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Plate I



ROBERT BOYLE

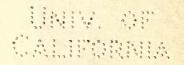
BY

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WITH EIGHT FULL-PAGE PLATES AND OVER FORTY DIAGRAMS IN THE TEXT



CASSELL AND COMPANY, LTD. London, New York, Toronto and Melbourne 1911

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PREFATORY NOTE

THE aim of the authors in this volume has been to produce neither a treatise on chemistry nor a dish of popular tit-bits from that science. Both of these tasks are at the present time unnecessary. But there seemed to be room for a volume intermediate to them. appealing, on the one hand, to the young student who is beginning a serious study of chemistry; and, on the other, to the intelligent general reader who, having a genuine interest in science, is nevertheless unable to follow up any one branch of it in close detail. No science can be made altogether easy, even in its elements: and in their choice of material the authors have not been concerned to evade the true difficulties of the subject. They have rather sought to expound, in suggestive outline, a few of the facts and theories of modern chemistry; to set the thoughtful reader thinking about some of Nature's constructive processes; and to stimulate him in the scientific spirit and method.



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CHAPTER I

SOME IDEAS ABOUT MATTER

I.—THE AIMS OF SCIENCE

THE stimulus to all learning and all science is the desire to *know*, which is one of the inherent properties of the human brain. This desire, becoming more eager and more insistent as mankind has advanced in civilisation, has been the motive power of all arts and all philosophies; it has led to the building of the noble temple of modern science, and it is guiding many explorers across the dark ways into the unknown.

It seems to arise from two apparently distinct needs of human nature. In the first place, man must live—eat, dress, and house himself. The more he knows about the things and laws of nature, the better he can accomplish this; and hence arises practical science—farming, cookery, metal-working, quarrying, engineering and the like. Man has desired to improve upon his knowledge of such arts as glass-making or dyeing, in order to satisfy his natural needs; and thus every branch of natural science has a great stock of such practical and "useful" knowledge to attend to.

But, over and above all this, there is, in the second place, the desire to know per se—the pure desire of

the mind. Man must think as well as live; he must fathom as far as may be the causes of things; he must soar to the beginning and to the end. Therefore there arises speculative or *theoretical* science—cosmogonies, atomic hypotheses, and so on.

These theories have done harm sometimes, but on the whole much more good. It has been evil for science when its two aspects have been held asunder. Progress has been rapid when they have worked hand in hand. Harness a theory to verifiable facts, and it is well for both; permit it to run amok, and invaluable truth may be overshadowed. The raison d'être of theoretical science is to interpret and to arrange the facts of practical science.

For these facts are many, varied and bewildering. The untutored mind, observing nature for the first time, is lost amid the labyrinth of the phenomena it perceives. And when it begins to inquire into the meaning and causes of what is seen, mystery is heaped upon mystery at every step. The perception of this mystery is the first step towards a real knowledge of nature. The familiar and the obvious are no less mysterious than the uncommon and out-of-the-way; we wonder over radium or a comet, but we accept, unquestioning, water or the movements of the moon.

Once the mind has been perplexed by the aspect of mystery, it must attempt to solve the riddle it has aroused; it begins to form a theory. If it does this in a scientific manner, it will make sure first of its observations; thence will issue some formula, or form of words, which will contain in itself a general expression of the whole of the facts. As thus: the movements of the moon are recorded over months, and provide

THE SCIENTIFIC METHOD

a confused array of figures; upon them we build the theory that the moon moves round the earth in such and such an orbit in a definite time; from this we infer the position of the moon at some future time. Does this turn out correct? If so, the theory is serviceable; it comprehends many facts in a simple statement.

This indicates the method to be adopted in science—the inductive method, from observation to inference, from practice to theory, the theory acting as the illuminator and interpreter and prophet of the real fact. This book, we hope, will be a simple illustration of the power and, at the same time, of the fascination of the scientific method.

II.—THE PROBLEMS OF CHEMISTRY

THE fundamental mystery of the science nowadays called chemistry is the nature of matter. By matter we mean the actual substratum of sensible things, the reality which is the ultimate basis of all the objects of sense. When we speak of the material world, we refer to that part of the universe of things that is perceptible by the senses. There are philosophers who, following out a strict logic, are sceptical concerning the real existence of matter. We have a sensation of hardness, of whiteness, of shape, and so on; these sensations blend in the mind into the image of a piece of wood; and we do not hesitate to say that there is a real piece of wood, an actual something, which exists apart from our sensations of colour, touch, etc., but which we cannot perceive without them. We may be wrong in our simple supposition; yet our belief is apparently in accord with thousands of everyday

experiences. The objects of our mind correspond with real objects outside it; and matter is the basis of all of these. What the nature of matter is—that is the question which philosophers have posed for themselves; they have answered it to their satisfaction, but not finally; and the patient labour of a century of chemists leaves the problem illumined, but still unsolved. How near and how far we are from the ultimate truth, we may be able to show; at least, our present theories have faced the riddling criticism of an army of experimental facts, and have been tempered accordingly.

What is the problem before us? It is to investigate the nature of wood, iron, water, air, granite, and the many thousand different kinds of matter with which we have become familiar. As we stand on the threshold of our task, the manifold variety of the substances with which we must deal might well appal us; and our difficulties are enlarged when we contemplate the changes through which every form of matter may pass under various circumstances. Wood can be charred; iron rusts; water evaporates; granite crumbles. These changes, and the conditions under which they occur, are all added to the burden of the student of chemistry. And certainly the science would be overloaded with its facts, if its theories did not come to the rescue. We shall see how they have educed from the chaos some sort of order; how diversity tends to give place to unity, and complexity to simplicity. The story of chemistry is, when fully told, a thrilling history of man's growing practical knowledge of the various kinds of matter-of metals, minerals, fluids, foods, drugs; it tells of a growing mastery over the

OBJECTS OF CHEMISTRY

processes of nature and the mutations of things; and it celebrates an ever-deepening insight into the fundamental laws and the ultimate constitution of the material universe.

III.—Achievements and Theories of the Ancients

From immemorial antiquity men have extracted metals from their ores; but the necessary processes, though chemical in their nature, were, of course, not understood, and were carried out entirely by rule-ofthumb methods. These must not, however, be hastily despised: rather is it matter for wonder that metals like iron, copper, or tin should ever have been made at all. Moreover, the Egyptians at least had attained real skill in the treatment of seven of the metals-gold, silver, copper, iron, lead, tin, and mercury; and there is every reason to believe that they were acquainted with the manufacture of glass. This implied a knowledge of soda, which had to be obtained from salt. The use of soda and potash in soap-making was also known to the ancients; and among other manufactured or extracted products very early known were turpentine, sugar (from starch), blue vitriol, and alum, the latter being employed in dyeing. Natural dyes and pigments were also known.

All this represents many centuries of progress, and is, in fact, a very remarkable body of achievements, considering the circumstances. Yet, while the hand had been industrious, the brain had not been idle. No science was possible until thought was made to operate upon the facts empirically known. But, unfortunately, thought disdained common practical matters;

it turned its face at once to the highest and most difficult problem of all: it sought to explain the constitution of matter, but took no heed of the known behaviour of matter in its most familiar forms. Thus much of it has vanished into ghost-land; it was from the first intangible and inane, having no relation to real things. Still, the intellectual activity implied in speculation was not wholly vain; it was a good thing in itself, and produced many valuable results. To Egypt came the Greeks; imbibed there the spirit of inquiry and the ambition to know; returned, and for many centuries were the scientific teachers of Europe.

Two very valuable ideas emerge from the bold and determined thinking of the Greek philosophers. | These are the idea of elements, and the atomic conceptions of Democritus. Probably, the first of these came originally from Egypt: the word, or the idea it conveys, is familiar in the thought of Thales, the earliest natural philosopher of Greece. But it is to Aristotle (384-322 B.C.) that we owe the fact that for a great many centuries the Greek elements were accepted as the real elements; indeed, the word has scarcely died out of figurative use at the present moment. Aristotle was a great philosopher—one of the world's mighty thinkers; but he was not a great scientist; and the best logic, unsupported by observation, is not competent to elucidate the constitution of matter. The influence of Aristotle's name upon the science of succeeding centuries was almost wholly bad; authority took the place of personal observation and thought, and the result was stagnation.

