gas, to which the name finally chosen for it, "argon," may now be applied. Now the proportion in which the constituents of a mixture of gases will dissolve in a solvent is conditioned first by their relative solubilities, and second, by their relative proportion. Thus, if air be considered to be simply a mixture of 1 volume of oxygen and 4 volumes of nitrogen, the gas extracted from water which has been shaken with air will have the composition—

Oxygen . . .	$1 \times 4{\cdot}5 = 4{\cdot}5$ volumes
Nitrogen . . .	$4 \times 1{\cdot}5 = 6{\cdot}0$ „

So that the proportion of oxygen to nitrogen in such a mixture of gases is considerably greater than in air: instead of being approximately 1 to 4, it is nearly 4·5 to 6. The discovery of this law concerning the composition of the gases dissolved in liquids was due to Dr. Henry, one of the biographers of Dalton.

The gases can be almost entirely extracted by

boiling the water. But to boil large quantities of water at one operation in a vessel suitable for collecting the escaping gas is not easy. It is much simpler to cause the water to pass slowly through a can below which there is a powerful flame, so that the water in its passage becomes heated to the boiling-point, and gives off its gas before it escapes. Of course the gas collected contained oxygen, but this was easily removed by the usual method of passing it over red-hot copper. The density of the residual gas was determined, and it was found to be at least as much greater than that of "atmospheric" nitrogen as the density of "atmospheric" nitrogen exceeded that from chemical sources. Hence it was to be concluded that the new constituent of air, argon, was being concentrated by dissolving air in water, and extracting the dissolved mixture of gases. A third proof that argon exists in air will be given farther on.

In order that the properties of the newly-discovered gas, argon, might be thoroughly investigated, it was necessary to prepare it on a much larger scale than had hitherto been attempted, and this was carried out by the two processes for removing the oxygen and nitrogen which have been

already described. Supposing the new gas to have the density 20 compared with oxygen as 16, the density of the atmospheric mixture of nitrogen and argon compared with that of nitrogen alone shows that air should, roughly speaking, contain less than one part of argon in one hundred. Hence, to obtain a litre of argon it was necessary to work up a large quantity of atmospheric nitrogen. Now, as has just been said, there are two ways of doing this. (1) One is to produce an electric flame between two pieces of stout platinum in air, confined in a large glass balloon of about 6 litres capacity, over a weak solution of caustic soda. For this purpose a very powerful rapidly alternating current is necessary. The latest, and apparently the best, method of carrying this out was described by Lord Rayleigh in his Royal Institution lecture in January 1896. The neck of the balloon is placed downwards, and connected by means of a glass tube, passing through a cork which closes the neck, with a rotating fan or paddle-wheel with curved blades, which forces through the tube a weak solution of caustic soda; another tube, also entering through the cork, conveys away the excess of soda to the fan, whence it is again forced into

the balloon. The soda solution makes a fountain in the balloon, and flows in a uniform stream down its sides, covering its inner surface with a thin layer of liquid. Through the cork the two electrodes, with their thick platinum terminals, enter; and there is

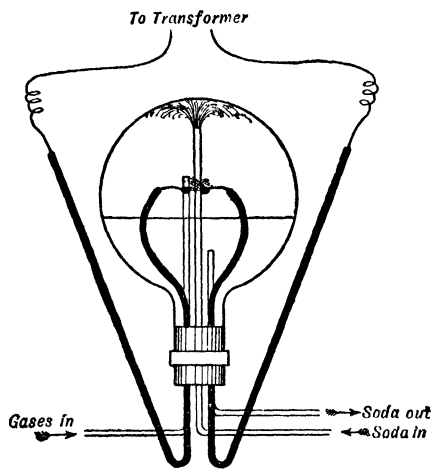


FIG. 3.

another tube besides, which conveys into the balloon a mixture of air and oxygen in such proportions that they combine completely on exposure to the flame. The layer of soda solution plays a double part. It prevents the undue heating of the gas balloon, which otherwise must be sunk in running water in order to keep it cool; and it exposes a very large

and constantly renewed surface of soda to the nitrous fumes which are produced by the combination of the nitrogen and the oxygen, and so removes them as quickly as they are formed. It appears probable that the union results initially in the formation of nitric oxide, NO, which then unites partially with oxygen to form some nitrogen peroxide, NO_2. This is absorbed by the soda, giving a mixture of nitrite and nitrate of sodium, $NaNO_2$ and $NaNO_3$. Working in this way, from 7 to 8 litres of mixed gases can be made to combine per hour. The rapidly alternating current is best obtained by the use of a transformer; and as the heating effect on the platinum terminals is very great, they must be made of stout rods.

(2) To prepare a large quantity of argon by the absorption of atmospheric nitrogen by magnesium is a somewhat tedious process. The air must be first freed from oxygen by means of red-hot copper, and the atmospheric nitrogen collected in a gas-holder. Long tubes of combustion-glass tubing, which stands a bright-red heat without becoming deformed, are packed with magnesium turnings and heated to redness in long gas furnaces, such as are used in organic analyses; and through these

the "atmospheric nitrogen," dried by passage over soda-lime and phosphorus pentoxide, is then passed. The magnesium begins to glow at that end of the tube nearest the entrance, owing to its combination with nitrogen, and a hot ring is seen to travel slowly down the tube to the other end, marking the place where such combustion is in progress. The gas issuing from the tube is collected in a small gasholder. When one tube of magnesium is exhausted, another is substituted for it. Each tube is capable of absorbing about seven litres of nitrogen, so that to obtain a litre of argon about one hundred litres of "atmospheric nitrogen" must be employed, and about fourteen tubes of magnesium are required. M. Maquenne, who has prepared the nitrides of several metals, found that a mixture of lime and magnesium, yielding metallic calcium, is more easily manipulated than pure magnesium, owing to the absorption of the nitrogen at a lower temperature. The process involves the preparation of pure lime by heating artificial carbonate. A mixture of equal amounts of magnesium powder and this pure lime may be readily heated in a glass tube, without danger of fusing the glass. All the nitrogen may

be removed by a single passage through a tube thus charged and heated; but hydrogen and carbonic oxide are introduced in small amount, and must subsequently be got rid of by passage over copper oxide and soda lime. Porcelain tubes are attacked by the magnesium, and crack on cooling; and iron tubes are difficult to clean out.

This preliminary operation, if magnesium alone be used, does not yield pure argon; it merely removes a large portion of the nitrogen. To free the argon from the remainder, it is caused to circulate (by means of a specially contrived mercury-pump, where each drop of mercury in falling down a narrow glass tube carries before it a small bubble of gas) through tubes containing red-hot copper, red-hot copper oxide, red-hot magnesium, and cold soda-lime and phosphoric anhydride. The copper serves to remove traces of oxygen; the copper oxide yields up its oxygen to any hydrogen or carbon compound—dust and the like—which may happen to be present; the soda-lime absorbs any carbon dioxide produced by the combustion of the carbon compounds, and at the same time partially dries the gas; while the phosphoric anhydride effectually dries the gas, previous to its passage over the red-hot magnesium,

which in its turn removes the nitrogen. It is necessary to continue this circulation for several days before the litre of gas is entirely freed from nitrogen. If, however, the lime-magnesium mixture be employed, argon free from nitrogen may be at once obtained.

It is difficult to choose between these two methods: both are troublesome, and require a considerable time, but in an ordinary laboratory the latter is probably the more easily set in operation, for the former requires a suitable electric current, and power, so as to rotate the water-fan. Up to the present date, the only sources which have yielded argon are atmospheric air, gases extracted from mineral waters or from springs, one meteorite, and one rare mineral, malacone. No animal or vegetable substance appears to contain it. Experiments were made in the summer of 1895 by Mr. George MacDonald and Mr. Alexander Kellas, in order to decide whether argon was a constituent of any living matter. Some peas were reduced to powder and dried; the carbon and hydrogen of the peas were burned to carbon dioxide and water by heating with oxide of copper, and under these circumstances the nitrogen is evolved in the state

of gas. Had argon been contained in the vegetable, it too would have accompanied the nitrogen. The nitrogen was then, as usual, absorbed for the most part by means of magnesium, and the small unabsorbed residue was mixed with oxygen and exposed to electric sparks for many hours, in presence of caustic soda. There was *no* residue left after absorbing the excess of oxygen : the gas was completely removed. Similar experiments carried out on animal tissue led to a similar conclusion. Two mice were chloroformed, and when dead they were dried in an oven until all the moisture of their bodies was completely driven off, and it was possible to reduce them to powder. It is interesting to note that one of these mice contained 73 per cent of water, and the other 70·5 per cent. The dried animals yielded about 11 per cent of their weight of nitrogen. Absolutely no residue of gas was obtained on causing this nitrogen to combine ; hence it appears to be a legitimate conclusion that neither animal nor vegetable tissue contains any appreciable amount of argon. It has been found, however, that the gas in the air-bladders of fish is richer in argon than atmospheric air.

But these experiments lead to a further

result. They show that nitrogen, procured from its compounds, when treated in the same way as atmospheric nitrogen, yields no trace of argon. And it must therefore be taken as proved without doubt that argon is actually present in the atmosphere as such, and is not produced by any process to which the nitrogen has been submitted in order to extract it.

This point having been settled, the actual percentage of argon in atmospheric air next invited inquiry. It is by no means very easy to absorb quantitatively the whole of the nitrogen from an accurately measured sample of air, for small gains and losses are apt to occur. It is necessary to keep the air out of contact with water as much as possible, because argon, being more soluble than nitrogen, dissolves in larger proportional amount in the water, and is thereby partially removed. The air was therefore entirely manipulated over mercury. The processes were like those previously employed: most of the nitrogen was removed with magnesium, and the residue was freed from all nitrogen by sparking with oxygen. Experiments directed to this end were carried out by Mr. Kellas in Professor Ramsay's laboratory, and independently

by M. H. Schloesing in Paris. The results were identical. "Atmospheric nitrogen" consists of pure nitrogen mixed with 1·186 per cent of its volume of argon.

It is now possible, knowing the percentage of crude argon in atmospheric nitrogen (for it will be seen later that other gases allied to argon are also present) and its density (19·94), to calculate whether Lord Rayleigh's determinations of the density of atmospheric nitrogen were correct. The weight of one litre of pure nitrogen is 1·25092 gram, and of argon, 1·7815 gram; hence a litre of a mixture of 98·814 volumes of pure nitrogen with 1·186 volume of argon must possess the weight 1·25711 gram. The actual number found by Lord Rayleigh was 1·25718 gram, which is almost exactly identical with the number calculated.

Mineral waters, as a rule, contain small quantities of argon mixed with oxygen, nitrogen, carbon dioxide, and in some cases sulphuretted hydrogen, helium, and neon—gases of which more hereafter. The waters actually examined were the Bath waters, which contain much nitrogen, a little argon, and traces of helium and neon; the Buxton waters, containing nitrogen and a little argon;

the water from "Allhusen's Well," Middlesborough, which evolved gas of an inflammable nature consisting mainly of nitrogen, but also containing marsh-gas, and argon to the extent of 0·4 per cent; water from boiling springs in Iceland evolved gas containing somewhat more argon than air does, viz. 1·14 per cent; and lastly, water from the Harrogate sulphur springs yielded a gas largely consisting of a mixture of sulphuretted hydrogen, carbon dioxide and nitrogen, but giving also an appreciable amount of argon. Such determinations show that argon is not merely confined to the atmosphere above the earth, but that it penetrates the earth and is contained in subterraneous water. These results have been obtained by Lord Rayleigh, Professor Ramsay, Mr. Travers, and Mr. Kellas.[1]

Similar experiments have been made by Dr. Bouchard in Paris[2] on effervescing waters from Cauterets in the Pyrenees. One of those springs yielded a mixture of nitrogen with a small amount of argon and helium; another yielded only nitrogen and argon; while a third gave nitrogen and

[1] *Proc. Roy. Soc.* vol. lix. p. 68. *Phil. Trans.* vol. clxxxvi. p. 227.
[2] *Compt. rend.* vol. cxxi. p. 394.

helium. Such are, up to the present, the sources of argon.

It is now of interest to inquire what are the properties of argon and how it is related to other elements.

CHAPTER VI

THE PROPERTIES OF ARGON

THE density of a gas is one of its most characteristic and important properties. Avogadro's law, which postulates that equal volumes of gases, at equal temperature and pressure, contain equal numbers of molecules, renders it possible to compare the weights of the molecules by determining the relative weights of the gases. Thus, as the ratio between the densities of nitrogen and oxygen is 7 to 8, a single molecule of nitrogen—the smallest portion which can exist in freedom, uncombined with other elements—is $\frac{7}{8}$ths of the weight of a single molecule of oxygen. Hence a determination of the density of argon leads directly to a knowledge of the relative weight of a single molecule of this gas.

But with what should the density of argon be compared? What gas must serve as the standard

of density? To answer this question it is necessary to give a short sketch of the development of chemical theory regarding the atomic weights of elements and their relative volumes.

Dalton proposed to adopt as the unit of atomic weight the weight of the lightest atom, namely, that of hydrogen. Taking, for example, water as one substance containing hydrogen, its percentage composition by weight is approximately—

Hydrogen	11·11 per cent
Oxygen	88·88 „

If the smallest portion of water capable of free existence contains one atom of hydrogen and one of oxygen, then, placing the weight of an atom of hydrogen as unity, the weight of an atom of oxygen is eight times as great. And although we do not know the absolute weight of any single atom, we are justified in supposing that an atom of oxygen is eight times as heavy as an atom of hydrogen. But have we any right to make the assumption that a molecule of water contains one atom of each element? Dalton came to the conclusion that this supposition was a justifiable one; but there are strong reasons against it. We have already

seen that Cavendish discovered approximately, and that Gay-Lussac and Humboldt determined accurately, that when hydrogen and oxygen unite to form water, two volumes of the former combine with one of the latter. Now it appears improbable on the face of it that any given volume of hydrogen should contain only half as many particles as an equal volume of oxygen; and it is still more improbable, when we take into consideration (1) Boyle's discovery that if the pressure on a gas be increased, the volume of the gas, whatever it may be, diminishes in like proportion; and (2) Gay-Lussac's and Dalton's discovery, that all gases, when equally raised in temperature, expand equally. It would be very remarkable if one gas, containing twice as many particles in unit volume as another, should show exactly similar behaviour towards pressure and temperature. Hence it appeared not unreasonable to suppose that the composition of water was expressed by one particle of oxygen in union with two particles of hydrogen. (The word "particle" is here used in the meaning of "small portion"; such particles may be molecules or they may be atoms.)

When steam is formed by the union of hydrogen with oxygen, it has a volume equal not to the sum

of the volumes of the hydrogen and the oxygen, but to two-thirds of the sum, or equal to that of the hydrogen alone, or twice that of the oxygen. And as steam, like hydrogen and oxygen, follows Boyle's and Gay-Lussac's laws it must be supposed that in the steam there are as many particles as in the hydrogen from which it was formed. But the particles of steam must necessarily be more complex than those of the hydrogen, inasmuch as the steam contains oxygen as well as hydrogen.

These difficulties may, however, be easily overcome by the following supposition, which was first formulated by Avogadro in 1811. The ordinary particles of hydrogen and of oxygen are complex, each containing at least two atoms, or smaller particles, which usually exist in combination with each other, or with atoms of some other element. Two volumes of hydrogen, therefore, contain twice as many particles as one volume of oxygen; to such particles the name "molecules" is now universally applied. And as these molecules are themselves each made up of two smaller particles, now termed atoms," there exist in two volumes of hydrogen twice as many atoms as in one volume of oxygen. On combination, the atoms

in the molecules of hydrogen and oxygen rearrange themselves, so that two atoms of hydrogen and one atom of oxygen combine to form a molecule of water-vapour, containing three atoms. The steam now contains as many molecules as did the hydrogen before combination; but whereas the molecules of hydrogen originally consisted of two atoms each, the molecules of steam contain three atoms. It is this which causes the contraction from three volumes to two when hydrogen and oxygen molecules exchange partners in forming water molecules.

Of course the difficulty would meet with an equally good explanation if it were supposed that the hydrogen molecules and the oxygen molecules each contained four atoms, or eight atoms; but there is no need to increase the complexity of the molecule, and the assumption that these molecules are "diatomic" completely serves the purpose. The composition of water is therefore believed to be two atoms of hydrogen in combination with one atom of oxygen; and when hydrogen and oxygen unite to form water, a transaction similar to an exchange of partners is supposed to occur; the atoms of hydrogen and oxygen are imagined to leave their partners of like kind, and to rearrange

themselves, so that groups of atoms, or molecules, each containing two atoms of hydrogen and one of oxygen, are formed. To such an arrangement the formula H_2O is applied, while ordinary hydrogen molecules may be represented as H_2, and molecules of oxygen as O_2.

It has been shown already (p. 153) how Lord Rayleigh obtained the number 15·882 for the density of oxygen compared with that of hydrogen. To determine the atomic weights of elements, the usual process has been to analyse their oxides, for only a few elements form compounds with hydrogen. Thus the analysis of copper oxide yields the numbers—

Copper . . .	79·96 per cent
Oxygen . . .	20·04 „

And as no compound of copper and hydrogen is known which lends itself to analysis, the atomic weight of copper is necessarily referred to that of oxygen. If the atomic weight of hydrogen be taken as unity, that of oxygen, from Lord Rayleigh's determination, must be 15·882, because, in comparing the weights of equal volumes of the gases, a comparison is made of the weights of equal numbers of molecules; and as it is reason-

able to suppose that each molecule of hydrogen and of oxygen contains two atoms, the number 15·882 represents the weight of an atom of oxygen compared with that of an atom of hydrogen taken as 1. But this number has not been regarded as sufficiently established by experiment. Other observers (for the importance of this ratio has been acknowledged since the beginning of the century) have obtained results differing from that given above, although not to any great extent. And as it is a matter of indifference what basis or standard be taken for atomic weights, which represent only relative numbers, it is common to accept the atomic weight of oxygen as 16, in which case that of hydrogen, if Lord Rayleigh's determination of its density be regarded as accurate, would be 1·0074. Hence if we place the atomic weight of oxygen as 16, that of copper would be 63·34. And as with copper, so with most other elements. It is very seldom that the atomic weight of an element has been directly compared with that of hydrogen; it is, in fact, almost always ascertained by analysis of its chloride, bromide, or oxide; and the atomic weights of chlorine and bromine have been very carefully compared with that of

oxygen. There is, besides, another convenience in accepting 16 as the atomic weight of oxygen: it is that many atomic weights are then represented by whole numbers instead of by fractions; thus, sulphur has the atomic weight 32, if oxygen be made 16, whereas, if it were 15·882, the atomic weight of sulphur would be 31·764, a number much more difficult to remember.

We see then that it is convenient to refer the density of argon to oxygen taken as 16. The density obtained by Professor Ramsay in February 1895, using a globe of small capacity (only 160 cubic centimetres), was 19·94; exactly the same result was given by Lord Rayleigh's experiments in June 1895 on argon prepared by means of the electric discharge, with a balloon of much greater capacity, which held over two litres of gas. Now as a molecule of oxygen consists of two atoms, the weight of a molecule is twice the atomic weight, or 32; and as a given volume of argon must contain as many molecules as the same volume of oxygen, the weight of a molecule of argon must be twice 19·94, or 39·88.

But this gives no information regarding the relative weight of an *atom* of argon. To ascertain

this important quantity two methods may be chosen. One is to make compounds of the element, and this will be first considered. Since an atom of an element is defined as the smallest amount which can exist in combination, then, if numerous compounds of an element be examined, that one which contains proportionally the least amount of the element may be regarded as containing an atom, unless there are reasons to the contrary. For example, reverting to the former instance of water, the relative proportions by weight of oxygen and hydrogen are, in round numbers, 16 to 2. Reasons have already been given showing why its formula should be H_2O and not HO; its molecule must contain two atoms of hydrogen. But another compound of oxygen and hydrogen is known in which the proportions are 16 parts by weight of oxygen to 1 part by weight of hydrogen. Here also there are reasons for believing that this compound, hydrogen peroxide, contains two atoms of hydrogen; whence it follows that it must contain two atoms of oxygen, or 32 parts by weight to 2 parts by weight of hydrogen, and must therefore have the formula H_2O_2. No other compound of oxygen and hydrogen is known; and it may be stated briefly that no compound of

oxygen with any element whatever is known in which less than 16 parts by weight enters—compared, of course, with the atomic weight of the other element or elements in the compound. Hence 16 is accepted on this ground as the atomic weight of oxygen.

If now it were possible to prepare compounds of argon, similar reasoning might be applied to them, and that compound containing least argon would be regarded as indicating its atomic weight. Many attempts were therefore made to induce argon to enter into combination. And the consistent failure of these attempts led to the choice of the name "argon" or "idle" for the newly discovered element. The methods employed to prepare argon free from nitrogen,—namely, by exposing the mixed gases to the action of oxygen in a discharge of electric sparks, and by passing them over red-hot magnesium,—show that it cannot be induced to combine with one of the most electro-negative of elements—oxygen, and one of the most electro-positive—magnesium. It also refuses to combine with hydrogen or with chlorine when sparked with these gases; nor is it absorbed or altered in volume by passage through a red-hot tube along with the vapours of phosphorus, sulphur,

tellurium, or sodium. Red-hot caustic soda, or a red-hot mixture of soda and lime, which attacks the exceedingly refractory metal platinum, was without action on argon. The combined influence of oxygen and an alkali in the shape of fused potassium nitrate or red-hot peroxide of sodium was also without effect. Gold would, however, have resisted such action, but would have been attacked by the next agent tried, viz. persulphide of sodium and calcium. This mixture was exposed at a red-heat to a current of argon, again without result. Nascent chlorine, or chlorine at the moment of liberation, obtained from a mixture of nitric and hydrochloric acids, and from permanganate of potassium and hydrochloric acid, was without action. A mixture of argon with fluorine, the most active of all the elements, was exposed to a rain of electric sparks by M. Moissan, the distinguished chemist who first succeeded in preparing large quantities of fluorine in a pure state, without his observing any sign of chemical combination.

An attempt was also made to cause argon to combine with carbon by making an electric arc between two rods of carbon in an atmosphere of argon. It was at first believed that combination

had taken place, for expansion occurred, the final volume of gas being larger than the volume taken; but subsequent experiments have shown that the expansion was due to the formation of some oxide of carbon from the oxygen adhering to the carbon rods. On absorption of this oxide by the usual absorbent, a mixture of cuprous chloride and ammonia, the argon was recovered unchanged.

M. Berthelot, the celebrated French chemist, has stated that, on exposing argon mixed with benzene vapour to a rain of electric sparks, he has succeeded in causing argon to combine. Its volume certainly decreases, but whether this decrease is to be attributed to true combination or not is very doubtful. The benzene is converted into a resinous mass, which coats the walls of the tube; and it is not improbable that the argon may be dissolved, or even mechanically retained, in the resinous deposit. Helium, a gas closely resembling argon in properties, may be made to enter into a similar combination with metallic platinum, if combination it can be called; but the amount absorbed in both cases is extremely minute, and the gas is evolved unchanged on heating the resin or the metal.

Professor Ramsay has also made experiments on the action of a silent electric discharge upon a mixture of argon with the vapour of carbon tetrachloride; the latter decomposes, giving, not a resin, but crystals of hexachlorobenzene and free chlorine; but the volume of the argon was unchanged. It was all recovered without loss. Next, the rare elements titanium and uranium have been heated to redness in a current of argon with no alteration or absorption of the gas. And more recently, attempts have been made to cause argon to combine with the very electro-positive elements, rubidium and caesium, by volatilising them in an atmosphere of argon. Numerous experiments, in which electric sparks have been passed through argon cooled with liquid air between poles of every attainable element, have also been made, but without result. It was hoped that possibly at a very low temperature, $-185°$ C., a compound of argon might be caught before it had time to decompose, and retained in the solid state as an incrustation on the walls of the tube. Just as nitrogen and oxygen can be made to combine in quantity, when electric sparks are passed through the mixture, provided the product, nitrogen per-

oxide, is withdrawn by caustic alkali as it is made, as in Cavendish and Lord Rayleigh's experiments, so it may be withdrawn by freezing, if the vessel be immersed in liquid air. But with argon, all results were negative. In short, all likely agents have been tried as absorbents for argon, but in no case has any true chemical combination been obtained.

These failures to produce compounds make it impossible to gain any knowledge regarding the atomic weight of argon by a study of its compounds, for it forms none. It is, indeed, in the highest degree improbable that, had compounds existed, none should have been found in Nature. There are, it is true, a few elements, such as platinum and those resembling it, which always occur native, *i.e.* in the elementary state; but even they yield to the attack of the agents tried with argon. It cannot, of course, be stated with absolute certainty that no element can combine with argon; but it appears at least improbable that any compounds will be formed.

It was therefore necessary to adopt some other method in attempting to determine the atomic weight of argon,—some method dependent on its

physical rather than its chemical properties, for argon, unlike almost all other elements, appears to be devoid of chemical properties.

In order better to follow the train of reasoning based on experiment, it will be well to begin with an account of why the atomic weight of mercury is accepted as 200. The amount of mercury which combines with 16 parts by weight of oxygen is easily found by heating a weighed quantity of oxide of mercury, as Priestley and Scheele did, and weighing the residue of metal. The results of the most accurate experiments show that 200·36 grams of mercury combine with 16 grams of oxygen, and if the compound consists of one atom of each element, 200·36 must be the atomic weight of mercury. The first idea which naturally occurs is to find out the relative weight of mercury gas. This has been done, and it is found to have the ratio to that of oxygen of 100 to 16. Doubling these numbers will give the molecular weights, since a molecule of oxygen consists of two atoms, and must therefore possess twice the weight of one atom. We thus obtain the numbers 200 and 32 as the molecular weights of mercury and oxygen respectively. It might therefore be concluded that 200 is not the

true atomic weight of mercury, but 100, and that the compound of mercury with oxygen contains not one but two atoms of mercury, and should therefore be represented by the formula Hg_2O, not HgO. But on surveying all known compounds of mercury, there is not one which contains less than 200 parts by weight of mercury in a molecule of the compound, or in which the mercury cannot be conceived to replace 2 parts by weight of hydrogen. And on weighing as gases the compounds of mercury with other elements, where such compounds do not decompose on heating like the oxide, the amount of mercury present must be always taken as 200, in order to add up to the molecular weight found. For example, a compound of mercury with carbon and hydrogen, named mercury methide, has a density of 120 compared with oxygen taken as 16; hence the comparative weight of its molecule must be 240. Now it is known to contain two atoms of carbon and six atoms of hydrogen, the atomic weights of which are $24 + 6 = 30$. And deducting 30 from 240, 210 remains as an approximation to the atomic weight of mercury. It might, it is true, be the weight of two atoms of mercury, but if so it is singular that

no compound contains a smaller proportion; and there is another reason, which follows immediately, that leads us to believe that 200 is correctly taken as the true weight of an atom.

It was discovered by Dulong and Petit, early in the century, that the higher the atomic weight of an element the less heat is required to raise its temperature through a given number of degrees. This heat can be measured by dropping a fragment of the element, carefully weighed and heated to a known temperature, into a known weight of cold water, and ascertaining what rise of temperature the water undergoes, owing to the heat communicated to it by the element. These comparative amounts of heat, if water is chosen as the standard, are termed specific heats. And as the specific heats of elements have been found by experiment to be inversely as their atomic weights, the product of the specific heat of any element and its atomic weight will give a constant number. If the quantity of element weighed is one gram, and its rise of temperature one degree, the numerical value of this product is about 6·4.

Now the specific heat of mercury has been found to equal 0·032; that is to say, it requires

only a fraction of the value of 0·032 of a unit of heat to raise the temperature of say 1 gram of mercury through one degree, whereas the amount of heat necessary to raise 1 gram of water through one degree is represented by the number 1. Hence this number, 0·032, multiplied by the atomic weight of mercury, should yield the product 6·4; and it is seen at once that that number must be 200, for $200 \times 0{\cdot}032 = 6{\cdot}4$. This is an additional reason for believing that the atomic weight of mercury must be represented by the number 200.

We come next to a confirmatory piece of evidence which greatly strengthens the view that the atomic weight of mercury must be 200; but before entering into detail let us see what an atomic weight of 200 involves. The density of mercury gas is 100, and its molecular weight must be 200. But if its atomic weight is also 200, it follows of necessity that its molecule and its atom must be identical; that unlike oxygen and hydrogen, its molecule consists, not of two atoms, but of one single atom. There is nothing strange in this conclusion; there is no evident reason why single atoms should not act as molecules, or independent

particles, able to exist in a free state, uncombined with each other or with any other molecules.

The specific heat of a gas is measured in much the same manner as that of a solid. A known volume of the gas is caused to pass through a spiral tube, heated to a certain definite high temperature; it then enters a vessel containing a known weight of water, traverses a spiral tube immersed in the water, and parts with its heat to the water. Knowing, therefore, the weight of the gas and its initial temperature, and also the rise of temperature of the water, the specific heat of the gas can be compared with that required to raise an equal weight of water through one degree. But gases are found to possess two specific heats. If the volume of the gas is kept constant, so that the gas does not contract during its loss of heat, one number for its specific heat is obtained; while if it is allowed to alter its volume a higher figure represents its specific heat. It will be necessary to consider the cause of this difference, in order to understand what conclusions can be drawn respecting the molecular nature of argon from a determination of the ratio between its two specific heats—that at constant pressure and that at constant volume.

If a gas is allowed to expand into a vertical cylinder so as to drive up a piston loaded with a weight, it is said to "do work." The work is measured by the weight on the piston, and also by the height to which it is raised. Thus, if the weight is one pound, and the height one foot, one foot-pound of work is done; if the mass is one gram and the height one centimetre, one gram-centimetre of work is done. During this process the gas must expand; and if it were enclosed in some form of casing through which heat could not pass—we know of no such casing, but we can contrive casings through which heat passes very slowly—the temperature of the gas would fall during its expansion, and it would lose heat. For each loss of one heat-unit or calory—*i.e.* the amount of heat given off by 1 gram of water in cooling through 1° Centigrade—the gas would perform 42,380 gram-centimetres of work; it would raise a weight of nearly $4\frac{1}{4}$ kilograms, or about $9\frac{1}{3}$ lbs., through 1 centimetre, or nearly half an inch.

When a gas expands into the atmosphere it may be regarded as "raising the atmosphere" through a certain height, for the atmosphere possesses weight, equal on the average to 1033

grams on each square centimetre of the earth's surface, or between 15 and 16 lbs. on each square inch. Suppose a quantity of air, weighing 1 gram, to be enclosed in a long cylindrical tube of one square centimetre in section. At the usual pressure of the atmosphere on the earth's surface, and at 0° Centigrade, the volume of the air would be 773·3 cubic centimetres; and, as the sectional area of the tube is 1 square centimetre, the air would occupy 773·3 centimetres' length of the tube. If heat be given to this air, so that its temperature is raised from 0° to 1°, it will expand, as Gay-Lussac showed, by $\frac{1}{273}$rd of its volume. Now the product of 773·3 and $\frac{1}{273}$ is 2·83 centimetres; the level of the surface of the air will rise in the tube through that amount. In doing so it will perform the work of raising 1033 grams through 2·83 centimetres, or 2927 gram-centimetres. Careful measurements have shown that, in order to do this work, heat to the amount of 0·0692 calory must be given to the gas. But it has been found that to heat the air through one degree, without allowing it to expand, requires 0·1683 calory; that is, the same amount of heat which would raise a gram of air through one degree, its volume being kept constant, will raise a

gram of water through 0·1683°; or, in other words, the specific heat of air is 0·1683. But if allowed to expand, more heat is required—an additional 0·0692 calory must be given it; consequently its specific heat at constant pressure is greater; it is actually the sum of these two numbers, 0·1683 + 0·0692 = 0·2375.

We have thus—

Specific heat at constant pressure .	0·2375
„ „ „ volume .	0·1683
Ratio between these numbers: $\frac{0·2375}{0·1683}$ =	1·41

This ratio is termed the ratio between the specific heats of air, and such a ratio is represented usually by the letter γ.