The mind's desire in facing the manifold variety of phenomena is simplification. Hence it was natural

THE FIVE ELEMENTS

that a mere thinker should conceive that the different substances were compounded of a few simpler materials in varying proportions; these simpler materials would be the elements out of which every kind of matter could be formed. The Greek philosopher could have known very little to support such a doctrine; the consequence is that his elements are not our elements, and that whereas our elements are, approximately at all events, the raw material of the universe, his turn out to be mere abstractions. It seems to have been Empedocles (c. 450 B.C.) who first clearly taught the definite doctrine of the four elements—air, fire, water, earth—as the origin of all things. Out of nothing, nothing comes: in the beginning were the elements, and out of them arose all the varied forms of matter. Later, further simplification was attempted; a fifth element, the quinta essentia, or quintessence, was supposed to unify the others, to be a more refined extract, as it were, common to all four. It is small wonder that such a doctrine captured the intellects of men who were bent on describing the world in the simplest and clearest terms. It was a most vital idea right into the eighteenth century. "Does not our life consist of the five elements?" asks Sir Toby Belch in Twelfth Night. It was the commonplace science of Shakespeare's day.

This theory of the five elements was the first chemical theory that had any force in it. We do not acknowledge the elements as such now; but we must be careful not to scorn them; our elements may quite well become the joke of a future day. One Greek philosopher, Anaxagoras (c. 550 B.C.), seems to have vaguely perceived that the five elements were not

sufficient; he assumed a large number of "seeds" of things, by whose interaction and combinations among themselves the varied materials of the universe arose. His speculations had, however, little or no influence; whereas those of Aristotle became a philosophical tradition, accepted unthinkingly. We are to learn from the Greek teachers, not that speculation is dangerous or wrong, but the futility of not checking them by an appeal to Nature and to experiment.

By Empedocles the four elements were, it appears, conceived as real material things, unchanging and unchangeable in themselves; but caused to unite or separate by "loves" and "hates," attractions and repulsions, which corresponded very closely to what modern chemistry calls chemical affinity. Some powder of the metal antimony will take fire readily in chlorine gas, but remains inert and unaltered in nitrogen gas: in some sense antimony "loves" chlorine, but not nitrogen; and if we ascribe the "love" to an attraction which results from opposite electrical conditions in the substances which "love" each other, we are still far from appreciating the real nature of the attraction: we have scarcely been able to conceive a theory of it as yet. And the picture of the world, as apparently conceived by Empedocles, is an acute and not contemptible one. He does not get lost among his abstractions. He sees the four material elements, held together by the play and interplay of non-material and imperceptible forces; whereas we see an uncertain number of elements, charged possibly with electricity, whose essence we know not, and endowed with nonmaterial energy, whose nature is almost as evanescent in the mind as the "loves" and "hates" of Empe-

GREEK SPECULATIONS

docles. It is told of him that, despairing of the possibility of penetrating to the ultimate essence of knowledge, he ended his life in the crater of Etna. We shall see that modern philosophers with their fuller knowledge of the nature of matter would have almost as good a reason as he to seek an untimely end.

The merit of Empedocles was that he was, in chemical matters, a materialist; he built his world out of real things-not essences, nor properties, nor any other abstraction. But he was not, and could not be, equipped with the accumulated statistics of science, which make the merest tyro in chemistry able to derange his speculations. He had undoubtedly watched such natural processes as came under his ken; and he had thought long and well about them. But there were not enough of them within his range; and another century did nothing to increase their number. So that when we come to Aristotle we find the four elements conceived in less clear and less materialistic forms. The Aristotelean elements were transformable among themselves, and thus had no right to the term element at all. In this later phase of Greek thought the "element" air was conceived as a combination of the properties of "hotness" and "moistness"; in fire, "hotness" and "dryness"—in water, "coldness" and "moistness"—in earth, "coldness" and "dryness" were united. Exchange moistness for dryness and you turn air into fire, or water into earth! Such a simple fact as the existence of a solid residue after the evaporation of natural waters was held to prove the transformation of water into earth. Thus, indeed, the earth was formed from the sea. This is evidently the reductio ad absurdum of speculation.

Contact with the actual world is lost; thought has become phantasm; and in the world of ghosts all twists and leaps are possible. In certain branches of natural knowledge—physics, astronomy, and natural history—the Greeks had begun, and were to continue, along the true path; but in chemistry they produced neither a Hipparchus nor an Archimedes.

The idea that there is, beneath the manifoldness of things, an underlying unity is attractive and possibly true. From this idea arose Aristotle's fifth element, the ether, the immaterial essence from which all material things originated, the Nirvana or nothingness of Buddhism, into which all things are ultimately developed. The idea of one fundamental element is, however, much older than Aristotle. Thales, in the sixth century B.C., probably deriving from Egypt, saw in water the primordial principle; his successor, Anaximenes, found in air the mainspring of all life and the foundation of all matter. Up to the present day the most scientific thinkers are fascinated by the thought that the diversity of matter will probably be reduced to simplicity, that one fundamental something lies at the basis of all the forms of matter. Armed with the unassailable suggestions of observed facts, we are eager to reduce our modern elements into our modern ether—as mysterious a quintessence as ever Aristotle's was. What we make of the ether, we shall see in our last chapter: what the other elements of the Greek speculators have become we are to gain a little notion of on the way thither. We at present convict the Greek elements of a vagueness in their definition; not until the time of Robert Boyle (1627-91) do we come upon a clear sense attributable to the word. His definition

ELEMENTS AND ATOMS

is ours. An element must be regarded as a substance which cannot be simplified or analysed into anything other than itself. Iron cannot be reduced into any form of matter simpler than itself; out of iron nothing but iron can yet be extracted; so, iron, with some eighty other substances, must at present be accounted an element. Chalk, on the other hand, can readily be reduced to simpler substances by the mere application of heat: it is not an element, therefore. We are to learn that some of the ancient elements will not stand the test of this definition. We must not rashly take general ideas in hand in science; they cannot be exactly expressed until the particular facts of which they are properly made have been examined and appraised.

The other theory of the Greeks, however, demands our notice on account of its acuteness and fruitfulness. It is unsatisfactory to be reducing matter—hard, material things—to "principles," quintessences, ethers -mere ideas of the brain! Let us follow Democritus, the materialist "laughing philosopher" of Abdera. He shivered matter into atoms. But the atom was still matter-matter in its indivisible, fundamental form. In the beginning was a concourse of falling atoms; somehow these atoms were formed into groups and aggregations; thus matter arose, sensible and gross. Democritus, and Lucretius after him, could find nothing in the universe but atoms and void and motion. Were the atoms all alike? Has each atom the same properties as matter itself has? Lucretius, expounding the subject in the first century A.D. in his De Rerum Natura, a true scientific poem, answers with full arguments, No! The differences between the varied forms

of matter demand atoms of different shapes and sizes, interposed by more or less void. A finite number of different kinds, he is careful to insist upon; so that he recognized a finite number of elements, much as we do, and, with splendid insight, developed a theory of the evolution of worlds. His poem is a monument of acute thought; the atomic hypothesis which it celebrates is perhaps the most profound scientific idea that antiquity has bequeathed to us. The thought slept for some eighteen centuries. The advance of chemistry made it necessary to us, and now it is the commonplace of science. In imagination we split matter into its ultimate "uncuttable" or atomic parts; we have notions about the properties of these atoms, and have even arrived at some tenable idea of their weight; we are even speculating further and reducing them to the finer electrons—showing that the atom, and consequently matter itself, is but a transient phenomenon after all. (See Chapter VII.)

IV -ALCHEMY

From the enlightened Greeks into the morass of the Dark Ages is an unpalatable step: confused, and largely unprofitable, were to be the workings of science for many centuries. The spirit of inquiry, so bright in Athens and Asia Minor, honourably kept aflame by such as Lucretius and Pliny in the golden time of Rome, did not so much as flicker in the waste of those ages. Chemistry in particular fell under an evil spell. Alchemy throve—among the ignorant largely by imposture, among the initiated by means of a vast lumber of incomprehensible jargon. Even when the Renaissance awoke Europe, it did not expel alchemy.

THE ALCHEMISTS

Ben Jonson has exposed the alchemist of his day in his vivid play of that title (1610), and certainly does not exaggerate the absurdity of the alchemist's formulæ and beliefs.

Read the following catechism of Face by his master Subtle, for an instance:—

Subtle: Sirrah, my varlet, stand you forth and preach to him
 Like a philosopher: answer in the language.
 Name the vexations, and the martyrizations
 Of metals in the work.

Face: Sir, putrefaction,
Solution, ablution, sublimation,
Cohobation, calcination, ceration and
Fixation.

Subtle: This is heathen Greek to you, now!—
And when comes vivification?

Face: After mortification.

Subtle: What's cohobation?

Face: 'Tis the pouring on

Your agag regis and

Your aqua regis, and then drawing him off, To the trine circle of the seven spheres.

Subtle: What's the proper passion of metals?

Face: Malleation.

Subtle: What's your ultimum supplicium auri?

Face: Antimonium.

Subtle: . . . And what's your mercury? How know you him?

Face: By his viscosity,

His oleosity and his suscitability.

Subtle: How do you sublime him?

Face: With the calce of egg-shells,
White marble, talc.

Subtle: Your magisterium now. What's that?

Face: Shifting, sir, your elements,

Dry into cold, cold into moist, moist into hot,

Hot into dry.

Subtle: . . Your lapis philosophicus?

Face: 'Tis a stone,
And not a stone; a spirit, a soul and a body:
Which if you do dissolve, it is dissolved.
If you coagulate, it is coagulated;
If you make it fly, it flieth.

All which is absurd—doubtless of malice afore-thought—but hardly a caricature of the real thing. Yet this was the only chemistry of the Middle Ages; and out of the dung a few grains of valuable facts can be extracted.

Alexandria seems to have been the birthplace of alchemy; in Egypt the practical arts of the chemist rubbed shoulders with the fantasies of the theorists. The processes of metallurgy attracted the one: the nature of the elements was the problem of the other. It is not difficult to see how, from the idea that the four elements could be transformed one into another, the belief arose in the possibility of transforming the metals into one another, and in particular the attractive chance of changing the base metals into gold.

Facts seemed to be on the side of the transmuters, too. For, is not a steel knife-blade covered with copper when it is plunged into a solution of blue vitriol? And is not the mixing of a little zinc with copper effective in changing at least the colour of the copper, so that it becomes more nearly golden? Steeped in the Greek theory of the elements, the alchemists found it easy enough to conceive their philosopher's stone, their universal solvent or elixir of life—different forms of the essence which could remove all the dross from things. They sought a simple scheme whereby to interpret all material phenomena; they insisted that simplicity was Nature's law, and developed their aim

ALCHEMY

in writings the most turbid and incomprehensible that have ever come from the human mind. Of course, they do not agree among themselves, and no one of them ever attained to a coherent doctrine. The Arabian, Geber, in the eighth century enjoyed as high a repute as any; and in our own country Roger Bacon (c. 1214-94) was famous (or infamous) for his knowledge of the magical arts. An acute, learned, and in some respects scientific thinker was this same Friar Bacon; but Basil Valentine, an alchemist of the seventeenth century, was a more creditable representative of his art. He made many valuable chemical discoveries, though he held to the doctrines of the earlier alchemists. From the confused mass of these, we may perhaps endeavour to sublime the essence; but it must not be supposed that any one alchemist ever had such a clear conception of his ideas.

There were, then, four elements, and a fifth essence transcending them. These "elements," as we have explained, were not material substances, but rather properties; too subtle, at all events, for man to be able to isolate them. But why stop at the four properties of hotness, coldness, dryness, moistness? Are there no others? There is colour, there is lustre: gold is a union of lustrousness and yellow! In order to make gold these properties have merely to be brought together; and that is what the philosopher's stone was to effect. The property of lustrousness exists supremely in mercury, the yellow substance in its pure condition is sulphur. Guessing vaguely upon the basis of these ideas, three "principles" came to be added to the four elements. These were mercury, sulphur, and salt. All metals were supposed to contain these

three "principles," not the three substances which we associate with their names, but the "principles" of lustre, colour, and solidity. The "salt" is a later addition, and not universal; the commoner view was that metals differed among themselves only in the proportion of mercury and sulphur that they contained; and if, by any process, the proportion of the sulphur-principle could be diminished, a step nearer to the noble metals was made. It was, therefore, the alchemist's aim to study those processes by which "sulphur" was driven out of the metals. They saw that the metallic characters of some metals were lost when sulphur was heated with them; naturally they inferred that sulphur was the evil spirit which thwarted the refinement of the mercury-principle in the metals.

It must be understood that the alchemists did not regard mercury or sulphur as identical with the substances thus named. They were conceived as compound principles formed from the four elements. Mercury was, according to their notions, produced when air acted upon water; sulphur when fire acted upon air; salt by the interaction of water and earth. Thus the metals were composed of the four elements, but only at second hand, as it were; other substances, such as clay, chalk, the metallic ores, were more impure and still more remote from the pure nature of the elements.

Fantastic theories like these, worked out in elaborate treatises and with a terrific apparatus of philosophical terms, arouse little more than a scoff to-day; but they were not wholly useless; they led to much calcination, sublimation, distillation, cohobation, filtration and what not, and incidentally to a large accumu-

IDEAS OF THE ALCHEMISTS

lation of chemical facts and preparations. The meaning of these experiments was often tortured to fit the theories; but the work done on acids and in the preparation of metallic salts was valuable all the same. The authority of the Greek conceptions hampered the alchemists as students of Nature: they were not men of science, because they did not face their facts with unprejudiced minds.

The alchemists did not confine themselves to the study of the metals in all cases. One of the most famous of them was Paracelsus (c. 1493-1541), who did much work on the connection between alchemy and medicine. Paracelsus, in spite of a violent gift of disputation, seems to have had the root of the matter in him; and to have spent his turbulent career in the pursuit of knowledge. The human body was supposed to be formed of the same elements and principles as other matter: mercury, sulphur, and salt unite in its composition; any excess of either produces some kind of illness; and the object of medicine was to prescribe drugs which re-establish the correct proportion.

Many preparations of mercury and sulphur, as well as other drugs such as laudanum, we owe to the medical experiments and theories of the alchemists. But we cannot pursue the matter here. It is sufficient to have indicated the point of view of those who, in whatever obscure corners, kept alight the torch of chemistry during the Middle Ages, and to have shown how an unscientific method made their speculations vain. As a result of the work of many learned seekers, we have a collection of facts (which they did not value much), but we are brought no nearer to their just comprehension; nor do we gain even a little light

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upon the fundamental problem which they attacked—the ultimate nature of matter. We do not complain because their ideas were wrong: probably transmutation of the elements has already passed out of dreamland into accomplished fact. They erred because they did not proceed in the right direction—from experiment to theory.

V.—CLEARER NOTIONS OF CHEMICAL ACTIONS

It was during the eighteenth century that the alchemists gradually became chemists, and the scientific examination of the nature of matter took a more promising turn. We find much attention now given to the "elements" air and fire-in modern language to the properties of gases and the facts of combustion. In our later chapters we shall explain as much of this work as seems needful; here let us merely state that by the year 1810 the true nature of air and water was known. Chemists had come to look upon weight as the sure criterion of a material substance; attention was fixed upon the actual matter, which was regarded as the unaltering reality at the basis of things. Careful weighings of all the substances used up in chemical operations and of all those produced led to the law, so far uncontradicted by a single reliable fact, that matter is indestructible; the total amount of matter—the total mass, as it is called-of all the substances engaged in a series of chemical changes can neither be increased nor diminished, whatever the changes may be. Matter may be transformed, but never obliterated. When one substance is transformed into another it is not by the loss or gain of certain non-material or evanescent

INDESTRUCTIBILITY OF MATTER

"principles"; it is by the elimination or addition of some other substances.