But it is not necessary to determine both kinds of specific heat in order to arrive at a knowledge of the value of this ratio. One plan, adopted by Gay-Lussac and Désormes at the suggestion of Laplace,[1] is to actually measure the fall of temperature by allowing a known volume of gas, of which the weight can of course be deduced, to expand from a pressure somewhat higher than that of the atmosphere to atmospheric pressure. It is

[1] *Méchanique céleste*, vol. v. p. 123.

true that heat will rapidly flow in through the walls of the vessel; but by choosing a sufficiently large vessel, and surrounding its walls with badly-conducting material, the entry of heat will be so slow that it may, for practical purposes, be neglected. The number for this ratio, actually found by Gay-Lussac and Welters for air, was 1·376; but subsequent and more accurate experiments have given as a result 1·405, which is almost identical with that calculated above.

This method, however, can be employed only when an unlimited supply of gas is at disposal, for it entails the use of large vessels, and the compressed gas must be allowed to escape into the atmosphere, and is lost. There is, fortunately, another method by which the same results can be obtained, and which requires only a small amount of gas.

Sir Isaac Newton calculated that the velocity of sound in a gas was dependent on its pressure and on its density, in such a manner that

$$c = \sqrt{\frac{p}{d}},$$

where c stands for velocity (celerity), p for pressure, and d for density. When waves of sound are transmitted through air, the air is compressed

in parts and rarefied in parts, in such a manner that compression follows rarefaction very rapidly, that part which is compressed at one instant being rarefied at the next, compressed again at a third, and rarefied at a fourth, and so on. Laplace was the first to point out that during such rapid changes of pressure as occur while a sound-wave is passing, the pressure will not rise proportionally to the density, as would be the case if Boyle's law were followed; for on sudden rise of pressure the temperature of the compressed portion of the gas will be increased; and, correspondingly, on sudden fall of pressure, the wave of compression having passed, the temperature will fall. He showed that instead of two pressures being inversely proportional to their two volumes, under such circumstances, as they are according to Boyle's law, or

$$\frac{p}{p_1} = \frac{v_1}{v},$$

they must be inversely proportional to the volumes raised to a power, the numerical expression of which is the ratio of the specific heats of the two gases, γ, thus;

$$\frac{p}{p_1} = \left(\frac{v_1}{v}\right)^{\gamma};$$

or as

$$v_1 : v :: d : d_1, \quad c = \sqrt{\gamma \frac{p}{d}}, \text{ and } \gamma = \frac{c^2 d}{p}.$$

The ratio of the two specific heats can therefore be determined by finding the velocity of sound in the gas, and by noting at the same time its density and its pressure.

To determine the velocity of sound in a gas it is not necessary to adopt the plan which has been successfully carried out with air; that is, to make a sudden sound at one spot and to measure the interval of time which the sound takes to travel to another spot some miles distant. There is a simpler method, depending on the fact that the lengths of the waves of compression and rarefaction are proportional to the velocity of the sound. So that, knowing the velocity of sound in air, the velocity in any other gas may be found by determining the relative length of the sound-waves in air and in that gas.

The simple apparatus with which such determinations are made is due to the physicist Kundt. It consists of a glass tube, through one end of which a glass rod passes, so that half the rod is enclosed in the tube, while the other half projects outside it. In the experiments on argon, the rod was

sealed into the tube; in other cases it is better to attach it with indiarubber, or to cause the rod to pass through a cork. The open end of the tube is connected with a supply of the gas, so that, after

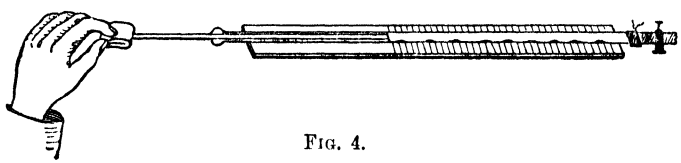


FIG. 4.

the tube has been pumped empty of air, the gas, in a pure and dry condition, can be admitted. Some light powder (and for this purpose lycopodium dust —the dried spores of a species of clubmoss—is best) is placed in the tube, and distributed uniformly throughout it, so that when the latter is in a horizontal position, a streak of the powder lies along it from end to end. The portion of rod outside the tube is rubbed with a rag wetted with alcohol, when it emits a shrill tone or squeak, due to longitudinal vibrations; the pitch of the tone depends, naturally, on the length of the rod, a long rod giving a deeper tone than a short one. The vibrations of the rod set the gas in the tube in motion, and the sound-waves are conveyed from end to end of the tube through the gas. As the tube is closed at the end through which the gas was admitted, these waves

echo back through it; and a great deal of care must be taken to make the echo strengthen the waves, so that the compressions produced by the back waves are coincident in position with the compressions produced by the forward waves travelling onwards from the rod. The gas, could we see it, would represent portions compressed and portions rarefied at regular intervals along the tube. Where the gas is compressed, it gathers the lycopodium dust together in small heaps, the position of each heap signifying a node of compression. Hence, comparing the distances between the nodes of compression for any gas and for air, we find the relative wave-lengths of sound in the two gases; and, as the velocity of sound in air has been accurately measured, we thus determine the velocity of sound-waves in the gas under experiment.

Such experiments were made by Kundt and by his co-worker Warburg on mercury gas, and they found that in this case the value of γ was 1·67; that is, in the equation

$$\gamma = \frac{c^2 d}{p}$$

the value of 1·67 had to be ascribed to γ, in order to

render it equal to the product of the square of the velocity into the density, divided by the pressure.

Similar experiments with argon led to the same result as Kundt and Warburg found for mercury gas; but the calculation becomes more simple if it is allowable to take for granted that the elasticity, or alteration of pressure produced by unit alteration of volume, is identical in the case of argon and air. The full equations are—

$$n\lambda_{\text{air}} = c_{\text{air}} = \sqrt{\gamma \frac{p}{d}(1 + \alpha t)_{\text{air}}},$$

and

$$n\lambda_{\text{argon}} = c_{\text{argon}} = \sqrt{\gamma \frac{p}{d}(1 + \alpha t)_{\text{argon}}},$$

where n is the number of vibrations per second, λ the wave-length of sound, and α the coefficient of the expansion of a gas for a rise of 1° in temperature, t, viz. 0·00367. Now if the expression $p(1 + \alpha t)$ can be shown to be identical for argon and for air, the value of γ for argon can be calculated by the very simple proportion—

$$\lambda^2 d_{\text{air}} : \lambda^2 d_{\text{argon}} :: 1{\cdot}408 : \gamma_{\text{argon}}.$$

This involved a measurement of the rate of rise of pressure of argon, p, per degree of rise of temperature, t; or, in other words, the verification

of Boyle's and Gay-Lussac's laws for argon; and this research was successfully carried out by Dr. Randall of the Johns Hopkins University of Baltimore, U.S.A., and Dr. Kuenen, of Leyden, working in Professor Ramsay's laboratory.[1] They made use of a constant volume thermometer, and measured the rise of pressure corresponding to a definite rise of temperature, comparing the gases argon and helium in this respect with air. The values found between 0° and 100° for air, argon, and helium were—

One volume in air, heated from 0° to 100°, raises pressure in the proportion of 1 to	1·3663
Argon	1·3668
Helium	1·3665

It may therefore be taken for certain that, within the limits of experimental error, the value of the expression $p\ (1+at)$ is identical for all three gases.

We see, then, that for argon, as for mercury gas, the value of γ, the ratio between the specific heats at constant volume and at constant pressure, is 1 to 1·66, whereas for air, hydrogen, oxygen, nitrogen, carbon monoxide, and nitric oxide, it is 1 to 1·4.

[1] *Proc. Roy. Soc.* vol. lix. p. 63.

We have now to consider what conclusion can be drawn from this difference.

On the usually accepted theory of the constitution of matter, it is held that for simplicity's sake atoms may be regarded as spheres, hard, elastic, smooth, and practically incompressible. True, we really know little or nothing regarding the properties of such particles, if particles there be; but in considering their behaviour it is necessary to make certain suppositions, and to see whether observed facts can be pictured to our minds in accordance with such postulates. If, from the known behaviour of large masses, conclusions can be drawn regarding small masses, and if these conclusions harmonise with what is found to be the behaviour of large numbers of small masses, acting at once, the justice of the supposition is, although not proved, at least rendered defensible as one mode of regarding natural phenomena.

Molecules, on this supposition, may consist of single atoms, or they may consist of pairs of such atoms, joined in some fashion like the bulged ends of a dumb-bell; or lastly, they may consist of greater numbers of atoms arranged in some different manner, the arrangements depending on their relative size

and attraction for each other. It must be clearly understood, however, that such mental pictures are not to be taken as actually representing the true constitution of matter, but merely as attempts to picture such forms as will allow of our drawing conclusions regarding their behaviour from known configurations of large masses.

The molecules of gases are imagined to be in a state of continual motion, up and down, backwards and forwards, and from side to side. It is true that they must also move in directions which cannot be described by any of these expressions, but such other directions may be conceived as partaking more or less of motions in the three directions specified; *i.e.* in being resolvable into these. To these motions have been applied the term "degrees of freedom." Such motions through space in which the molecule is transported from one position in space to another, form three of the possible six degrees of freedom which a molecule may possess, and the molecules are said to possess "energy of translation" in virtue of this motion. The other three consist in rotations in three planes at right angles to each other.

Now, it can be shown that the product of pres-

sure and volume of a gas, pv, is equal to $\frac{2}{3}$rds of the energy of translation of all molecules of the gas, or

$$pv = \tfrac{2}{3}\mathrm{NR},$$

where N stands for the number of molecules in unit volume, and R for their energy of translation; inasmuch as a pressure diminishing a volume is of the nature of work, or energy. For one gram of air at 0° C. and 76 cms. pressure (normal temperature and pressure), the pressure (p), measured in grams per square centimetre, is 1033, and the volume (v) is 773·3 cubic centimetres; and the raising of the temperature through 1°, as was shown before, requires 2927 gram-centimetres of work. Further, since the product of pressure into volume is equal to $\frac{2}{3}$rds of the energy due to motion, or the translational energy of the gas,

$$\mathrm{NR} = \tfrac{3}{2}pv = \tfrac{3}{2} \times 2927 = 4391 \text{ gram-centimetres.}$$

Dividing this number by 42,380, the mechanical equivalent of heat, or the number of gram-centimetres corresponding to one calory, the quotient is 0·1040 calory. If the energy of the air were due to the translational motion of its molecules, we should expect this number, 0·1040, to stand for the specific

heat of air at constant volume; but it has been found equal to 0·1683, as already shown.

We have seen that to convert specific heat at constant volume into specific heat at constant pressure 0·0692 must be added. Hence at constant pressure the specific heat of such an ideal gas should be 0·1732. And the relation between specific heat at constant volume and that at constant pressure should be 0·1040 to 0·1732, or 1 to $1\frac{2}{3}$. The conclusion to be drawn from these numbers for air, 0·1683 and 0·2375, which bear to each other the ratio of 1 : 1·41, is that air cannot be such an ideal gas; that in communicating heat to it some of that heat must be employed in performing some kind of work other than that of raising its temperature. What this work may possibly be we shall consider later.

But Kundt and Warburg found, from their experiments on the ratio between the specific heats of mercury gas, this ideal ratio, 1 to $1\frac{2}{3}$; and Professor Ramsay obtained the same ideal ratio, or one very close to it indeed, 1 to 1·659, for argon. He subsequently found this ideal ratio also to hold for helium (1 to 1·652), and also for three other gases of the same group, and it must therefore be con-

cluded that such gases possess only three degrees of freedom; or, in other words, their molecules, when heated, expend all the energy imparted to them in translational motion through space.

This is the consequence which we should infer from the supposition that such molecules are hard, smooth, elastic spheres. Were they each composed of two atoms, we should have to picture them as dumb-bell-like structures; and here we enter on a theoretical conception put forward by Professor Boltzmann, but which has not been accepted universally by physicists.

Boltzmann imagines that to the three "degrees of freedom" of a single-atom molecule there may be added, provided the molecule consists of two atoms, two other degrees of freedom, namely, freedom to rotate about two planes at right angles to each other. The knobs at the end of each imaginary dumb-bell may revolve round a central point in the handle joining them, and it is clear that they may revolve in one horizontal and in one vertical plane, as shown in Fig. 5. Such diatomic molecules are said to possess five "degrees of freedom." They will not, it is supposed, rotate round the line joining the centres of the spheres,

because, as before said, the atoms are pictured as perfectly smooth. But if the molecules are triatomic—as, for example, CO_2 or N_2O—they will have six degrees of freedom, for with the addition of an additional atom they have an additional plane of rotation (see Fig. 6). Boltzmann has attempted

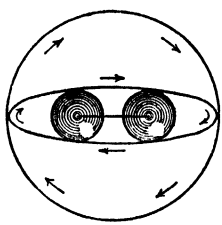


FIG. 5.

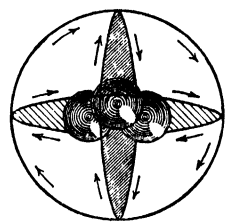


FIG. 6.

to show that the ratio of the specific heats of diatomic molecules should be as 1 to 1·4. In actual fact it approximates to that number. For the commoner gases it is—

Oxygen	1·402
Nitrogen	1·411
Hydrogen	1·412
Carbon monoxide	1·418

In all cases the numbers are too large, and this is a serious difficulty, because any tendency to rotate round the central line would cause the values to be less, not greater than 1·4. For triatomic molecules the calculated value of γ is $1\frac{1}{3}$, but in actual

fact the ratio in the case of triatomic molecules, such as H_2O, CO_2, N_2O, etc., is always less than $1\frac{1}{3}$. These speculations stand on a basis very different from the first conception, namely, that all heat must be employed in communicating translational motion to molecules of mercury gas, argon, neon, krypton, xenon, and helium, and it appears that the atoms of these six elements must necessarily be regarded as having the properties of smooth elastic spheres. The atoms and the molecules must in their several cases be identical. And, inasmuch as the chemical evidence regarding mercury leads to the same conclusion, it appears legitimate to infer that argon and its congeners must also be monatomic elements.

CHAPTER VII

THE POSITION OF ARGON AMONG THE ELEMENTS

FROM what has been said in the preceding chapter there can be no doubt that the molecular weight of argon is 39·88. We have now to consider what this conclusion involves. Taken in conjunction with the fact that the ratio between its specific heat at constant volume and that at constant pressure is $1\frac{2}{3}$, it follows that energy imparted to it is employed solely in communicating translational motion to its molecules. In the case of mercury gas such behaviour is taken as evidence that the conclusion following from the formulae of its compounds, from the density of its compounds in the gaseous state, and from its own vapour-density, as well as from its specific heat in the liquid state, namely, that its molecules are monatomic, is correct. Is it legitimate to conclude that because

argon in the gaseous state has the same ratio of specific heats, therefore it also is a monatomic gas?

The conclusion will depend on our conception of an atom and a molecule, and in the present state of our ignorance regarding these abstract entities no positive answer can be given. It appears certain that, on raising the temperature of argon, very little, if any, energy is absorbed in imparting vibrational motion to its molecules; and our choice lies between our ability or inability to conceive of a molecule so constituted as to be incapable of internal motion. If there be any truth underlying Professor Boltzmann's conception, a molecule of argon cannot consist of any complex structure of atoms, otherwise it would possess more than three degrees of freedom, and heat would be utilised in causing rotational motions. As we know for a fact that the ratio between the specific heats of gases diminishes with the increasing complexity of their molecules, perhaps the safest conclusion is the one adopted by the discoverers of argon, that the balance of evidence drawn from *this* source is in favour of its monatomic nature.

But this hypothesis raises difficulties which are

not lightly to be met. These difficulties arise from a consideration of the position of argon when it is classified with other elements.

After a preliminary attempt by de Chancourtois, which met with no attention, Mr. John Newlands pointed out in 1863, in a letter to the *Chemical News*, that if the elements be arranged in the order of their atomic weights in a tabular form, they fall naturally into such groups that elements similar to each other in chemical behaviour occur in the same columns. This idea was elaborated further in 1869 by Professor Mendeléeff of St. Petersburg and by the late Professor Lothar Meyer, and the table may be made to assume the subjoined form (the

THE ELEMENTS ARRANGED IN

Lithium . 7·0	Beryllium . 9·1	Boron . . 11·0	Carbon . . 12·0
Sodium . . 23·0	Magnesium 24·4	Aluminium 27·1	Silicon . . 28·4
Potassium . 39·1	Calcium . 40·0	Scandium . 44·1	Titanium
Rubidium . 85·4	Strontium . 87·6	Yttrium . 89·0	Zirconium
Caesium 133·0	Barium . . 137·4	Lanthanum 138·0	Cerium .
? . . . . 170·0	? . . . . 172·0	Ytterbium 173·0	? . . .
? . . . . 221·0	Radium . 225·0	? . . . . 230·0	Thorium

atomic weights are given with only approximate accuracy):—

The elements in the first column all agree in that they are white soft substances, with metallic lustre, but tarnish rapidly in air, owing to the action of water-vapour; they are all violently attacked by water, and they are without exception monads,—that is, they replace hydrogen in its compounds atom for atom. The elements in column two are also all white metals, attacked by water with more or less ease; but in their case one atom replaces two atoms of hydrogen, whence they are called dyads, or bivalent elements (worth two). And

THE PERIODIC SYSTEM.

		Hydrogen . 1·01	Helium . 4·0
Nitrogen . 14·0	Oxygen . 16·0	Fluorine . 19·0	Neon . . 20·0
Phosphorus 31·0	Sulphur . 32·1	Chlorine . 35·5	Argon . . 39·9
Arsenic . 75·0	Selenium . 79·1	Bromine . 80·0	Krypton . 81·8
Antimony . 120·0	Tellurium . 127·6	Iodine . . 126·9	Xenon . . 128·0
Erbium . 166·0	? . . . . 167·0	? . . . . 169·0	?
Bismuth . 208·5	? . . . . 214·0	? . . . . 219·0	Niton . . 222·4 [1]

[1] See p. 283.

so on with the other columns. All elements in vertical columns exhibit chemical similarity, and, indeed, are often strikingly like in properties.

The subdivision, produced by folding the loose slip, is intended to show that the elements represented on it have a double set of resemblances. But there are various anomalous and inexplicable phenomena still attached to this arrangement of elements. For example, copper, although it replaces one atom of hydrogen in some of its compounds, and is thus a monad, forms more numerous and more stable compounds in acting as a dyad and replacing two atoms of hydrogen. Gold, which belongs to the same column, is at once univalent and tervalent; mercury, both univalent and bivalent; thallium, univalent and tervalent; tin and lead, bivalent and quadrivalent, and so on. It is as if some elements had a tendency to enter a column not their own.

Again, on comparing the atomic weights of the elements, it is seen that the differences are far from being regular. As a rule, the difference in the vertical columns between any single element and the one following it is approximately 16, or some multiple of 16. Thus we have lithium, sodium,

and potassium; beryllium, magnesium, and calcium; boron, aluminium, and scandium; carbon and silicon; oxygen and sulphur; fluorine and chlorine—all with a difference of 16 approximately. But here we come to a break: silicon and titanium, phosphorus and vanadium, sulphur and chromium, chlorine and manganese, each show a difference of about 20.

Passing on, between the atomic weights of potassium, rubidium. and caesium there is a difference of about 16×3; a similar difference between calcium, strontium, and barium; between scandium and yttrium; between titanium, zirconium, and cerium, and so on; but with wider and wider divergence from the supposed constant, $48 = 16 \times 3$. In short, we have a seeming regularity, but only a very approximate one—a regularity, in fact, in which a vivid imagination must play a conspicuous part in order to detect it.

Now, up to the present, no reason has been suggested to account for the divergence from this irregular regularity, which a little expenditure of time will enable any one to trace through all these numbers. But one thing has been remarked: there is the same seeming regularity between

certain physical properties of elements and their compounds: their specific volumes, their melting-points, their refractive indices, and other properties vary from member to member of the same column in a manner bearing more or less similarity to the periodic variation of the atomic weights.

It happens that among compounds of carbon we are acquainted with series of compounds which, in variation of molecular weights and gradation of properties, bear a striking resemblance to the elements thus arranged. Thus we have the series :—

CH_4	Methane	16
C_2H_6	Ethane	30
C_3H_8	Propane	44
C_4H_{10}	Butane	58
C_5H_{12}	Pentane	72

and a host of others up to a compound of the formula $C_{30}H_{62}$; in each case there is a constant difference of 14 between the molecular weight of any one hydrocarbon and that immediately preceding or succeeding it in the column. Such a series is termed a homologous series. The analogy is very tempting; to suppose that a similar constant difference should exist in the relations of the atomic weights of the elements, and that they too

are undecomposable compounds of two unknown elements, is an attractive hypothesis, but one for which there exists no proof; indeed, it is rendered improbable by the irregularities just pointed out.

But there is one noticeable feature in the periodic arrangement of the elements. It is, that although the differences are irregular (*e.g.* between B = 11 and C = 12 the difference is 1, while between O = 16 and F = 19 the difference is 3), yet there are two marked displacements in the *order* of arrangement of the elements, inasmuch as two elements have atomic weights *lower* than those preceding them in the horizontal line. It is tellurium and iodine, and nickel and cobalt which are thus misplaced; and the same is evidently the case with potassium and argon. With an atomic weight of 39·88, the natural position of argon would lie between potassium and calcium; but there is no room for it. And for this reason considerable doubt has been thrown on the validity of the conclusion to be drawn from the found ratio of its specific heats, $1\frac{2}{3}$, viz. that its molecule and its atom are identical. If it were a diatomic gas, like chlorine or hydrogen, its atomic weight

would be 19·94, and it would find a fitting position after fluorine and before sodium. And the difference between its atomic weight and that of helium, to which the atomic weight 2·0 would for the same reasons then attach, would be 17·94, one not incomparable with 16. But, as before remarked, it is difficult, if not altogether impossible, to conceive of a diatomic structure to which all energy imparted in the form of heat should result in translational motion, and as a matter of fact none such is known.

There are two methods of escape from this dilemma. If the gases termed argon and helium are not single elements, but mixtures of monatomic elements, then what has been termed their atomic weights will represent the mean of the atomic weights of two or more elements, taken in the proportion in which they occur. For example, supposing that argon is a mixture of an element of atomic weight 37 with one of atomic weight 82, the found atomic weight, nearly 40, would imply a mixture of 93·3 per cent of the lighter, with 6·7 per cent of the heavier element. We must therefore carefully examine all evidence for or against the supposition that argon is a mixture of elements.

It is well known that elements with high atomic weights have, as a rule, higher boiling-points than those with low atomic weights in the same columns. Perhaps the most striking case is that of the elements fluorine, chlorine, bromine, and iodine. Whereas fluorine has only lately been liquefied (chiefly owing to difficulties of manipulation, due to its extraordinarily energetic action on almost every element and compound), and boils at about $-185°$, chlorine boils at $-34°$, bromine at 59°, and iodine at 184°. And if a mixture of chlorine and bromine gases be cooled, the bromine, if present in sufficient amount, will condense first, in a fairly pure state, little chlorine condensing with it. But in a mixture containing only 7 per cent of bromine with 93 per cent of chlorine (analagous to a mixture of the two supposed constituents of the argon mixture) the pressure of the bromine gas in the mixture would be only $\frac{7}{100}$ths of the normal pressure, or 53·2 millimetres. At this pressure the boiling-point of bromine is about $-5°$, so that, on cooling to that temperature, bromine would begin to show signs of liquefaction. This is, however, still nearly 30° above the boiling-point of chlorine; and there

would therefore be no difficulty whatever in detecting such a percentage of bromine in a mixture of chlorine and bromine gases on cooling the mixture to a moderately low temperature.[1]

Argon was first liquefied in 1895. A sample of pure argon was sent by Professor Ramsay to Professor Olszewski of Cracow, well known for his accurate researches at low temperatures; and he found the boiling-point of argon at atmospheric pressure to be $-186{\cdot}9°$, and its melting-point to be $-189{\cdot}6°$.[2] There was no appearance of liquid before the boiling-point was reached, nor was there any alteration of temperature as the argon boiled away, and these are signs of a single substance, not of a mixture; moreover, the melting-point was a definite one; and here again, mixtures never melt suddenly, but always show signs of softening before melting. So far as this evidence goes, therefore, it points to the conclusion that argon is not a mixture of elements.

Other evidence may be sought for in the spectrum of argon, which has been carefully ex-

[1] These considerations would hold on the assumption that no combination takes place between chlorine and bromine.

[2] Later determinations by Ramsay and Travers have altered these numbers to $-186{\cdot}1°$ and $-187{\cdot}9°$ (*Phil. Trans.* 1901, A, p. 41).

amined by Sir William Crookes and others. It consists of a great number of lines, extending all through the spectrum, from far down in the red to far beyond the visible violet; the invisible lines were examined by the aid of photography, for ultra-violet light, although invisible to the eye, impresses a photographic plate. The most striking feature of this spectrum is the change which can be produced in it by altering the intensity of the electric discharge which is passed through the tube containing argon at a low pressure. By interposing a Leyden jar between the secondary terminals of the induction-coil from which sparks are taken through the gas, the colour of the light in the tube changes from a brilliant red to an equally brilliant blue. A large number of lines in the red spectrum disappear, on interposing the jar, while many lines in the blue-green, blue, and violet part of the spectrum, invisible before, shine out with great brilliancy. There is no other gas in which a similar alteration of intensity of discharge produces such a marked difference, although in many gases, supposed to be simple substances, similar changes may be produced. So far as we know at present, however, such a change cannot be definitely

ascribed to the presence of a mixture of two elements, although it is in itself a very remarkable phenomenon.

On the other hand, Professors Runge and Paschen, in a paper communicated to the Royal Academy of Science of Berlin in July 1895, adduced reasons for concluding that helium, the gas from cleveite, is a mixture; it appears to show lines belonging to two spectra, each series of lines exhibiting certain regularities. But this is also the case with oxygen, which is not considered to be a mixture of gases.

One method of separating the constituents of a mixture is by taking advantage of their different solubilities in water, or in some other appropriate solvent. And as argon was found to have the solubility of 4 volumes in 100 of water, while helium is more sparingly soluble,—only 1·4 volume per 100,—it is not unreasonable to suppose that, if argon consisted of a mixture of elements in argon, one should be more soluble than another; but Lord Rayleigh has made experiments which render it very improbable that any separation of its constituents can be thus effected. Wishing to ascertain if there were any helium in the air, he

shook up atmospheric argon with water, until a very small fraction remained undissolved. The spectrum of this small residue was identical with that of the original argon, from which it would appear that this method, at least, did not effect any separation.

The evidence was therefore at first distinctly against the supposition that argon is a mixture of two or more elements.

There is, however, another possible method of accounting for the high atomic weight of argon, which, if it could be reduced by a few units, would fall into its place after chlorine and before potassium. It is that argon consists of a mixture of many monatomic, with comparatively few diatomic, molecules. If there were only about 500 molecules of diatomic argon in every 10,000 molecules of the gas, its density, supposing it to consist entirely of monatomic molecules, would be 19, and its atomic and molecular weights 38—a number which would fit between the atomic weight of chlorine, 35·5, and that of potassium, 39·1. Several instances of this kind are known. Chlorine itself, when heated to high temperatures, changes from diatomic to monatomic molecules, and the

density decreases with the change. For example, at 1000° the found density of chlorine is 27, implying a molecular weight of 54; now 54 is neither the weight of a monatomic molecule of chlorine, viz. 35·5, nor of a diatomic molecule, which is 71; but it corresponds to that of a mixture of monatomic and diatomic molecules. Here fall of temperature causes combination of monatomic molecules with each other to form diatomic molecules; and rise of temperature increases the number of monatomic molecules, at the expense of the diatomic molecules. Is there no sign of similar behaviour with argon?

It has already been mentioned that the rise of pressure of argon with rise of temperature has been carefully measured by Drs. Randal and Kuenen, and that it is quite normal; no sign of splitting has been observed. But the range of temperature was not great (it was only from 0° to 280°), and it is quite possible that the change, if there was one, was so minute as to have escaped detection. Again, a more delicate method of detecting such a change is in the measurement of the ratio of the specific heats. The most trustworthy number obtained was 1·659 for the ratio, instead of 1·667, the theoretical

figure. A mixture of 5 per cent of diatomic molecules should have reduced this ratio to 1·648. Here the evidence is, however, inconclusive. But on the whole, the presumption is against the hypothesis that argon is a mixture of monatomic with diatomic molecules.

CHAPTER VIII

THE OTHER INACTIVE GASES: HELIUM, NEON, KRYPTON, AND XENON

In 1868 an eclipse of the sun was visible in India. The spectroscope was then for the first time employed to examine the chromosphere, or coloured atmosphere round the sun; and a brilliant yellow line was observed, and supposed to be the "D" lines of sodium. The well-known French astronomer, M. Janssen, however, noted its non-coincidence with those lines; and it was supposed to be due to hydrogen, or to water-vapour; but all attempts to reproduce the line in the laboratory failed. Messrs. Lockyer and Frankland, who investigated the chromosphere spectrum, found that the line which was distinguished as "D_3" could not be ascribed to the spectrum of any known element; and as a matter of convenient reference, Frankland suggested

the provisional name of "helium," a name derived from the Greek word for the sun, ἥλιος.

No certain proof that this supposed element existed on the earth was obtained, although a specimen of gas from a mud-volcano near Vesuvius was said to have exhibited the line.

In seeking for compounds of argon, Professor Ramsay was reminded by Professor Miers that Dr. Hillebrand, of the U.S. Geological Survey, had obtained relatively considerable volumes of gas, which was supposed to be nitrogen, by heating a rare mineral named cleveite, after Cleve, the Professor of Chemistry at Upsala. Of course, if a substance were found, from which argon could be obtained on heating, it would give a clue to the elements with which an attempt to cause argon to combine might be successful. A sample of cleveite was procured, and heated with sulphuric acid; and a gas was collected, which, after purification by sparking with oxygen in presence of caustic soda, was examined with the spectroscope. The chief characteristic of the spectrum was a brilliant yellow line, much overpowering the others in intensity; and the first idea was that it must have been due to the discharge making the soda in the glass of

the vacuum-tube incandescent. The position of the line was not coincident, however, with that of the sodium lines thrown into the field of vision for the purpose of comparison; the preconceived idea that the line was due to sodium was hard to eradicate; and the spectroscope was dismantled, the prisms readjusted, and the spectra again compared. This time there could be no doubt; the lines were not coincident. Reference to a table of the solar spectrum soon made the matter clear, and terrestrial helium was discovered.[1] Like argon, it is a gas, with no pronounced tendency towards combination; it is, like argon, nearly insoluble in water; while 100 volumes of water at atmospheric temperature (15° C.) dissolve 4·1 volumes of argon, they dissolve only 1·4 volumes of helium; for the solubility of helium is nearly the same as that of nitrogen, the least soluble of gases. Attempts made to induce helium to enter into combination failed, like those made with argon; and it is therefore reasonable to place it in the same class of elements as argon, especially as the ratio between its specific heats shows it to resemble argon in

[1] It was somewhat later, but independently, rediscovered by Langlet, in Cleve's laboratory.

being a monatomic gas. Its density is nearly 2·0 —that of oxygen being taken at 16·0; next to hydrogen, the density of which is 1·007, it is the lightest gas known.

It was subsequently found that many minerals, chiefly those which contain the rare element uranium (the element of highest atomic weight known), contain helium, and give it off when heated; among these are bröggerite, fergusonite (which turns white-hot during the evolution of helium), and monazite, a mineral now mined in large quantity in Brazil, and used as a source of the thoria of which incandescent gas-mantles are made. The curious behaviour of fergusonite deserves explanation.

It is familiar to all that a burning object, such as coals, or a candle, gives out heat. This is generally the case when chemical combination takes place. Even when chlorine combines with elements such as iron or phosphorus, heat is evolved. Now, there are compounds which are formed not with evolution of heat, but with absorption. And such substances give off heat when they decompose; indeed they usually decompose with explosion. Gun-cotton and the newer forms

of smokeless powders are instances in point; another is acetylene gas, which owes its high luminosity to the great heat given off when it decomposes; this heat adds itself to that evolved by the burning of the carbon and hydrogen of which it consists, and the particles of carbon which separate in the flame are raised to brighter incandescence than if they owed their temperature to the heat due to the burning of the carbon and hydrogen alone, as is the case with ordinary coal-gas. Compounds which behave thus are termed "endothermic," and fergusonite is an endothermic compound. Now it is found that endothermic compounds are not readily produced from their elements; for chemical combination takes place generally only when heat is evolved during combination—when the reaction is "exothermic." But it is possible to produce endothermic compounds directly; that can be achieved if energy is given them during combination. For example, nitrogen does not burn in oxygen; if it did, our atmosphere would be inflammable. But if an electric discharge be passed through a mixture of nitrogen and oxygen, combination does occur: that is one of the methods employed for removing nitrogen

from a mixture of that gas with argon or helium. Now, the fact that fergusonite decomposes with evolution of heat implies that the helium which it evolves when heated must have entered into combination with the constituents of the mineral with absorption of heat, or that some rearrangement of molecules takes place on heating.