Let us follow a simple case. A piece of sulphur is burned; it disappears in the form of a choking fume. According to ancient theory, sulphur consisted of air and fire; if you burn it, the fire-element or principle escapes, leaving an impure air. No: we ask for something more tangible. We weigh, say, I oz. of sulphur; we can weigh the resulting fumes, and find them 2 oz. The loss of the fire-element has made the sulphur heavier then? It is unthinkable now. Evidently the sulphur must have had some matter, some substance, added to it somehow, in order that it might become sulphur-fumes. We now know that it is the air that vields this additional substance—one ounce of it to every ounce of sulphur. Cork a little sulphur in a glass flask, and weigh it. Then gently warm the sulphur until it takes fire. When the burning ceases, weigh again, and you will find neither loss nor gain in weight. The matter in the flask, sulphur and air, has been altered and transfigured; it is still there, every grain of it. The greater the care taken, and the more refined the experiment, the more striking is the confirmation of the law that matter is not destroyed or created. This is not, it will be seen, a mere speculation: it is science Its credit is not derived from Aristotle or from Roger Bacon, but from Nature and experiment.

It will be seen that it was the use of the balance that gave the death-blow to the ancient theory of elements. Air, water, and earth are material things because they can be weighed. It was not yet recognized that fire, *i.e.* heat, stands in a different category: the true nature of heat was left to the nineteenth

century to elucidate; while the twentieth century is concerned with the ether as the possible ultimate quintessence of things. It is possible that matter can be resolved under certain very special conditions into something which is not matter, in the sense that it is capable of being weighed. However this may be, it is very important to realise that air is as truly a material thing or substance as wood or water. A piece of copper becomes heavier when it tarnishes, because something heavy from the air has been added to it. In reality the copper has been partly transformed into a new substance, copper oxide, by the union of some of it with the oxygen of the air. Such a change as this, involving the formation of new substances, is called a chemical change. It is by the careful study of such changes that the science of chemistry has been built up and our knowledge of the properties of matter in its many forms greatly increased.

A chemical change may consist, as in the case of the tarnishing copper above mentioned, in the formation of a complex substance from two or more simpler ones; such a process is called a *synthesis*. The process is not called chemical, it must be observed, unless a new substance is formed, different from the originals. The red copper and airy oxygen are very different from the black tarnish which nevertheless contains them both. Whatever the copper and oxygen themselves may be, clearly the black tarnish is not an entirely simple substance; it is what is called a chemical *compound* of copper and oxygen, to be very carefully distinguished from a *mixture* of the two in which neither is changed. Thus the results of the processes of synthesis are compounds of continually

CHEMICAL CHANGES

growing complexity. Many of the beautiful aniline dyes are compounds of a complex nature, formed by synthesis from simpler compounds found in coal-tar.

The opposite process to synthesis is called analysis, and is equally powerful as a weapon of investigation and discovery. Any substance which, by the aid of heat alone and in the absence of all other substances, yields us two or more other substances must clearly be a compound of these, although these in their turn are not necessarily simple. Thus heat is able to analyse chalk into two constituents, lime and carbonic acid gas-revealing the fact that chalk is a compound substance. Other processes, however, are needed to show that both lime and carbonic acid gas are compounds also. The methods of analysis are numerous and varied; their results, notwithstanding, can generally be confirmed by synthesis. It is as easy to form the compound chalk by a union under suitable circumstances of its components, lime and carbonic acid gas, as it is to decompose it into them.

Applied to all substances alike, the methods of chemical analysis lead us to our modern conception of *elements*. They are simply those substances which cannot be analysed in any way into simpler substances. There are some eighty or ninety of such undecomposable forms of matter known to us at present, and additions are being made to the list from time to time, chiefly in the form of very rare metals. Of the original Greek "elements" none belongs to our modern category. Water, for example, can easily be shown, both by analysis and by synthesis, to be a true chemical compound of two substances, hydrogen and oxygen, which in their turn are, according to

present knowledge, true elements. But, it must be remembered that our modern elements are real material substances, not indefinable "principles"; and our present state of knowledge forces us to suppose that there are at least eighty or ninety different kinds of matter contributing to the architecture of the material universe. The nature of the forces which regulate the combinations of the elements, whether we name them chemical affinity or electrical attractions, is still unknown to us—is as mysterious to us as the "principles" which the Greeks associated with and ascribed to their four elements.

Our problem in chemistry, however, is not primarily this; we are chiefly concerned with the nature of matter, and the nature of matter means the ultimate nature of our eighty or ninety elements. From these arise the manifold compounds which in their thousands are found in the earth or are manufactured artificially; from them we can in imagination form the crystal, the living organism, the utmost stars. But what are they? The infinite is reduced to eighty: the mind insists upon reducing the eighty still further. Eighty different kinds of fundamental stuffs are too many for our philosophical instinct; we hanker for the simple four, or for the quinta essentia, of the Greek thinkers. In our last chapter we shall see what is to be said scientifically in response to our natural desire. This much we may say here: no substances were more like elements in their behaviour, in their possession of a unique property, than the alkalis potash and soda, until Sir Humphry Davy decomposed them by the then new process of electrolysis, and gave us the extraordinarily active elements, potassium and

SIMPLIFICATION OF THE ELEMENTS

sodium; so that it may well be that the metals will be shown by some new-found and up-to-date philosopher's stone to be not elements, but compounds. It is, however, necessary for the present to regard our eighty elements as the foundation-materials for our study of matter.

VI.—THE NEW THEORY OF ATOMS

In the hands of Lavoisier, Cavendish, and the other pioneers of scientific chemistry, the problems of analysis and synthesis reduced themselves to a quantitative, and not merely a qualitative, determination of the elements present in compounds. It is not enough to know that water contains hydrogen and oxygen; we must go further, and know that the weights of each are in the proportion 1:8. Now, experiments tending towards the exact determination of these proportional weights in a number of compounds were carried out in the first instance by a Spaniard named Proust; and after him came John Dalton with a series of classical researches which formed the basis of the atomic theory of chemical changes with which his name will be permanently associated. Proust's experiments led him to the truth, which Dalton's work clinched, that chemical compounds were of fixed and unchanging composition. Wherever we find water, for example, we shall find its composition to be that stated above. In 9 oz. of water there will always be I oz. of hydrogen and 8 oz. of oxygen. This constancy and uniformity of composition has become, in fact, the criterion of a pure chemical substance; and any chemist who came across a contradictory result would at once suspect either the method of his experi-

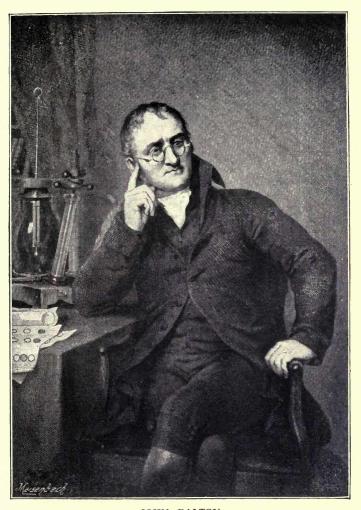
ment or the purity of his materials. This law of "Definite Proportions" is indeed the bedrock of exact chemical science.

Dalton's work was done with the crudest of apparatus, but it led to still further results of great consequence to the future of chemistry. It was known to him that two gases, then known as carburetted hydrogen and olefiant gas, now named respectively methane and ethylene, were both reducible to the same two elements, carbon and hydrogen. Each of these two gases being a chemical compound has its own constant composition: that of methane shows I part by weight of hydrogen for every 3 parts of carbon; while in ethylene the proportions are 1:6. Dalton's results were not exactly these; but they were good enough to enable him to deduce from them the laws and the theory which will always go by his name. For it will be seen that in ethylene there is twice as much carbon, proportionally to the hydrogen, as we find in methane. The same sort of result issued from a study of other compounds; in particular, we ask our readers to note the following further case:-

In carbonic acid gas there are 3 parts of carbon to 8 parts of oxygen.

In carbonic oxide gas there are 6 parts of carbon to 8 parts of oxygen,

It will be observed that it is precisely 8 parts of oxygen that unite with I part of hydrogen (by weight in each case) to form water. These reciprocal connections between the three elements, carbon, hydrogen, and oxygen, were made by Dalton the basis of his laws of chemical combination.



JOHN DALTON



JOHN DALTON

The question now arises—in true scientific sequence—how are these facts and laws, irrefragably based upon experiment as they are, to be interpreted and explained? Can a theory be evolved from them, wherewith the mind can form for itself a picture of the whole process? Dalton has it ready for us in the guise of the old atomic theory of Democritus and the Lucretius.

John Dalton (1766-1844), the founder of modern theoretical chemistry, was an unobtrusive and humble personality, who retained to the last the broad Cumbrian accent of his early days. His early life was hard, and he lived throughout with Quaker simplicity, and on the frugal fare of the typical philosopher. After a period of private tutorship in Cumberland, he went to Manchester as teacher and lecturer in physics and chemistry; it was there that he wrote the memoirs and made the experiments which led to his new theory. His chemical work dealt mainly with gases; and, considering the rudeness of his appliances, he obtained some remarkable results. His experiments were naturally not very accurate; but he had a genius for generalization, and rarely failed to extract some valuable teaching from his observations. The laws of chemical combination explained above were his most enduring, but not his only, contribution to science. And his conception of the chemical atom was the fitting crown to his work.

The atom was a familiar idea to others before Dalton's time. Newton figured the atoms as hard material particles surrounded by spheres of force; and others had felt that the facts of expansion and contraction made an atomic structure of matter necessary.

It was the existence of diffusion among gases that first threw Dalton on to the atoms. For how could a light vapour like steam be thoroughly mixed with the heavier gases of the air, unless the smallest particles of both were free to move in and out among one another? If it were not for this thorough mixture of the atoms, surely steam would rise to the upper surface of the air, just as cork bodily rises to the surface of water and floats there.

Having obtained a prejudice for the idea of atoms, both from his reading and from his experimental work, Dalton proceeded to apply it to his chemical results. He supposed—and we now suppose with him—that when chemical change takes place it is the ultimate atoms of the acting substances that take part in it. Thus, in a simple case: if we heat a little copper and sulphur together, a black powder, known as copper sulphide, results from the union of the two. This union is not that of a mass of copper with a mass of sulphur; but every atom of copper takes part separately, and combines with one or more sulphur atoms, the result of the whole action being a number of "atoms" of copper sulphide, each one containing both copper atoms and sulphur atoms. We have only to suppose that every "atom" of copper sulphide contains a fixed number of atoms of its two constituents to enable the atomic idea to explain the fixed constitution of chemical compounds. But we must here steer away from a possible source of confusion. The atoms are literally the uncuttable things (Greek à, not; τέμνω. I cut): the atom of sulphur means, therefore, the smallest conceivable particle of sulphur. This smallest particle of copper sulphide, however, cannot

ATOMS AND MOLECULES

be an uncuttable thing; it must at least contain one atom of copper and one atom of sulphur; and consequently it is only the elements whose fundamental particles can be in the strict sense atoms. The term molecule is applied to the collection of atoms that forms the smallest thinkable particle of a compound substance. The term is also applied to groups of similar atoms, which form the smallest particles of the elements that are capable of a separate existence; a jar of hydrogen gas consists of many molecules, each of which we have good reasons for believing to contain two hydrogen-atoms.

Now, suppose that all the atoms of any one element have the same weight and the same properties; we shall then have no difficulty in showing how the atomic theory, thus extended, comprises the laws of combination, discovered by Dalton and verified by many hundreds of later experiments. For, let us suppose that the symbols (H), (O), (C), stand for

the atoms of hydrogen, oxygen, and carbon, and that the relative weights of these atoms are 1, 8, and 3 units respectively. Then clearly the simplest possible combination of carbon and oxygen would be that in which one atom of each is concerned, and we should obtain:

$$\bigcirc$$
 + \bigcirc = \bigcirc \bigcirc \bigcirc (carbonic acid gas).

Relative weights: 8 + 3 = II

Now, if there be any other compound of these atoms, the next simple of the many possible arrangements would be that in which the molecule formed would contain two atoms of the one element along with one of the other: thus—

Relative weights:
$$8 + 3 + 3 = 14$$
 (carbonic oxide gas).

The atoms of carbon being indivisible and all of the same weight, it is easy to see why the proportion of carbon in the second compound must be exactly doubled.

In the case of the other combinations mentioned, our symbolical atomic representation of the composition of each would be—

$$H$$
 + C = H C (methane).
 H + C + C = C H C (ethylene).
 H + O = H O (water).

The reader may easily check the weights involved from the numbers previously given (p. 24). He will also be able to understand how such atoms as Dalton conceived are competent to explain the laws of chemical action. He will also perceive the possibility of affixing to each atom a definite atomic weight, which shall tell, not indeed the actual weight of the atom, but its weight in relation to that of some standard atom. Taking the atom of hydrogen as a standard, so that H weighs I unit, he would be inclined, like Dalton, to write O = 8, and C = 3, as the atomic weights of oxygen and carbon respectively; and those

THE ATOMIC THEORY

the facts given to take into consideration. But Dalton was like many another pioneer: he opened new country, but could not occupy the whole of it. He was conscious of difficulties, which only his successors could overcome. One of these was the consideration of the space occupied by the atoms. Is this the same for all atoms? We will express his difficulty in the form of a simple experimental fact. If hydrogen gas and oxygen gas are brought under suitable conditions, it will be found that only when the hydrogen occupies twice the space taken by the oxygen is the whole of the mixture turned into water. Assuming all atoms to occupy equal space, we should then have—

$$O + H + H = H O H$$
(water).

Relative weights: $16 + I + I = 18$

$$Volumes: I + 2 = 3$$

Thus, one atom of oxygen would unite with two atoms of hydrogen and make one atom of steam; but experiment shows that the steam formed really occupies the same space as the hydrogen did at first, i.e. the same space as two atoms of hydrogen. Here is a discrepancy that Dalton felt: the theory must give way, and all atoms declared not necessarily to occupy an equal space. The difficulty is got over by the assumption that the molecules of all gases, under the same physical conditions, occupy an equal space. The molecule is defined as the smallest particle of any gas that can exist free. If we have a jar of oxygen gas, the gas consists of a vast number of molecules, all alike and all occupying an equal space each. But

each molecule can be imagined split into the smaller atoms, which do not exist alone but (in the case of oxygen) in pairs. [When the molecule has three oxygen-atoms we obtain a rather different gas, ozone.] The molecules of oxygen are split when it enters into chemical combinations, wherein the atoms are the all-important actors.

With this addition the atomic theory of Dalton has been harmonized with all the facts known to chemical science. Our symbols and atomic weights are not those of Dalton; but they spring from his idea. We now represent each atom by a suitable letter or abbreviation of the name of the element; thus H, O, and C stand for the atoms of hydrogen, oxygen, and carbon respectively, each bearing its own atomic weight. Various considerations have led to the choice of the number 16 for oxygen and 12 for carbon, hydrogen still being I. These numbers bear an obvious relation to those given on p. 28. The crude and clumsy symbols (or formulæ) for compound substances are replaced by a more expeditious shorthand; as—

All compounds that can be analysed can be given a formula of this kind, no matter how complex the

CHEMICAL FORMULÆ

substance may be. The mode of calculation can easily be followed from the appended example. Formic acid is the substance examined.

Result of Analysis						Relativ	e S	Simplest
								propor-
Element		Percenta	ge u	veight	0	f atom	is	tion
Carbon		26.1	+	12		2.12	٠.	I
Hydrogen		4.3	÷	I		4.3		2
Oxygen		69.6	+	16		4'3		2
Simplest possible formula—CH ₂ O ₂ .								