That helium is a pretty abundant constituent of the earth is proved by its being contained in many mineral waters. The springs at Cauterets, in the Pyrenees, evolve it in fair quantity; and, nearer home, the mineral waters of Bath are rich in it. It doubtless escapes from the soil in many places; and, as will hereafter appear, it is a constituent of our atmosphere. Like argon, helium has neither taste nor smell; indeed, its inactive character would have rendered this probable, even without direct evidence. It also resembles argon in being a monatomic gas; for the ratio of its specific heats is 1 to $1\frac{2}{3}$, as explained on p. 203; and with such a ratio, the atom and the molecule are identical.

The spectrum of helium is a very brilliant one. Besides the particularly brilliant yellow line, by means of which it was originally recognised as the

sun's chromosphere and in many of the fixed stars, it exhibits two red lines, of which one is fairly brilliant; also, besides other fainter ones, a green line, a peacock-blue line, and a violet line. It was at first conjectured that what was named helium was a mixture of two gases, and, indeed, the name "parhelium" or "asterium" was given to the supposed partner; but this supposition was found to be erroneous, for the arguments in its favour (namely, that the various lines in its spectrum could be arranged in two series, the lines in each series exhibiting numerical relations to each other, if arranged according to the frequency of vibration of the light-waves) were shown to apply equally to oxygen; and it is not believed that oxygen is a compound gas. Professors Kayser and Runge, who made this suggestion, afterwards disproved it; and another suggested argument, which was that diffusing the gas through porous pipe-clay separated a light from a heavy portion, the one giving a more brilliant green, and the other a more brilliant yellow line, also turned out to be inaccurate; as a matter of fact, if the pressure in a vacuum-tube containing helium is reduced, the yellow line is relatively weakened in intensity,

while the green line grows stronger and more luminous. Careful experiments, by which helium was fractionally diffused many hundred times, also proved the homogeneity of helium. The spectrum of helium, too, like that of argon, is altered by the interposition of a jar and a spark-gap; but the change is by no means so striking as with argon.

After the discovery of helium, it appeared certain that other gases remained to be discovered, similar to those which had already been isolated. The reasons for this belief were stated by Professor Ramsay in an address given to the Chemical Section of the British Association, at its meeting at Toronto in 1897. As it may appear wonderful that the existence of new and undiscovered elements can be thus prophesied, an attempt will be made to make clear the arguments in favour of the forecast.

Not long after John Dalton, in 1803, had reintroduced the old Greek hypothesis of the atomic constitution of matter, and had made his somewhat unsuccessful attempt to determine the relative weights of the atoms of the elements, speculation began as to some possible relationship between the weights of these atoms. These speculations finally,

as has already been remarked, culminated in the periodic table, reproduced on p. 220. The last column of that table contains the elements helium and argon. The elements of preceding groups show approximately regular differences between their atomic weights; thus, for example, the difference between the atomic weights of nitrogen, 14, and phosphorus, 31, is 17; that between oxygen, 16, and sulphur, 32, is 16; hydrogen and fluorine show a difference of 18, and fluorine and chlorine of 16·5; and lithium, sodium, and potassium have differences of 16 and 16·1 respectively. It was highly probable, therefore, that an element should exist, having an atomic weight about 16 units higher than that of neon, and about 17 or 18 units lower than that of argon. It should have a brilliant spectrum; it should be a gas with a boiling-point when liquefied higher than that of helium, yet lower than that of argon; like them it should be monatomic, and it should display inactivity in resisting combination with other elements. Similar arguments would lead to the conclusion that other two elements of higher atomic weights should also be found—one with an atomic weight somewhat higher than that of

bromine, 80, but somewhat lower than that of rubidium, 85·4; and that a third should succeed iodine, with atomic weight greater than 127, but less than 133. As no elements are known in the chlorine or sodium column with still higher atomic weights, it was imagined that it would be unlikely that any element with a higher atomic weight than, say, 130 would be discovered belonging to the helium column.

But where were these elements to be sought? A very large number of minerals were heated in a vacuum, and the gases they gave off extracted by pumping; some few yielded no gas whatever; but the majority evolved carbon monoxide and dioxide, and hydrogen, in small quantity, while a considerable number evolved helium, and one, a mineral named malacone, containing zirconium, evolved both helium and argon. The spectra of the inactive gases were carefully examined, but showed no unknown lines. The helium from mineral waters, too, was introduced into vacuum-tubes, but its spectrum likewise failed to show the presence of any new constituent. The diffusion of helium, which might have been expected to separate a light from a heavy constituent of the

mixture, was also unsuccessful in revealing any impurity, except a trace of argon; the only clue, and that not a very hopeful one, was that argon, when systematically diffused, gave two portions—one slightly heavier, the other slightly lighter, than the original gas. But the difference was extremely minute, and was probably to have been accounted for by experimental error.

However, as all other possible sources had been examined, it appeared to be the only one left untried; and after an examination of sea-water, which proved fruitless, a large quantity of argon was separated from the atmosphere, with the view of its liquefaction and distillation—a process which would separate small quantities of light and heavy constituents more perfectly than any other method.

The boiling-point of argon, at atmospheric pressure, is 86·9° absolute, or −186·1° centigrade; hence, in order to liquefy it, a plentiful supply of liquid air was necessary. Dr. William Hampson, who had devised an apparatus which yields liquid air easily and in large quantity, kindly placed a litre at the disposal of Professor Ramsay and his coadjutor Dr. Travers. This liquid air was not used, however, for the liquefaction of argon, but

experiments were made with it, to obtain practice in manipulation, before risking the fifteen litres of argon which were ready for liquefaction. On the chance that the "dregs" or last residues of this air might contain some one of the supposed higher-boiling constituents of the atmosphere, the final portions, after almost all had boiled away, were collected; the sample consisted largely of oxygen, because, as nitrogen has a lower boiling-point than oxygen, and is more volatile, the spontaneous evaporation of the air had deprived it of most of this constituent. On removal of the oxygen by means of red-hot metallic copper, and of nitrogen by magnesium, the inert residue was examined spectroscopically. While it showed the well-known argon spectrum, two brilliant lines were also visible—one in the yellow and the other in the green part of the spectrum. The density of the sample was 22·47; hence it was considerably higher than that of argon, which, it will be remembered, is approximately 20. The ratio of the specific heats of the sample was found to be normal, viz. 1·66; hence this gas, like helium and argon, is also monatomic. This gas was discovered on May 30, 1898, and was named

"krypton," or *hidden*—a name which had previously been considered as a possible one for argon.

The fifteen litres of argon were next liquefied, by causing it to enter a bulb, surrounded by liquid air, boiling under reduced pressure. The liquid argon, which occupied about 11 cubic centimetres, was seen to be a colourless, mobile liquid; it could easily be frozen, by a slight reduction of temperature; and it then formed a white, ice-like solid.

The first portions of the gas which boiled off this liquid were collected separately, and examined with a spectroscope; a complicated and extremely beautiful spectrum was observed, consisting of a great number of red, orange, and yellow lines. The density of this sample was 14·67. These densities, of course, must not be taken as final numbers, but merely as indicating that the argon obtained by the evaporation of air contained a heavier companion, and that the gas distilled from liquid argon contained a lighter constituent, than argon itself. To this constituent the name "neon" or *new* was given.

The recognition of the presence of new gases in the atmosphere, and their separation on a scale sufficiently large for their study, are two very

different things. While the gases were discovered in June 1898, it was not until October 1900 that the investigation of their properties was completed.

It was first necessary to prepare them in considerable quantity. And two quite distinct operations were required to separate the lighter constituent, neon, from air, and the heavier constituent, krypton. Although both processes were immediately commenced, as soon as a suitable machine for producing liquid air had been procured from the Brin Oxygen Company, through Dr. Hampson, it will conduce to clearness to describe the operations separately.

The preparation of neon was carried out by liquefying air, compressed to about 1-150th of its volume; this is achieved by allowing the compressed air to pass downwards through a tightly-wound copper coil, enclosed in a thin metal box, which box is itself surrounded by a packing of wool, contained in an exterior case. The air escapes at the bottom of the coil. Air, thus compressed, approximates to a liquid, in so far as its molecules or ultimate particles are so close together that they attract one another. Now, in order to separate particles of water from each

other, two methods are possible: either heat may be applied, when the water changes to steam, a body occupying a much larger volume than the same weight of water; or if pressure is removed from the surface of the water by means of a pump, the particles at the surface fly off, while the temperature of the water is lowered. With compressed air, allowed to expand through a valve, a somewhat similar phenomenon takes place. The air-particles, separating suddenly from each other, absorb heat, for the attraction between the particles is overcome, and to effect this, heat is necessary; as, however, little external heat is allowed to enter, the heat is derived from the air itself, during the act of expansion; and the air is cooled. The cold air passes upwards over the copper coils through which the compressed air is passing downwards; and the copper pipe is cooled. The effect naturally is that the air passing downwards is progressively cooled to a lower and lower temperature; and finally, its temperature is so greatly reduced that it issues in the state of liquid. The process is a wonderfully rapid one; in less than ten minutes after the compression-pump starts, liquid air begins to escape through the valve.

Of the two main constituents of air, nitrogen has the lower boiling-point, −194·4°, for oxygen boils at −183°. Hence, the liquefied portion of air, which probably does not exceed one-twentieth of what passes through the coils, contains a relatively larger proportion of oxygen than of nitrogen, while the escaping portion consists more largely of nitrogen. The connecting pipes were so arranged that the issuing gas returned to the compressor, to be again forced into the coils, and partly liquefied. In this manner, the heavier constituents of the air were condensed out, and the lighter constituents, on compressing the remainder at a pressure of about two atmospheres into a bulb immersed in liquid air made to boil at a low temperature (about −205°), by being connected with a vacuum-pump, were liquefied. This liquefied portion, of course, contained the lower-boiling constituents. Air was then blown through the liquefied portion, causing it to evaporate; and about one-third was collected in a large gas-holder. The operation was repeated until a considerable quantity had been obtained. It was then freed from nitrogen by help of magnesium dust and lime; and the residue, consisting chiefly of argon,

but containing also neon, was liquefied and fractionated by distillation.

And next began a tedious and troublesome process of repeated fractionation; the gas was liquefied, distilled, and collected in successive fractions in a methodical manner, until the heavier and higher boiling argon had been separated from lighter and lower boiling constituents. Finally, a quantity of gas free from argon was obtained, which would not liquefy, however much the temperature of the liquid air which was used as a cooling agent was lowered. This gas showed the spectrum previously described as that of neon; but in addition, it showed the well-known lines of helium. The spectrum of helium had previously been recognised in that of atmospheric argon by Drs. Kayser and Friedländer, but it was not believed to contain helium in such considerable amount. The helium appeared to form about one-third of the total volume of gas; the remaining two-thirds were neon. As neither of these gases can be liquefied at the temperature of liquid air, even when its temperature is lowered as far as possible by boiling it in a vacuum, it was impracticable to separate them by distillation.

Many months were spent in attempting to effect a separation by diffusion; partial success was attained, but perfect separation was impossible. Dissolving the gases in liquid oxygen, and fractionation from the solvent were also attempted, but without success. Finally, an apparatus somewhat similar in design to Dr. Hampson's air-liquefying apparatus was constructed by Dr. Travers, in which hydrogen was liquefied, and at the very low temperature of boiling hydrogen, 20·5° absolute, the neon froze solid, while the helium remained gaseous; the helium was removed by help of a pump, and the solid neon was allowed to warm up, gasified, and collected separately. It may be mentioned incidentally that, on removing the liquid hydrogen from the bulb which contained solid neon, the atmospheric air froze on it, and encrusted it with a snowball of solid air, which melted, dropped, and evaporated.

The krypton was prepared in a different manner. It was left in the residue from about thirty litres of liquid air, which had been used for various operations. Instead of allowing the last fractions of this air to boil away and mix with the atmosphere, they were collected sepa-

rately and deprived of oxygen, which formed the main bulk, and also of nitrogen, in the usual manner. The residue consisted mainly of argon;

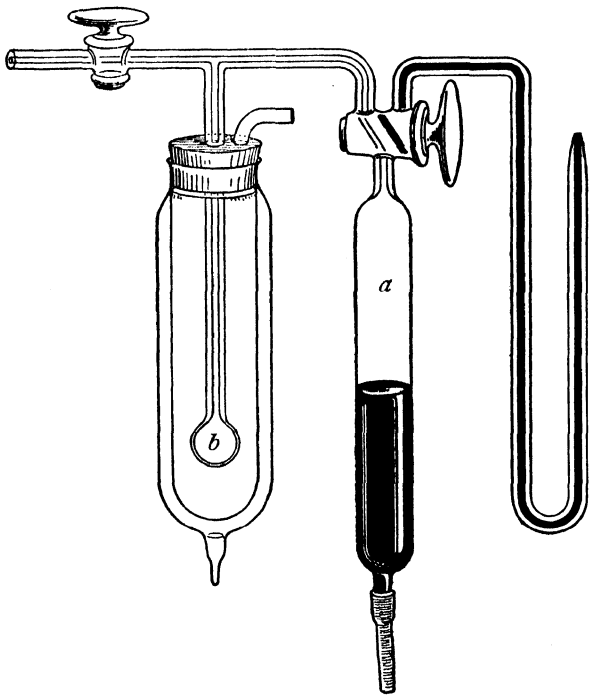


FIG. 7.

and the lighter gases, helium and neon, had already evaporated. This argon, which amounted in bulk to several litres, was liquefied, and fractionated in an apparatus of which an idea may be gained from the annexed figure. The bulb (*b*)

was cooled by being immersed in liquid air; the argon was introduced from a reservoir (a) through the stopcock, under some pressure, and liquefied; and the first portions were allowed to boil back into the gas-holder. The remainder was again liquefied, and separated into six fractions.

It was found, on inspecting the spectrum of the lowest boiling of these fractions, that little krypton was present, and that the gas consisted mainly of argon. It is fortunate that the brilliant yellow and green lines of krypton render its recognition especially easy; hence we had no hesitation in rejecting gas in the spectrum of which these lines were not visible; but the intensity of the spectrum misled us at first in estimating the relative quantity of krypton in the gaseous mixture.

The remaining fractions were re-fractionated again and again; but we found that anomalous results were being obtained, for it appeared that while krypton could be pumped away slowly, even while the bulb was surrounded by liquid air, a residue remained which, after removal of the air-jacket, gasified. It turned out to be still

another gas, to which the name "xenon," or *the stranger*, was given.

To describe in detail the numerous fractionations by which a separation of argon, krypton, and xenon were effected would be tedious. The final result was that two gases were obtained which were not further altered by repeated fractionation—one of density 40·8, and the other of density 64·0. These numbers imply the atomic weights 81·6 and 128, for reasons already given on p. 197. The total amount of these gases was disappointingly small; for the krypton was only about half a fluid ounce (about 15 cubic centimetres) in volume, while the xenon had barely a quarter of that volume.

An attempt has been made to estimate approximately the amounts of these gases in atmospheric air. The process for krypton and xenon was to compress the ordinary atmospheric air, and to run it through the liquefier; the air which had escaped condensation was passed through a large gas-meter. During the experiment no less than 179·7 kilograms, or nearly 400 lbs. of air, passed the meter, or about 4500 cubic feet, while 11·4 kilograms or 25 lbs. were liquefied. The total

quantity was therefore 191 kilograms of air. It may be remarked in passing that the liquid air contained twice the normal quantity of argon, for during liquefaction more argon liquefies proportionally than nitrogen.

The liquid air was boiled down in a large glass flask under a partial vacuum; its boiling-point was $-195°$ C.; the residue measured about 200 cubic centimetres. This liquid was then allowed to boil, and the resulting gas was passed over red-hot copper contained in a large tube; much oxygen was absorbed, and the final volume of gas was 50 litres; after all nitrogen had been removed by magnesium-lime mixture, the argon left measured 12·5 litres. It was then fractionally distilled, so as to separate the argon, boiling at a low temperature, from the krypton and xenon, of which the boiling-points are much higher. Then the gases were separated from each other by a long series of operations of the same kind.

On comparing the volumes of krypton and xenon with that of the air from which they had been obtained, surprisingly small quantities were obtained.

The estimation of the helium and neon was

made in quite a different manner. Sir James Dewar made the ingenious discovery that if air be admitted into a vessel containing charcoal cooled to a low temperature by liquid air surrounding it, the oxygen and nitrogen are absorbed, while the helium remains uncondensed, and not much neon condenses. This property of gases to be absorbed by charcoal has been long known; but Dewar was the first to apply it at low temperatures.

A measured quantity of air, about 17 litres, was admitted to a bulb containing 100 grams of cocoa-nut charcoal, cooled to $-100°$ C. A large proportion of the oxygen and nitrogen was absorbed, but the neon and helium remained unabsorbed. The unabsorbed gas was pumped off, and again treated in the same manner with a smaller quantity of charcoal, so as to remove most of the oxygen and nitrogen. The remaining mixture, which still contained a little nitrogen and oxygen, was mixed with excess of oxygen, and sparked over caustic soda. The residue of inert gases was measured, after withdrawal of excess of oxygen by phosphorus. The mixture of neon and helium was then admitted to a bulb containing charcoal cooled to $-185°$ C., when the neon was

almost completely absorbed, the helium being left. It was pumped off and measured, and when the charcoal warmed up, the neon was also collected and measured.

The amounts of these rare gases in crude argon were found to be—

Helium	.	1	part	in	2300	of argon	by volume.
Neon	.	1	„	„	757	„	„ „
Krypton	.	1	„	„	200,000	„	„
Xenon	.	1	„	„	1,700,000	„	„

In air, the gases are present in the following proportions, approximately—

Helium	.	.	1	part in	245,300 by volume.
Neon	.	.	1	„	80,800 „
Argon	.	.	1	„	106·8 „
Krypton	.	.	1	„	20 millions „
Xenon	.	.	1	„	170 millions „

It is surprising to think that there is much more gold in an average sample of sea-water than there is xenon in the air.

The density of pure argon, freed from these gases, was determined by Sir William Ramsay and Dr. Travers; the two most reliable determinations gave the figures 19·952 and 19·961. But knowing the relative volume of neon and helium in crude

argon and their density, the density of pure argon can be calculated; it is 19·953—a number in close agreement with the result of direct experiment.

To determine the properties of these elements, apparatus had to be constructed on a very minute scale. The boiling-points of argon, krypton, and xenon were determined at all pressures between a few millimetres and forty metres of mercury; that of argon at atmospheric pressure is 186·1° below zero centigrade; that of krypton, 151·7°; and that of xenon, 109·1°. On compressing these gases, the highest temperature at which liquefaction occurs, or the critical temperature, is for argon, −117·4°, for krypton, −62·5°, and for xenon, +14·7°; hence on compressing xenon to about 50 atmospheres on a cold day, it liquefies. They all form transparent, colourless liquids, indistinguishable in appearance from water; and they likewise all freeze to white, ice-like solids.

The position of the atmospheric elements in the periodic table may be seen on p. 221. But it will conduce to clearness if the elements are placed in juxtaposition to those of neighbouring atomic weights; and an excerpt from the periodic table is therefore introduced.

THE POSITION OF THE INACTIVE ELEMENTS IN THE PERIODIC TABLE.

Hydrogen.	Helium.	Lithium.	Beryllium,
1	4	7	9
Fluorine.	Neon.	Sodium.	Magnesium.
19	20	23	24
Chlorine.	Argon.	Potassium.	Calcium.
35·5	40	39	40
Bromine.	Krypton.	Rubidium.	Strontium.
80	82	85	87
Iodine.	Xenon.	Caesium.	Barium.
127	128	133	137

Professors Lothar Meyer and Mendeléeff, after constructing the periodic table of the elements, drew attention to the fact that the physical properties of the elements are periodic functions of, or vary regularly with, the atomic weights of the elements in each column: thus, for example, we have in the first column of the elements, in the table above, the elements hydrogen, fluorine, chlorine, bromine, and iodine. For some unknown reason, the first element of such a column diverges considerably in properties from the rest; thus there is no great analogy between the behaviour of hydrogen and that of the halogens, as the remain-

ing elements of the column are termed. But contrasting the latter among themselves, we see that while the colour of fluorine is pale yellow, that of chlorine is a darker greenish-yellow; that of bromine-gas red, and that of iodine-gas violet. Again, fluorine has the lowest boiling-point, and iodine the highest; fluorine is the most active, or in this column the most highly electro-negative element of the group, and iodine the least; for fluorine attacks almost every other element, and indeed compound, forming fluorides; while iodine is comparatively inactive, and is somewhat difficult to induce to combine with electro-negative elements. On the other hand, while iodine forms relatively stable compounds with that other highly electro-negative element, oxygen, no compound of fluorine and oxygen has been isolated.

Now in certain cases such properties admit of a numerical value being attached to them. For example, the volume of liquid or solid occupied by a weight of the element taken in grams, at some suitable temperature, implying the same condition for each, is seen to vary progressively, with increase in atomic weight. Thus, in the instance chosen the volumes in the liquid state at the boiling-point

of 1 gram of hydrogen, of 19 grams of fluorine, of 35·5 grams of chlorine, of 80 grams of bromine, and of 127 grams of iodine are—

	Hydrogen.	Fluorine.	Chlorine.	Bromine.	Iodine.
C.cs. . .	14·3	17·15	23·5	27·1	34·2

In the annexed figure it will be seen that with ordinates as atomic weights, and with abscissae as

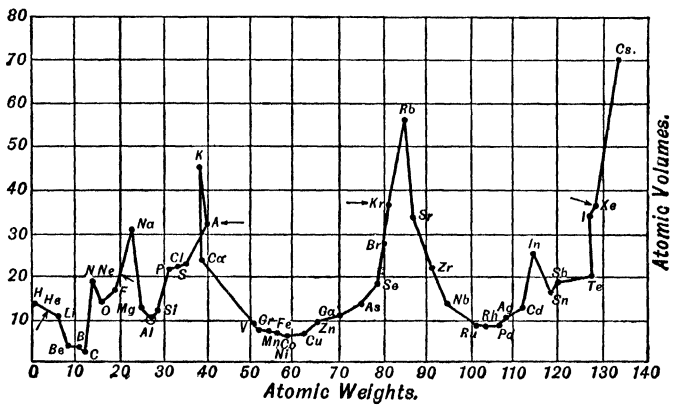


FIG. 8.

atomic volumes, broken curves are obtained both in the fluorine and in the argon column of elements which show such periodic variation. The same kind of irregular variation of properties with atomic weights is to be found if other properties be considered. Thus, when light passes through any transparent material, it suffers more or less retarda-

tion, depending on the nature of the material. If the retardation due to passage through a known length of air at a certain temperature and pressure is taken as unity, that due to passage through the same length of the new gases under similar conditions of temperature and pressure is shown below—

Helium.	Neon.	Argon.	Krypton.	Xenon.
0·124	0·235	0·968	1·450	2·364

Here, again, the increase with rise in atomic weight is well defined. These numbers display among themselves a very simple relationship, as has been pointed out by Mr. Clive Cuthbertson. If the value of the refractivity of helium be taken as $\frac{1}{2}$, then the series becomes

Helium.	Neon.	Argon.	Krypton.	Xenon.
$\frac{1}{2}$	1	4	6	10

Mr. Cuthbertson has also shown that a similar relationship holds for other elements which can be obtained in the form of gas. Thus, if certain columns of the periodic table (see p. 221) be considered, we have, if we take neon as 139—

			Helium.
			$139 \times \frac{1}{2}$
Nitrogen.	Oxygen.	Fluorine.	Neon.
297×1	270×1	192×1	139×1
Phosphorus.	Sulphur.	Chlorine.	Argon.
297×4	270×4	192×4	139×4
Arsenic.	Selenium.	Bromine.	Krypton.
?	?	192×6	139×6
Antimony.	Tellurium.	Iodine.	Xenon.
?	?	192×10	139×10

These numbers are values of the expression $(\mu - 1) \times 10^6$, and are proportional to the retardation of light in passing through equal numbers of molecules of the gases, or of the elements in the gaseous state. Their significance has not yet met with any explanation, but it is evident that the exceedingly simple relation must be connected with some fundamental facts relating to the constitution of matter.

The same periodicity is manifest with other properties, such as the melting and boiling-points of argon, krypton, and xenon, the critical temperatures, and, indeed, the whole curve of vapour-pressures. Moreover, the properties of these elements are functions, not merely of their atomic weights considered in reference to each other, but

also in reference to those of other elements: thus, for example, while the atomic volume of sulphur (atomic weight, 32) is 21·6, that of chlorine (35·5) is 23·5, that of argon (39·9) is 32·9, and that of potassium (39·1) 45·4.

But it is the electric behaviour of these new elements which has most interest. For while fluorine, chlorine, bromine, and iodine are the most electro-negative of the elements, being separated from their compounds with metals at the positive pole,—and while elements of the sodium group, namely, lithium, sodium, potassium, rubidium, and caesium, are the most electro-positive of the elements, separating at the negative pole when a solution of one of their compounds, or the fused compound, provided it is a conductor of electricity, is electrolysed,—these elements occurred in contiguous columns in the periodic table of the elements. Now it is difficult to see how elements of such opposite properties should be next each other, without some transition. "*Natura nihil fit per saltum*"; and it would be reasonable to expect a bridge to unite columns containing elements of such opposite properties. This bridge has now been discovered: it consists of the neutral

elements of the argon group, which have no electric polarity, seeing that they form no compounds. It is owing to this neutrality and to their low boiling-points that they occur in the atmosphere. The boiling-point of any substance appears to be influenced greatly by its molecular weight, as well as by the nature of the elements forming the compound; and these gases, being molecularly simple (for their molecules are identical with their atoms), have especially low boiling-points, and therefore occur only as permanent gases.

It is curious that although the presence of helium is revealed in the sun and in many of the fixed stars by its spectrum, that of argon has not been detected. This leads to the suspicion that a hypothesis put forward by Dr. Johnstone Stoney contains a considerable element of truth. It is that gases are continually leaving our atmosphere, owing to the intrinsic rate of motion of their molecules. A molecule of hydrogen, for example, when it arrives at the confines of our atmosphere, may escape, provided its rate of motion is sufficiently rapid. And it may be proved that some molecules of hydrogen possess sufficient velocity to carry them beyond the sphere of the earth's attraction;

it would follow that, given sufficient time, all molecules of hydrogen would ultimately fly off and would find a home when they reached a body of sufficient mass, and therefore of sufficient attractive force to retain them permanently. Such a body is the sun; and it has been abundantly proved that free hydrogen exists in quantity in the solar atmosphere. But M. Gautier and Lord Rayleigh have shown that our terrestrial atmosphere contains a detectible quantity of free hydrogen; and Sir William Ramsay and Dr. Travers have proved it to contain helium. Why do these gases remain in our atmosphere? Why, in the course of ages, do they not leave it, each molecule pursuing its way as an independent wanderer, until it comes under the sway of the sun, or of some planet of sufficient mass to retain it in its atmosphere?

The answer to this question must be that hydrogen and helium are continually being evolved from the earth in such quantity as to replenish the drainage of these gases into space. The existence of helium in the gases from mineral waters leads to the very probable guess that that gas must be escaping in appreciable quantity from the soil; and it is well known that hydrogen is produced by

imperfect combustion, and thus finds its way into our atmosphere.

The absence of the spectrum of argon from the sun's atmosphere is more puzzling. The explanation may perhaps lie in the fact that the spectrum of argon is easily masked by that of other gases. It is impossible to see argon lines in a mixture containing a small amount of nitrogen; and the spectrum is much enfeebled, too, if oxygen be present in the vacuum-tube. If this is not the explanation, it must be concluded that the relative quantity of argon in the sun's chromosphere is small compared with that in the atmosphere of the earth; or possibly that the compounds of argon are stable at the enormously high temperature of the sun,—a suggestion which has something in its favour; for compounds which are formed with absorption of heat acquire greater stability the higher the temperature; and it is not inconceivable that although argon, at atmospheric temperature, and under atmospheric conditions, refuses to combine, it may yet form compounds under the much greater extremes of electric disturbances and high temperature which obtain in the sun and in the fixed stars. It is only recently that the spectrum

of oxygen has been recognised in the sun, and a possible reason of its feebleness may be the stability of some of its compounds endothermic under normal conditions.

Shortly after the wave-lengths of the lines in the spectrum of krypton were published, Sir William Huggins, in a private letter, suggested to Sir William Ramsay that its brilliant green line appeared to be identical with that seen in the spectrum of the aurora borealis. The same remark was made somewhat later by Professor Schuster, in a letter to *Nature*.

The *aurora borealis* or Northern Lights generally appears in the north, on frosty evenings, as a luminous arch, from which streamers descend, and emit light, sometimes white, sometimes green, and sometimes crimson. The height of this arch appears to be from 50 to 125 miles. The spectrum contains numerous lines, all of which have been shown by Mr. Baly to be identical with strong lines in the spectrum of krypton, but the strongest is one of wave-length 5570 Ångstrom units.

Now this krypton line persists at great rarefactions. Even when the amount of krypton is reduced to one twenty-three-millionth part of its

normal pressure, the line still is visible. It can be calculated that the pressure of the atmosphere would be equal to that amount at a height of 80 miles, a number which falls within the limits given above.

Sir William Ramsay has succeeded in producing an artificial aurora by causing a ring-shaped discharge to take place through krypton in the interior of a flask, and by a powerful electromagnet, suitably placed, the "streamers" can also be reproduced. Such an aurora shows all the peculiarities of the natural aurora, including the spectrum characteristic of krypton.

The progress of events has resulted in the discovery of new atmospheric gases, the peculiarity of which is their short life; and the next chapter will be devoted to a description of their sources and properties.

CHAPTER IX

THE RADIOACTIVE GASES: THE "EMANATIONS"

THE year 1896 was remarkable for the discovery by M. Henri Becquerel that the metal uranium and its salts were capable of impressing a photographic plate, even after they had been kept for years in the dark; they appeared to be able to emit a constant and unceasing flow of something analogous to light. Moreover, the rays emitted were found to discharge an electrified body, so that no charged object could retain its charge in their immediate neighbourhood. But the effect of such "uranium rays" was feeble. Madame Curie, two years later, announced that she had succeeded in extracting from pitchblende, the natural ore of uranium, a metal resembling bismuth, to which she gave the name "polonium"—a word derived from Poland, of which she is a native. This sup-

posed metal possessed these properties of uranium, but in a much higher degree. Shortly afterwards, she announced the discovery of another element still more active, and happily named it "radium." Compounds of the element thorium were also found to exhibit similar properties; and later, another substance was separated from pitchblende by M. Debierne and by Professor Giesel, named by the former "actinium," and by the latter "emanium." The property of emitting "rays," which were at first imagined to resemble those of light, has been termed "radioactivity."