The full theory enables us very often to go further and to decide whether $\mathrm{CH_2O_2}$ or $\mathrm{C_2H_4O_4}$ or some larger number of atoms in the same proportional number constitutes the real molecule of the substance. And even more: by the careful study of the actions of a substance we can often gain an indispensable insight into the arrangement of the atoms in respect to one another in its molecule.

In the case of a compound substance the formula is made to stand for the molecule of the substance. The formula CO₂ stands for one molecule of carbonic acid gas, containing three atoms—one of carbon and two of oxygen. Now, in any chemical change, what really occurs is that all the atoms involved redistribute themselves in new combinations, form new molecules, but are never destroyed. This fact enables us to construct chemical equations to represent all the substances that are in any way concerned in a chemical operation, under the condition that not an atom is either destroyed or created. We take a random example from many thousands. When the gases methane and oxygen are exploded together in the correct proportion, they are

completely changed into a mixture of carbonic acid gas and water. We know the formula of each of these substances; we therefore construct our equation—

$$CH_4 + O_2 = CO_2 + H_2O$$

Relative weights: 16 32 44 18

Now, although this quite accurately represents the actual nature of all the materials used or produced, it is in error, because in the original molecules of methane and oxygen we have altogether four atoms of hydrogen, only two of which appear in the final molecules. Two atoms of hydrogen have disappeared in the atomic shuffling that has taken place; and, it will be seen also, one new atom of oxygen has come to light. There is no evidence that two hydrogen atoms can be transformed into one oxygen atom; we, therefore, attempt to reconstruct the equation thus:—

This equation is correct, because in the first place it represents no loss or gain of matter from the operation, and in the second it also represents the proportion in which the gases must be mixed to give the change complete. If more oxygen is taken than is represented in the equation, it will be left unchanged at the finish. This, and all that is implied in the equation, can be completely tested and verified by experiments. Equations of similar nature can be built up from the facts of any and every chemical change, all of which are found to verify the assumption we make, that matter, as tested by weight, is indestructible.

CHEMICAL EOUATIONS

We have thus arrived at this position. The material universe contains a vast number of different kinds of matter. Most of these are compound substances. We can reduce these compound substances to a certain number of undecomposable and, as far as we can at present go, simple substances called elements. The elements themselves are further conceived as made up of the ultimate and indivisible atoms. There is good reason for believing in the reality of these atoms; we assign to them certain definite properties, and call upon them to interpret our chemical laws.

The fundamental question of speculative chemistry is now—what is the nature of the atoms? Are there really eighty different kinds, or are they reducible to few or one? What is the nature of the forces that hold them together, or drive them apart? The various atoms behave in a strangely fastidious manner in obedience to the directions of these forces. The atoms of hydrogen and oxygen hold together firmly in the molecule of water (H₂O), but loosely in that of hydrogen peroxide (H₂O₂), and will not hold together at all in any other proportions. The atoms of nitrogen and hydrogen combine stably in the proportion 1:3 and give us ammonia gas (NH₃); but in the opposite proportion of 3:1, we obtain a violently explosive compound known as azo-imide (N3H). And while all the metals are ready enough to form compounds with oxygen gas; almost all of them agree to refuse hydrogen. The atoms show these preferences, and any theory of the atom must account for them. And again: an atom of oxygen will not exist with one atom of hydrogen alone combined with it, and must needs have two before it will settle down into a stable molecule of

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water (H₂O); whereas one atom of zinc suffices for it in the formation of the molecule of zinc oxide (ZnO). One atom of zinc, therefore, carries the same chemical effect in combination as two atoms of hydrogen; it has a double chemical value, or *valency*, as we call it. Each elementary atom has its own valency—hydrogen is monovalent, zinc divalent, aluminium trivalent, and so on—and thus another property of the atoms enters to confuse us. A picture of the atom which is to rise to the dignity of a scientific speculation must take all these properties into account.

The determination of the atomic weight of an element is the most important of the chemical processes concerning it, and to this problem have been brought together the highest manipulative skill and the best thought of some of our best chemists. The first step is the determination of the equivalent of the element, which is defined as that quantity of it that will take the place of one unit-weight of hydrogen in any compound*. The weight of the element thus obtained is clearly that which is chemically equivalent to the unit-weight of the standard element. We shall see later on that hydrogen is easily liberated from dilute acids by many metals; we find, for example, that 12 grams of magnesium are required to liberate one gram of hydrogen from diluted sulphuric acid; and so, this number 12 is deemed the equivalent of magnesium.

^{*} In spite of much careful experimental work on the composition of water, the equivalent of oxygen cannot be said to be settled with absolute accuracy; and, as it is generally easier to find equivalents by means of combinations with oxygen, O = 8 is most commonly adopted by chemists as the standard of equivalents. But this does not affect our argument.

ATOMIC WEIGHTS

Many elements, however, do not act in this way towards acids; but they often combine easily with elements whose equivalent is known. Thus, when a piece of charcoal (or better, a diamond, which is pure carbon) is heated in oxygen gas, we find 3 grams of carbon always uniting with 8 grams of oxygen; that is to say, 3 grams of carbon are in the chemical sense equivalent to I gram of hydrogen, because in the formation of water, I gram of hydrogen is combined with 8 grams of oxygen. Hence, the equivalent of carbon will be 3. By similar methods we are able to find the equivalents of most of the elements with great accuracy.

The equivalent is not, however, the atomic weight. It would be so if all elements had an equal combining power or valency. In various indirect ways we are able to arrive at an element's valency with a reasonable certainty. Let us suppose that we have discovered, as we can assuredly discover, that the atom of magnesium is divalent; each atom of magnesium will therefore be able to do the work, or fill the place, of two atoms of hydrogen. The weight of two atoms of hydrogen is 2: hence the weight of one atom of magnesium will be $2 \times 12 = 24$, since 12 is the equivalent of the metal. Similarly in the case of carbon: the atom is found, only with great probability rather than certainty, to be tetravalent (Gr. tetra = four). Its atomic weight is therefore $4 \times 3 = 12$, as we have mentioned previously. Of course, it is not necessary to repeat that all these weights are merely relative to that of the atom of hydrogen, taken as standard; but even so they are of indispensable value in the science of chemistry, and for practical purposes a knowledge

of the actual weights of the atoms would not add to their usefulness.

The method most commonly adopted for the determination of atomic weights in the present day depends upon a different, but no less interesting, principle from that outlined above. Compounds of carbon, for example, can be analysed and have their molecular weights determined with considerable accuracy. Now, the weight of carbon in any molecule can never be less than that of one atom, though, of course, it may be greater; and among all the molecules of carbon compounds that we have yet analysed, we have never found one which contains less than 12 parts of carbon by weight. We therefore adopt 12 as the atomic weight of the element.

In this book the five elements of the Greeks are taken as the text of five lessons in modern chemistry; wherein we show how we have reached the true conception of those elements, and how our studies of these have thrown light upon the great questions which were working in the minds of Empedocles and his like more than 2,000 years ago. On the way we shall see how fruitful a scientific chemistry has been in great discoveries and achievements of a practical nature; in pursuing our inquiries into the mysteries of Nature, guided only by the determination to arrive at truth, we have been rewarded at the same time with a noble philosophy of matter and a long series of invaluable new substances and processes.

CHAPTER II

AIR

I.—EARLY VIEWS ABOUT AIR

OF the four elements of the ancients, none surely was more wonderful and mysterious than the air which was so obviously necessary to human existence. Earth, water, and fire—each cherished its mysteries, but at least they could be seen. So the air—invisible, yet ever present; peaceful, yet prone to violence; capable of irresistible motion—touched the imaginative powers more nearly, and awakened a quicker speculation.

The demand for a motive power behind the phenomena of the air led a crude philosophy to people it with gods; and our word gas, which is our general term for all air-like substances, originated in the German Geist, ghost, and reminds us of such primitive notions. To Anaximenes (c. 500 B.C.) came the thought that air was the element. Did he not perceive in his soul something akin to the air—something ever moving, tending to uplift, yet ever invisible? And, just as the soul is the beginning of man, his permanent and essential element, so must air be the beginning of external things. Does not water come from the air, earth from water, and fire from earth? Looked at with the science of Anaximenes, air is clearly the parent of the other elements!