Perhaps the simplest way to test for radioactivity is to place the substance under examination on the top of an ordinary photographic plate, wrapped up in black paper, so that no light can reach it. But the photographic method is not well fitted for quantitative experiments. A much more satisfactory instrument is the gold-leaf electroscope. It consists of a metal chamber with two windows of glass or mica opposite each other, through which the gold-leaf can be observed. A tin oil-can forms an efficient chamber. It is closed by an india-rubber cork, perforated with two holes. Through one hole passes a thin brass rod, to the lower end

of which a short rod of fused silica is attached. A slip of brass, about $\frac{1}{32}$ inch thick, $\frac{1}{4}$ inch wide, and $2\frac{1}{2}$ inches long, is cemented on to the lower end of the silica rod; and attached by a dash of gum to the upper end of this brass slip is a strip of gold leaf of the same length and width, which hangs down parallel to the brass slip, so long as it is not electrified, but when charged, the gold leaf stands out more or less from the brass slip like an Λ with one leg vertical (the strip), and the thin leg representing the gold leaf. To impart a charge to the gold leaf and strip, a stiff brass wire passes through the second hole in the india-rubber cork; this wire is bent at the lower end, so that on twisting it round, the lower end makes contact with the brass slip. By rubbing a piece of ebonite or sealing-wax, it is charged, and on touching the wire with it, the wire being in contact with the brass slip, the latter is charged, and the gold leaf diverges. The wire is then twisted, so as to break contact with the slip; and it is then advisable to connect the charging wire to earth, by means of a piece of thin wire attached to a gas-pipe. The bottom of the oil can should be removable; and it is well to pierce the india-rubber cork with a third

hole through which a glass tube passes, in order that it may be possible to introduce a gas into the metal chamber. If a solid is to be tested for radioactivity, the electroscope is charged, and the solid is laid on the bottom, which is then replaced. Rays from the radioactive substance have an effect on the air contained in the can, termed "ionisation"; ionised air has the property of discharging an electrified body; and the amount of ionisation, and therefore the rate of discharge, is proportional to the intensity of the radiation of the radioactive substance. If a radioactive gas is to be tested, a measured quantity is blown through the glass tube into the can; it will discharge the electroscope more or less quickly according to the extent of its radioactivity. By observing the rate of fall of the charged gold leaf through a telescope fitted with a scale in its eye-piece, comparative experiments may be made, and the relative radioactivity of two substances compared.

More accurate measurements may be made with an electrometer; but enough has been said to give a fair idea of a practicable method of testing for and estimating radioactivity.

Compounds of radium, thorium, and uranium

differ from those of uranium and polonium in that they continuously evolve gases; but these gases are unlike others with which we are acquainted, for they decompose or disintegrate in a short time. Only one of the products of such decomposition has been identified with any known chemical element; it is helium, which is produced from the gas evolved from compounds of radium. To these gases the name "emanation" has been given by Professor Rutherford, the discoverer of the first of these to be observed—namely, the emanation from thorium. The thorium emanation, like other gases, mixes with air, and air, thus mixed, acquires and retains the property of discharging an electroscope, so long as the emanation remains undecomposed. In conjuction with Mr. Frederick Soddy, Rutherford showed that the emanation can be condensed by passing it through a tube cooled below - 154° C. by means of liquid air; this, as the reader has observed, is now a familiar method of separating two gases from each other.

Monsieur and Madame Curie observed that radium compounds, too, had the power of imparting radioactivity, lasting for a considerable time, to air with which they were in contact; but they did not divine

the true cause of the radioactivity—namely, the evolution of a gas. The radium-gas was also investigated by Rutherford and Soddy, and found to be condensable, like the thorium gas.

In 1900, Professor Geitel and Mr. C. T. R. Wilson independently discovered that a positively or negatively charged body, placed in a closed vessel, gradually lost its charge. And Elster and Geitel in 1901 tried to extract the radioactive substance from the air, believing that the loss of charge in the closed vessel was due to some radioactive constituent of the atmosphere. Their method of extraction depended on an observation made by Rutherford, that the gas from thorium was attracted by a negatively charged object, and could be made to deposit its decomposition-product on it; and as this decomposition-product is also radioactive, its presence could be detected, and its comparative quantity measured. The same method would attract the radium emanation, and lead to its detection.

This method of detecting radioactive substances by means of their discharging power is incomparably more delicate than the most delicate chemical or spectroscopic test; the amount which is at the

disposal of the experimenter is extremely small. Moreover, the products of their decomposition are also quite invisible. Their presence or absence can be detected only by their power of ionising air, and thus affecting an electroscope: and they are differentiated from each other by the time during which they retain that power. For example, the radium emanation, mixed with air, is measured; a known fraction of the whole—that is, a certain number of cubic centimetres of the radioactive gas—is blown into an electroscope, and the rate at which the leaf falls is measured. That quantity contains a certain amount of emanation which we shall call x; its absolute amount is unknown. The stock of air is now kept for 92·6 hours, and a fresh portion, the same in volume as the former, is blown into the electroscope. It is again discharged, but the time required is twice as long as the first, for one half of the emanation has been changed into products which are non-volatile but also radioactive. If these deposit on the sides of the vessel containing the electroscope, the vessel would become radioactive; hence it is necessary, after the first measurement, to remove the bottom of the vessel, and take care to expel the residual emanation completely

by a current of air. After a second period of 92·6 hours, a third equal quantity of the emanation, which has now been kept for 185·2 hours, is admitted: the time required for discharge is now four times as long as the original time—that is, only one quarter of the original emanation has survived. An example of actual measurements is given below.

Age of Emanation in hours.	Conductivity of Air in Electroscope.	Age of Emanation in hours.	Conductivity of Air in Electroscope.
0	345	241	57·5
123·5	143	316	31·4
168	96·2	363	19·5
196	75·2	484·5	7·7

The conductivity is inversely proportional to the time of discharge of the electroscope; it is evident that it falls off as the emanation grows older and until it reaches nearly a zero value.

The law of decrease is a well known one; it may be likened to the inverse of the law of compound interest. If a sum of money is lent, it is customary to pay interest on it at stated intervals; for example, a yearly interval is usual. Thus, at four per cent per annum, a sum of £100 yields, at the end of a year, £4 interest. Supposing it to be

agreed that the intrest is to be payable at the rate of four per cent per half-year, then it is clear that £100 in six months will have increased to £102. During the second six months, the interest at 4 per cent accrues not on £100, but on £102; it is therefore £2, *i.e.* the interest on £100 for six months, plus about 9½d., the interest on £2 for six months at 4 per cent. If it be agreed to pay at the rate of 4 per cent per quarter, then the interest works out as follows:—

Interest on	£100	0	0	for 3 months	at 4 p.c.	=	£1	0	0
„	101	0	0	„	„	=	1	0	$2\frac{4}{10}$
„	101	0	$2\frac{4}{10}$	„	„	=	1	0	$4\frac{1}{2}$
„	101	0	$4\frac{1}{2}$	„	„	=	1	0	$6\frac{7}{10}$
							£4	1	$1\frac{4}{10}$

By this method, therefore, the interest at the end of the year will be increased by about 1s. 1½d. If the period of payment were monthly, instead of quarterly, it is clear that the sum gained would be still larger; if daily, hourly, once every minute, once every second, the increase would be progressively greater. Stated generally, the rate of increase of the principal at any moment depends on the amount of the principal at that moment.

Now the decay of the emanation is an inverse

case of this. Let us take a supposititious instance. Imagine, for simplicity's sake, that in each day one tenth of the total quantity of emanation present decomposes. Then we should have—

Time.	Amount of Emanation present.	Amount Decomposed per day.
0 – 1	1·000	0·1 × 1·000 = 0·100
1 – 2	(1·000 – 0·100) = 0·900	0·1 × 0·900 = 0·090
2 – 3	(0·900 – 0·090) = 0·810	0·1 × 0·890 = 0·081
3 – 4	(0·810 – 0·081) = 0·729	0·1 × 0·729 = 0·073
4 – 5	(0·729 – 0·073) = 0·656	0·1 × 0·656 = 0·066
etc.	etc.	etc.

At each moment the amount decomposing, however, is proportional to the quantity present. Now the mathematical expression for this is

$$\frac{I_t}{I_0} = e^{-\lambda t},$$

where I_0 is the amount present at the beginning of the change, I_t, the amount present in time, t, e a number equal to 2·718 . . ., and λ a constant. The value of λ may be defined as the reciprocal of the average life of a particle of the emanation.

In the case of the radium emanation, $\lambda = \frac{1}{463{,}000}$; it means that that proportion of the total amount of emanation present decomposes in a second. The average life of a particle of this emanation is there-

fore 463,000 seconds, or 5 days, 9 hours. The thorium emanation has a much shorter life: it is 87 seconds, and λ has the value $\frac{1}{87}$. Still shorter is the life of the emanation from actinium: it is only 5·8 seconds; nearly $\frac{1}{6}$th of the whole emanation decomposes each second.

The gases from a solution of a radium salt (the bromide is commonly used) consist for the most part of a mixture of oxygen and hydrogen; about 10 cubic centimetres per gram of radium per day are evolved. There is always a small excess of hydrogen, which amounts to about 6 per cent of the total volume of the mixed gases. The gases are evidently derived from the decomposition of the water of the solution; but it is not easy to account for the excess of hydrogen: it may be due to the formation of bromate of radium, $Rd(BrO_3)_2$, although this has not been satisfactorily ascertained. Mixed with these gases is the emanation, in extremely minute amount.

Rutherford and Soddy investigated to some extent the action of chemical agents on the thorium and radium emanations. In each case they resemble the inert gases of the atmosphere. Copper oxide at a red heat, red-hot zinc dust, and red-hot

platinum black in presence of oxygen are without effect on them; their discharging power, property of condensation, etc., are unaffected. And Ramsay and Soddy confirmed this evidence of their indifference towards reagents: neither sparking with oxygen in presence of caustic potash, nor passage over red-hot magnesium-lime mixture in any way altered the radium emanation. It must, therefore, be concluded that they resemble most the gases of the argon group in this respect.

Now it is remarkable that those elements which display radioactivity have all a very high atomic weight. Thus radium belongs to the barium series, with a probable atomic weight of 226; thorium is allied to silicon, but has the high atomic weight 232; and uranium is the element with the highest atomic weight known—240.

It has been shown, however, by Dr. Hahn, working under Ramsay's direction, that the impure thoria from thorianite contains a substance for which the name "radiothorium" has been proposed, of intense radioactivity. Indeed, it appears to bear to thoria the same sort of relationship as radium to uranium. It was separated, along with radium, from a sample of a mineral from

Ceylon, named thorianite. This substance was left behind along with barium and radium sulphates, after the mineral had been fused with hydrogen sodium sulphate. Its bromide is more soluble than that of radium; moreover, unlike radium, it is precipitable by ammonia. The quantity obtained is too small to have made it possible to determine its atomic weight; its activity, however, is at least half-a-million times that of the crude thoria from which it was separated. The emanation which it evolves is identical in every respect with that evolved from salts thorium; and the natural conclusion is that it is the substance to which thorium compounds owe their radioactivity. It is still doubtful whether thorium has a radioactivity of its own, like uranium; the assertion has been made by two different observers that thorium oxide from certain minerals is non-radioactive. Like thorium salts, too, salts of this substance give on precipitation with ammonia a filtrate containing thorium X, a body which is at first strongly radioactive, but which soon loses its radioactivity; while the precipitate from which the thorium X has been separated is less radioactive, and regains its activity at a rate precisely the same as that at which the thorium X loses activity.

We do not know the atomic weights of the gases evolved from radiothorium or from actinium. That of "niton," the gas evolved from radium, is, however, known, for its density has been determined by Ramsay and Whytlaw-Gray. Experiments made with the view of determining this quantity by comparing their rates of diffusion with those of gases of known density can hardly be pronounced satisfactory. Perhaps the best of such experiments is the one made by Debierne with "niton," the name now adopted instead of the cumbrous "radium emanation." He caused the gas to issue through a minute hole in a diaphragm of platinum, and found the molecular weight of the niton to be nearly 220.

The density, and consequently the molecular weight, of niton was determined in 1910 by Ramsay and Whytlaw-Gray, by means of a "microbalance," an instrument constructed for the purpose of weighing exceedingly minute quantities. A good ordinary balance, constructed with a brass or aluminium beam resting on an agate knife-edge bearing on an agate plate, turns with the tenth part of a milligram, when the pans are loaded with 20 or 30 grams. An assay-balance, made on

essentially the same principle, but with a much lighter beam, may turn with $\frac{1}{50}$th or even $\frac{1}{100}$th of a milligram. But such a degree of sensitiveness is by no means sufficient for the determination of the weight of the niton produced from an obtainable weight of radium. The volume of niton in equilibrium with 1 gram of metallic radium is only 0·6 cubic millimetre; and Ramsay and Whytlaw-Gray had about the sixth part of this at their disposal, 0·1 cubic millimetre, a quantity barely visible with the unaided eye in a capillary tube. Its weight was found to be about 2 thousandths of a milligram; and in order to reach a reasonably accurate result, the balance required should be able to show the 200th part of that weight, or the 1/100,000th of a milligram. The sensitiveness attained was indeed five times as great; the balance "turned" with the 500,000th part of a milligram.

The beam was constructed of thin silica rods, fused together with an oxy-coal-gas blowpipe; its shape was like that of an ordinary balance. It rested on a knife-edge of polished silica bearing on a polished silica plate. From one end of the beam hung a counterpoise of silica by a silica fibre; from the other a hook, to which the apparatus

could be suspended. The advantage of silica as a material for the balance is its hardly being affected by temperature; it barely expands when heated; besides, it is very strong, and very thin fibres of silica can support comparatively heavy weights. To the centre of the balance was fused a small silvered mirror, from which a beam of light could be reflected on to a vertical scale; this served as a pointer, and had the great advantage that the pointer is weightless, for a beam of light has no weight. The balance was enclosed in an air-tight brass case, resting on a brass plate; a vacuum could be made in the case, and air could be admitted, so as to have any required air-pressure; the actual pressure was read by means of a mercury gauge.

Hanging suspended by a silica fibre from the end of the beam opposite to that carrying the counterpoise was a small silica bulb; the capacity of the bulb used was 22·2 cubic millimetres. It contained air, weighing 0·027 milligram. Now this air would be counterpoised, as it were, by the air in the balance-case, if the latter contained air at atmospheric pressure; but if all air were withdrawn from the balance-case, it would be equivalent to putting a weight of 0·027 milligram on the end

of the beam. For intermediate pressures the apparent weight of the air in the bulb is proportional; thus at a pressure of half an atmosphere, or 380 millimetres of mercury, the air in the little bulb would act as a weight of 0·027/2, or 0·0136 milligram. It was possible to read a difference of pressure on the gauge of 0·1 millimetre, or 1/7600th part of the atmospheric pressure; and this corresponded to putting on or taking off a weight of 0·027/7600 milligram, or 0·00000355 milligram; that is a little more than 3 millionths of a milligram.

The niton was generated (along with oxygen and hydrogen) from about half a gram of bromide of radium in 8 or 9 days; after explosion, the residue consisted of a little hydrogen containing the niton. It was forced up by mercury into a very narrow capillary tube, the tip of which was then cooled with liquid air, so as to freeze the niton. The volume was then greatly increased, so as to diminish to insignificance the amount of hydrogen in the capillary tube; and this was then sealed off, "full" of niton.

The capillary tube was then placed in a little glass "bucket," suspended from the balance, and

counterpoised by a suitable piece of silica rod, hung on the opposite arm of the balance. Silica is slightly volatile; so after suitable pieces had been drawn off from this piece of rod, originally too heavy, exact counterpoise was obtained by directing the tip of the blowpipe flame on what remained, until the counterpoise was exact. The air-pressure was then adjusted so that complete equilibrium ensued.

Next the "bucket" was removed with forceps, and the pointed end of the capillary tube was broken by pressure in the "bucket"; this made certain that no little pieces of glass could scatter, for the drawn-out part of the capillary tube fitted the "bucket" pretty accurately. The "bucket" and capillary were then replaced on the balance, and the air-pressure in the case adjusted until equilibrium again set in. The weight of the niton was then ascertained in terms of the buoyancy of the air in the little bulb, and that was translated into actual weight. The volume of the niton was calculated from measurements previously carried out with radium, the amount produced in a given time being known.

The mean of five such weighings gave the

molecular weight of niton as 223; and as the molecular weight of a monatomic gas is the same as its atomic weight (see pp. 200-216), it follows that the atomic weight of niton is also 223.

But Ramsay and Whytlaw-Gray carried the matter further. Radium, when it changes into niton, parts with an atom of helium; niton, in its turn, yields Radium A, and another atom of helium is shot off; Radium A changes into Radium B, but no helium is here lost; Radium B gives Radium C, and again an atom of helium separates. All these changes are fairly rapid; in three months, it may be said, appreciably all the niton has changed into Radium D, which is a pretty permanent body, keeping its identity for many years. Is it possible to find the loss of weight caused by the loss of helium?

A sealed capillary tube was left in the "bucket" of the balance for four months, and was then counterpoised. By that time all the niton had changed into solid Radium D and helium. The tip of the capillary was broken as usual, and a vacuum was made in the balance-case so as to pump all the helium out of the capillary; the weight was again taken; the loss was 27 millionths

of a milligram. But the weight of the helium from the amount of niton in the tube should have been 38 millionths.

It has been mentioned that the molecules (or atoms) of niton "explode" when they change into Radium A; and the other products, B and C, shoot out each an atom of helium during their change. Was it not possible that some of the helium had been shot into the walls of the glass capillary? That was easily tested. The capillary tube was placed inside a little tube of quartz, and all air was removed by pumping. A little oxygen was then admitted. Then heat was applied, so as to fuse the glass capillary, and all gas was pumped off. The oxygen was condensed out by cooling a bulb containing cocoa-nut charcoal in connection with the tube containing the gas, and the small residue of helium was measured, and from the volume the weight was calculated; it came to 8 millionths of a milligram. Adding 8 to the 27 millionths previously weighed, the total weight of the helium is 35 millionths of a milligram, instead of the calculated 38. And making the little measuring-tube into a Plücker tube by wrapping tin-foil round its ends, and passing a discharge, the

spectrum of pure helium was seen. Hence the idea that niton, in changing into radium D, gives off three atoms of helium was proved to be correct.

Dr. Whytlaw-Gray and the writer have also liquefied and solidified niton, observing it in a capillary tube through a microscope. The liquid, which can be produced by compression at the ordinary temperature, shines with a bright purple light; the solid, formed by cooling the liquid with liquid air, looks like a miniature arc-light—a very brilliant luminous point. The melting-point of the solid and the boiling-point of the liquid were determined.

It would be desirable to carry out a similar series of experiments with the emanations from thorium and actinium, but unfortunately it is impossible; these substances are too transient, and cannot be kept long enough to handle. We have therefore no direct knowledge of their atomic weights, and can only speculate.

An experiment made with actinium emanation appears to point to its being a light gas. If a piece of paper containing an actinium salt (of course in a very impure condition, for salts of

actinium have never been obtained free from impurities) be held about the middle of a cardboard screen, covered over with phosphorescent zinc sulphide, at about half an inch from the screen, it can be seen that the gas rises. Suppose the screen to be represented by the line, and the paper by the dot, then in the position _ · _ there is hardly any luminosity produced on the screen. In the position ¯ · ¯ the screen becomes intensely luminous. In the positions / and \ the evidence is again that the emanation rises, care of course being taken to avoid convection currents of air. The actinium emanation is particularly well adapted for such experiments, for its effect is very transitory; it can be blown away, and it takes an appreciable time to reappear. The phenomenon is a very striking one, and conveys the conviction that an invisible substance is streaming on to the screen to excite luminosity where it touches the phosphorescent covering. Now, if the gas from actinium is lighter than air, it must have a density of considerably less than 14·5 (hydrogen being taken as unity). This, however, is very improbable; the upward streaming is doubtless due to the heat of the actinium preparation expanding the air.

It has been already mentioned that radium emanation undergoes decomposition, and that one of its products is helium. Professor Rutherford and Mr. Soddy, after finding that thorium emanation was an indifferent gas, remarked: "The speculation naturally arises whether the presence of helium in minerals and its invariable association with uranium and thorium may not be connected with their radioactivity." The state in which helium is retained in minerals, too, is analogous to the state in which radium emanation is retained in salts of radium. It cannot be pronounced to be combined; it is almost certainly molecularly entangled in the interior of the solid, and escapes only when heat is applied. This state has been imitated by decomposing a compound of nitrogen, mixed with a solid, when the nitrogen is similarly retained.

The discovery that radium emanation, during its change, is converted partially into helium was the result of an unsuccessful attempt to obtain the spectrum of the emanation. It was at first imagined that if the emanation were mixed with a gas of simple spectrum, such as helium, its lines might be visible. But it soon became evident

that the amount of emanation present was so small that specially minute apparatus would have to be constructed in order to deal with it. The Plücker tube, instead of being of dimensions measurable in inches, was constructed in dimensions measurable in millimetres (1 inch = 25 millimetres). And the volume tube, in which the amount of emanation obtainable from a given weight of radium in a given time was measured, was of the finest capillary tubing. It has been mentioned that the gases evolved from a solution of radium bromide consist of a mixture of hydrogen and oxygen in nearly the proportion of two to one, with a small excess of hydrogen, and that the emanation is mixed with these gases. The gases evolved in eight days from 60 milligrams of radium bromide in aqueous solution were exploded by a spark in a small explosion burette; the residue of hydrogen was left in contact with moist caustic potash for some time in order that any carbon dioxide which might have arisen from dust on the surface of the glass being burnt, should be absorbed. The residual hydrogen, containing the emanation, passed through a tube containing phosphorus pentoxide so as to remove water-vapour; and it was driven upwards, by

means of mercury, until it entered a small bulb, to the top part of which a capillary tube of known bore was sealed. The bulb was then cooled with liquid air, so as to condense the emanation, and the hydrogen was entirely removed by pumping. The jacket of liquid air was then removed, and the emanation evaporated; by raising the mercury column, it was made to enter the capillary tube, where it was measured.

It was a brightly luminous gas; its volume was nearly the fortieth of a cubic millimetre—that is, the forty-thousandth of a cubic centimetre. It was found to follow Boyle's law—the volume decreased in proportion as the pressure was increased. From day to day the volume decreased, until after four weeks less than one two-thousandth of a cubic millimetre was left. This minute bubble, however, was as brightly luminous as at first, although, of course, there was much less of it.

The mercury was drawn down the capillary tube into the bulb, and was there frozen. On heating the glass so as to expel helium, and passing a discharge, the helium spectrum was visible. It appears then that the emanation contracts to

practically nothing in about four weeks; that helium is formed from it, which penetrates the walls of the glass tube, probably because the molecules are shot off with enormous velocity; and that, on heating, some at least of the helium is expelled, so that it can be recognised by its spectrum.

In a second experiment, in which a capillary tube of a different kind of glass was used, there was no contraction, but, on the contrary, an expansion. The initial volume of emanation was practically identical with that which had previously been found; but it expanded to about ten times its original volume in three weeks. The gas was then removed by pumping, and it showed a brilliant helium spectrum; some gas had also been absorbed.

It is easy to calculate from these data the amount of emanation produced from one gram of radium. It appears to be about one cubic centimetre from one gram in a year. But as this goes on, the radium will continually decrease in weight, and hence the actual amount of emanation evolved will continually diminish, again according to the inverse law of compound interest. It can be cal-

culated that the average life of an atom of radium is about 1730 years, supposing that the only product of its initial decomposition (not of subsequent changes, in which the emanation is concerned) is emanation.

Now if radium is changing at this rate, its production must keep pace with its waste; else it would all have disappeared during the enormous period of time of existence of the minerals in which it is found. The natural supposition is that uranium, the main constituent of the pitchblende in which radium invariably occurs, may be changing continuously into radium. This conjecture is strengthened by the fact that the amount of radium in such minerals always bears a constant ratio to that of uranium. But very careful experiments by Mr. Soddy, in which he freed a solution of a uranium salt completely from radium by repeated precipitation of the radium with sulphuric acid in presence of a barium salt, showed that the rate of formation is by no means so rapid. That radium is formed appeared to be proved; but not at the expected rate.

The spectrum of the radium emanation has also been observed. The process of obtaining the pure

gas was practically the same as the one already described; but a minute Plücker's tube was substituted for the capillary measuring tube. The character of the spectrum is analogous to that of the inert gases; it is characterised by a number of clearly-cut lines, chiefly in the green region. Their position has been accurately mapped by Watson and others. These lines have been observed to be present in the spectra of many of the fixed stars.

The disruption of the radium molecule is accompanied by a relatively enormous heat evolution. Rutherford has found that of this heat, 75 per cent is derived from the emanation and its subsequent products of change. The Curies found that 1 gram of radium evolves no less than 100 calories per hour; hence 1·3 cubic millimetres, the amount of emanation yielded per hour by one gram of radium, must be responsible for 75 calories. Comparing this with the heat evolved by a violent chemical change of the ordinary character, the difference is enormous. One cubic centimetre of emanation, were it possible to obtain it, would evolve about seven and a half million calories during its complete change; while a cubic centi-

metre of mixed oxygen and hydrogen gases evolves on explosion only 2·05 calories, or 3·4 million times less than the heat of disruption of an equal volume of emanation—that is, on the ordinary assumption of an equal number of molecules. The process of change of an atom, therefore, while the same in kind as an ordinary chemical reaction, differs entirely in the magnitude of the result: the amount of energy parted with during the disruption of an atom is hardly commensurable with that due to its combination with another atom to form a compound.

That a charged electroscope always leaks on standing, and is slowly discharged, has been a subject of annoyance to physicists ever since its invention. It was for long supposed to be due to damp. As a matter of fact, if the insulating rod from which the gold-leaf is suspended be of glass, the discharge of the electroscope is closely connected with the hygrometric state of the atmosphere; for glass is attacked by water, especially if, as is always the case in natural air, carbon dioxide is present. The solution of carbonic acid, no doubt, decomposes the glass, forming sodium carbonate; and in moist weather a conducting film is formed

on the glass consisting of a solution of that salt. Hence leakage takes place along the supposed insulator. But if material be employed which is not acted on by water, such as sulphur, ebonite, amber, or fused quartz, the electroscope still slowly discharges; and it has often been shown that the moisture of the air has no connection with the observed leakage. The earth appears to be negatively electrified: for if a wire, in contact with the earth, extends upwards into the air, a negative charge continuously leaks away. And the leakage, if the wire be insulated from the earth, is less in damp than in dry weather; indeed it is least during a fog. The ions of atmospheric gases are trapped by the small water-particles of a fog and removed; and as the leakage depends on the pressure of such ions, anything which diminishes the number of ions in the air produces a corresponding diminution of leakage of electricity. Now, negative ions induce the formation of fog. If air containing moisture be cooled, the moisture will condense. In order that it may condense, unless the degree of cooling be very great, nuclei are necessary. These nuclei may be minute solid particles, such as those of smoke; or they may be ions, either

positive or negative. The negative ions attract the fog particles, and induce liquefaction at a higher temperature than do the positive ions. Hence the negative ions are removed as the fog precipitates, leaving the positive ions still free in the atmosphere. And thus these positive ions discharge a negatively electrified body.

Owing to the rarity of radium and thorium, it was long ere it was suspected that the ionisation of the atmosphere was due to their presence in the soil. But as soon as it was discovered that radio-active gases are products of their disintegration, it became evident that it is owing to the presence of such gases that the atmosphere acquires its discharging power. It was observed by Elster and Geitel, to whom most of our knowledge of atmospheric electricity is due, that the air in underground cellars has a much greater discharging power than that of the free atmosphere; and this suggested a source for the ionisation of the air—namely, the presence of a greater amount of radio-active gas.

Now Rutherford showed that when the thorium-emanation decomposes, its products are attracted by a negatively electrified body, such as a platinum

wire connected with the negative pole of a battery of several hundred volts. Elster and Geitel, therefore, tested for such products by connecting an insulated wire, suspended in the air, with such a source of negative potential for several hours; and it was easy to prove, by coiling the wire and transferring it to an electroscope, that the "induced activity" due to the presence of the decomposition product of radium emanation was present on it. That this is really a material coating on the wire is shown by the fact that it can be removed by polishing the wire with sand-paper, or by treating it with an acid, so as to dissolve off the superficial layer. The coating is specially rich if the negatively charged wire is exposed to air from subterraneous sources. The activity has usually been traced to radium emanation, though proof has been obtained that the decomposition of thorium emanation is also responsible for the radioactivity. This can be done by measuring the period of decay of the "induced activity," which differs in the two cases.

Closely connected with these phenomena is the radioactivity of mineral waters. The waters of Bath and of Harrogate, as well as those of some

German mineral springs, have been shown to contain radium emanation in solution; and Strutt has found that the deposit on the sides of the Bath springs contains a minute trace of radium. J. J. Thomson, too, has proved that water from deep wells near Cambridge is radioactive. Indeed, radium appears to be a widely-spread element, although it occurs in almost infinitesimal quantity. Such waters, no doubt, give off their emanation to the air; and as the life of the radium emanation may be taken as about a month, much survives in the air and, by ionising its gaseous constituents, confers on them the power of discharging an electroscope. The emanation from thorium, or rather from radiothorium, has a much shorter period of life; it may be reckoned as at the most ten minutes; hence its radioactive power is soon exhausted, and it can be detected only near the soil. It is a remarkable fact that thorium emanation is produced from some soils in quantity much greater than can be accounted for by the thorium which they contain, and it is to be presumed that this is due to the presence of radiothorium in quantity far too small for detection by any analytical process.

One other fact remains to be noted in relation to the gases of the argon group: we can tell the origin of helium and neon in the atmosphere. Much, if not all, of the helium is the product of the change of radium, thorium, and actinium; whence comes the neon?

It was noticed in certain experiments carried out by Cameron and Ramsay, on the action of niton on water, that besides decomposing water into its constituent elements, oxygen and hydrogen, and besides setting free helium, which was easily recognised by its spectrum, the spectrum of neon was observable, so bright that it could not have been due to mere traces. The theory was put forward that both helium and oxygen being "nascent," that is, in process of being formed, it was not inconceivable that combination might occur; the atomic weight of oxygen, 16, plus that of helium, 4, gives when added 20, which is almost exactly the atomic weight of neon.

Additional evidence is found in the gases which escape from the hot springs of Bath. They consist mostly of nitrogen, but contain both helium and neon; argon is also present. The water contains an appreciable amount of radium, and the gases

which escape are rich in niton, relatively to ordinary air. Now in these gases there exist about three-quarters as much argon as is present in atmospheric air, one hundred and eighty-eight times as much neon, and seventy-three times as much helium. It cannot be doubted, therefore, that both the helium and the neon are products of changes produced by radium in presence of water.

Professor Norman Collie, and simultaneously and independently Mr. Patterson, found that on passing a high tension discharge from a Ruhmkorff coil through rarified hydrogen, between electrodes of aluminium, the hydrogen rapidly disappeared, and on examining the contents of such tubes both helium and neon were found. This was confirmed by frequent experiments; and Mr. Irvine Masson was also able to prove the presence of helium in the gases pumped out of a Cooper-Hewitt lamp of fused silica, under conditions which precluded its entry from the air. It would appear, therefore, that helium and neon can be formed by powerful electric discharge. For the formation of the latter, oxygen is apparently necessary; for if the apparatus be so arranged that the glass tube is not bombarded by the kathode rays, little if any neon is formed.

The formation of helium and neon has also been shown by Sir J. J. Thomson, in a similar manner, but testing for their presence by a totally different method of great ingenuity. Their presence is undoubted, but Sir Joseph does not unreservedly adhere to the view that they have been "synthesised"; he prefers to reserve judgment.

It would seem not improbable that the passage of lightning through ordinary moist air may be accompanied by the transmutation of certain atmospheric gases into neon and helium, and that their presence in air is at least partially due to that source. The writer has also evidence, which, however, he does not regard as conclusive, that argon may be formed by submitting sulphur vapour and hydrogen to a continued passage of kathode rays. But further research is needed before it can be positively affirmed that that is the case.

The investigation of these remarkable gases is still very far from complete; we know only where niton should be placed in the periodic table, that is, below xenon; but in all probability the other two active gases also belong to the argon group. They must now be reckoned with as normal constituents

of the atmosphere; and although the proportion in which they are found is almost inconceivably small, it is still possible that the enormous quantity of energy with which they part when they undergo their inevitable change may make them potent factors in relation to living plants and animals. To sum up: we see that the words of Boyle, quoted on p. 9, are almost prophetic when he stated that "Our atmosphere, in my opinion . . . consists in great number of numberless exhalations of the terraqueous globe . . . with perhaps some substantial emanations from the celestial bodies." It is indeed conjectured that corpuscles, almost inconceivably minute, which have been termed "electrons," and which are shot off with enormous rapidity during the changes which the radioactive elements undergo, are actually constituents of our atmosphere; that they owe their origin to the sun; and that they contribute to the electrification of the atmosphere, and are the cause of the Northern Lights, or *aurora borealis*.

THE END

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