But Empedocles levelled air to the rank of fire, water, and earth; it was no longer prima materia,

but became a spirit, a ghost, a gas, in which guise it remained. Careful experiment, extending the field of familiar observation, was wanted; not for many centuries was this, the method of science, to be applied. We find, however, that in the days of the Roman Empire the rise of water in pumps was attributed to the weight of the air. Weight cannot be ascribed to spirits, and it was something gained when air had a material property attached to it. But through the dark centuries, when alchemy was the only chemistry, this fact was lost, and no real attempt was made to elucidate the nature of air. On the contrary, darkness became deeper as substances were endowed with "air," which had no claim to the name. Thus, sulphur, producing a sharp-smelling fume when burnt, was therefore said to contain the element air, although it must have been obvious that the choking fumes were vastly different from atmospheric air. Indeed, whatever we now define as a gas was in those days described as an air; but it was not until the eighteenth century that it was clearly realised that all airs are not alike, and that gases differ among themselves as sharply as solids do. The actual truth about the nature of air was held back almost to the end of that century. But the Hon. Robert Boyle (1627-91), a good experimenter and a shrewd reasoner, had first established the important truth that air was matter by demonstrating its weight and its "spring," or elastic force, when compressed. What is true of air is true of other gases: they can be weighed and compressed.

In our study of air we shall follow broadly the footsteps of history, and consider it first in its beha-

AIR A MATERIAL SUBSTANCE

viour as a substance in the gaseous form, without inquiry about its inherent nature. We shall consider, first, those physical changes which do not alter the air intrinsically, leaving the more difficult chemical changes, which do involve a change in its actual material nature, to a later stage. Thus, an investigation of the weight of the air, a study of its expansion under heat, a description of the principles by which it has been brought into the liquid state—these are physical inquiries, because they do not suppose any change in the composition of the substance: the air is air throughout. But if a piece of wood is burned in the air, we shall see that the new air is now different from the old air, though its physical properties are the same.

II.—PRESSURE OF THE AIR

That air has weight and can exert pressure is suggested by the force of the winds; but it is advis-

able to weigh the air directly, and that may be done by a very simple experiment. A flask is fitted with a cork and glass tube, as in Fig. 1, and a long piece of india-rubber tubing is fitted on the glass. Place the whole on a balance, and weigh it. Then suck as much air out of the flask as possible; pinch the Fig. 1.-Apparatus rubber and tie it in a knot, so as to prevent the re-entry of air. Weigh again,

for showing the

and the flask will be found to be lighter now-of course, by the weight of the air sucked out.

Possessed, therefore, of weight, the air must be competent to exert pressure. Place a few pieces of

any light substance upon a piece of paper which floats on the surface of water in a tumbler about half-full (Fig. 2). On bringing over the top of the paper an inverted wine-glass, that can be comfortably accommodated in the tumbler, and gently pressing it down into the water, the paper and its contents will appear to sink beneath the surface, and may be pushed almost to the bottom of the tumbler. What pushes the substance down? Evidently something in the wine-glass;

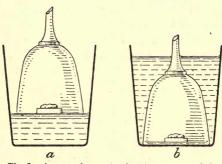


Fig. 2.—An experiment showing the pressure of air.

and evidently, also, that something is the air which by its pressure prevents water from entering the glass. A keen observer would notice that a small amount of water does enter the wine-glass; this shows that the air inside is capable of compression. Neglecting this for the present, we note that on carefully raising the tumbler the substance on the paper has not been wetted. Clearly the air is capable of exerting enough pressure to push down the water.

This pressure is in *all* directions, upwards as well as downwards. Place a cardboard slip over the mouth of a tumbler full of water, and carefully invert it, as in Fig. 3. The upward pressure of the air is

PRESSURE OF THE AIR

great enough to support the water in the tumbler, and the card does not fall off or the water flow out.

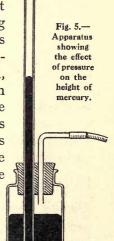
If the air did not thus exert its pressure in all directions the roofs of buildings could not withstand the onesided pressure to which they would be subjected. A tin can with its lid sealed on is pressed perfectly flat by the air outside it, when the pressure is withdrawn from the interior.



Fig. 3.-A simple experiment for showing the pressure of air.

The actual pressure exerted by the air is a valuable piece of information which can be obtained with very considerable accuracy by means

of a barometer. The essential part of a barometer is a straight glass tube, about one yard long and closed at one end. It is filled with mercury and inverted in a basin of that liquid, as shown in Fig. 4. A portion of the mercury falls out of the tube, but about 30 inches always remain in it. How is it supported, if not by the pressure of the air? That the height of the column is dependent upon the pressure of the air on the mercury Fig. 4. - A surface we can prove consimple baro- clusively by the apparatus



meter.

suggested by Fig. 5. Here the mercury reservoir is a bottle which has a tight-fitting cork with two holes. The barometer tube passes through one hole.

and a tube by which air can be sucked out or blown into the bottle passes through the other. When air is sucked out, the mercury in the tube falls; if more air is blown in, the mercury rises. If the closed end of the tube be cracked, all the mercury will fall out, because the pressure of the outside air then becomes operative inside the tube.

The space above the mercury in a barometer, of course, contains no air, and would be a complete vacuum were it not for a few molecules of mercury which escape from the liquid in the form of gas or vapour. If the tube be inclined a little, the mercury will be seen to flow into the vacuum, meeting no impediment to its motion. This space, containing no matter worth speaking of, was first recognised by Torricelli in 1643.

By carefully measuring the height of the mercury in the tube above the surface of the mercury in the basin, we can, by a very simple calculation, express the pressure of the air in pounds to the square inch. A given volume of mercury weighs 13.6 times as much as the same volume of water; that is to say, I cubic foot of mercury weighs 13.6 \times 62.5 lb. Thus, 30 inches of mercury standing on a base of a square inch would weigh $\frac{30}{1728} \times 13.6 \times 62.5$, or about 15 lb.

The air is therefore able to support, and so must exert, a pressure of 15 lb. per square inch, which is a very remarkable amount when we try to realise it.

A barometer might be made by using water for the liquid; but it would, of course, have to be 13.6 times as long as a mercury barometer need be. The air will support 34 feet of water, but no more. Baro-

THE BAROMETER

meters are sometimes constructed with glycerine when very delicate changes have to be recorded; but they, too, are absurdly cumbrous for ordinary purposes. Many improvements have been made in order to make the reading of the mercury barometer as accurate as possible, and to make the instrument more convenient for practical use. Aneroid barometers are also made, in which no mercury is used at all. They can, however, only be graduated by reference to the mercury barometer as standard.

However accurate the barometer, the record it gives has the same meaning: namely, that the air is really a material substance, exerting a very substantial pressure, which varies from place to place, and from hour to hour, but rarely falls below 28 inches of mercury or rises beyond 31 inches. The variation of the pressure may be caused by an alteration in the observer's position or by a change in the air itself. If the observer ascends a mountain with a barometer, he will find the pressure diminishing; and it is possible for him, from the change of pressure indicated, to calculate how high he has ascended. When the air is very moist, or when it is tending to rise from the surface of the ground, or when it is in rapid horizontal motion, it will exert less pressure, and the mercury will fall. Conversely, a high barometer tells of a dry air, or of downward currents, or of little wind; hence its use as a weather indicator. The changes in the pressure of the air are, in fact, our best guides in forecasting the weather.

III.—EVAPORATION

The disappearance of water into the air must have attracted attention from the most cursory observers;

but the fact that the water is still there requires thought, and it was very much more natural for the philosophic mind, untutored by scientific processes, to postulate that "water" is simply transformed into "air." But the material, water, does exist in the air, thoroughly mixed with it in the form of vapour; the water has put on the invisible garb of a gas, apparently of itself; but its molecules are no further changed. Let us consider how modern science explains the loss of the liquid "element," i.e. the process of evaporation.

The molecules of matter have to be supposed to be endowed with motion, and it is this motion which, as we shall later see, confers upon them their heat. In a liquid, apparently still, every molecule is moving, some faster and some slower than a certain average which gives the external temperature of the liquid. The more rapid molecules, the hotter ones, may occasionally be carried out of the surface of the liquid into the air-space above. These molecules, therefore, will have left their liquid condition; the liquid thus partly evaporates, and, as the slower molecules are left behind, the evaporating liquid will have become colder. We may therefore describe evaporation as the process by which a liquid becomes a vapour by the expenditure of its own inherent energy.

We always find matter associated with energy in some form, by virtue of which it is capable of doing work. This energy may be due either to motion, as in the case of the steam-hammer, or to position as in the case of a wound-up watch-spring. Molecular energy has as genuine an existence as these more obvious forms, and if we utilise some of the molecular energy of any body there will be less of it left. Now, when

EVAPORATION

evaporation takes place, some of the liquid's molecular energy is expended in overcoming the cohesive forces between its molecules and in doing work against the atmospheric pressure; and it is this loss of molecular energy that is responsible for the cold which is always produced during the process of evaporation. This cold is always noticeable, and often very intense.

The vapour which results from evaporation enters the air and adds to the pressure of the air its own vapour-pressure. If the pressure exerted by the air itself is diminished, evaporation will evidently be easier; the molecules of liquid have greater freedom, and so a greater chance of escape.

The behaviour of a gas or vapour shows us that its molecules can move more freely than those of a liquid. In the latter case the molecules must be held together by some cohesive force which is inoperative in the gaseous condition; by artificially cooling a vapour we cause its molecules to move more slowly, and thus tend to re-form the liquid from which it arose. The vapour is then said to *condense*, and when we combine the vaporisation of a liquid with subse quent condensation, the whole process is known as distillation.

In many practical operations which involve distillation and the concentration of solutions, it is necessary to convert the liquid into vapour quickly, and we must then supply more heat, or molecular energy, than it contains. The molecules can then be made to move more rapidly and so pass more freely into the air, until by continuing the addition of heat we arrive at a point when the vapour-pressure of the liquid is equal to the pressure of the air above it. At

this point all the molecules of liquid will have acquired enough energy to pass into the air, and the liquid is said to boil. From what we have said, the boiling-point, or temperature of boiling, will be seen to be dependent upon the pressure of the air. Reduce the pressure and we lower the boiling-point. This is a very important fact in a number of industrial operations. Suppose liquids like benzene or chloroform to be necessary for the solution of certain substances. Such liquids are valuable, and must not be thrown away like water, if the process in which they are used is to be worked economically. The smallest expenditure of energy upon fuel gives the soundest economy, since the liquid then uses its own energy; consequently the liquids are placed in vacuum stills, so constructed that the pressure of the air upon them can be reduced. On slightly raising the temperature of the liquid by passing steam through coils immersed in the stills, boiling at once takes place, and the vapour produced is afterwards condensed. Thus the valuable liquid is separated from the dissolved material, and recovered for future use. The method is safe as well as economical; the low temperature of boiling very greatly diminishes the danger from inflammable liquids taking fire; no vapour is lost by escape from the condensers.

Many liquids also, such as glycerine or syrup, begin to change when the attempt is made to concentrate them in the air at its ordinary pressure. The use of vacuum stills in distilling glycerine, and of vacuum pans in concentrating sugar solutions, has made it possible to carry out such processes without loss by the decomposition of the substance.

BOILING OF LIQUIDS

IV.—AIR-PUMPS

Since a reduced pressure is so useful, it will be worth while taking a momentary glance at the processes by which it may be obtained. The introduction of the air-pump is due to that pioneer of our science of gases, Robert Boyle. A simple form is sketched in Fig. 6.

A is the vessel to be exhausted, and P is the piston which moves tightly in the brass cylinder c. At the

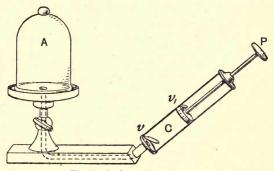


Fig. 6.-A simple air-pump

bottom of c, where it is in connection with A, there is a valve, v, which can only open into c; and in P there is another valve, v_1 , which can only open outward. Consider now what happens during one complete stroke of P. Beginning at the bottom of the cylinder, P is drawn up; at once air, coming from A, lifts the valve v and passes into the cylinder. Arrived at its limit, P is then pressed down. The air in the cylinder, unable to pass back into A by reason of v, will now lift v_1 and escape into the atmosphere. Thus the to and fro movement of P will have withdrawn from A a quantity

of air enough to fill c. Every similar stroke of P will reduce the pressure in A still further, although it will never give us a perfect vacuum.

Various improvements in this simple pump have been made, whereby its efficiency and convenience have been increased. Large pumps, worked by electrical or mechanical means, have superseded the hand-

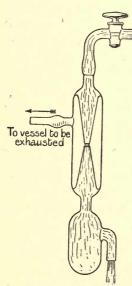


Fig. 7.-A filter-pump.

worked instruments, and find their uses in such industries as we have previously mentioned, and in other instances where vacua are essential. A vacuum is almost impervious to heat. Glass bottles or tumblers, having a double wall enclosing a vacuum, as in the well-known Thermos flask, are often used to preserve hot liquids or very cold liquids at temperatures very different from that of the air.

For the production of vacua, or partial vacua, in small vessels, a T-piece of glass tubing, fastened to a fairly

high-pressure water supply is remarkably efficient. The pressure of the water along the main tube causes bubbles of air from the side tip to be carried along with it; and consequently any vessel connected with this tip suffers a partial exhaustion. The laboratory filter-pump (Fig. 7) is based upon this principle, and is particularly useful when distilling operations have to be performed with small quantities of

PRODUCTION OF VACUA

liquid. On the same principle also is based the very efficient Sprengel pump, much used for evacuating vessels like electric glow lamps. A long column of mercury is allowed to fall past a narrow horizontal tube on which the lamp is affixed. Each thread of mercury carries away some air from the lamp, and the globe is thus ultimately evacuated.

By reference to Fig. 6, the reader will notice that, if the valves v and v_1 are arranged to open in the reverse direction, air would be pumped *into* A when the piston is worked. Hence, the air in A would be compressed, and its high pressure could be utilised to do work if such a pump could be constructed on a larger scale and worked by other than hand-power. Compressed air can be used, for example, to promote the efficient stirring of liquids. A series of pipes is arranged along the bottom of a vessel. Each pipe contains a large number of fine orifices, and compressed air forced through them causes gentle agitation and effective contact of the substances to be mixed. Such a device is used for making the intimate mixture of water and milk of lime employed for softening hard water.

V.—How Air exerts Pressure: Boyle's Law

Our experiments on air have so far taught us that it exerts pressure upon surrounding objects. It is obvious there must be a cause for such an effect; and we shall endeavour to find what the cause is. It must be remembered that gases, along with liquids and solids, are coarse-grained; they have the molecular structure. The gaseous molecules are, however, animated with much faster movements than those of liquids and of solids, and in the course of their

E

movements the molecules are continually bombarding the walls of the containing vessel. The sum total of these molecular impacts constitutes the pressure exerted by the gas. Suppose, now, we confine a given amount of air in a cylinder in which moves the familiar, yet purely hypothetical, frictionless piston P (Fig. 8). By placing weights upon P we

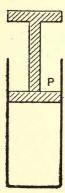


Fig. 8. — I lus. trating the effect of pressure on air.

diminish the volume of the air, but the pressure of the confined air has increased, since a balance is maintained between the upward pressure of the air and the downward pressure of the atmosphere and added weights. Hence the pressure of the gas has increased. In terms of our molecular theory this must certainly follow; for, on diminishing the striking area of the molecules, we must increase the number of impacts, thereby increasing the pressure. It will be clear that, if we reduce the striking area to one-half its original value, the number of impacts will be doubled; or, by halving the volume,

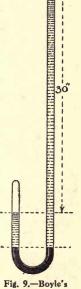
we double the pressure. Explanations of the behaviour of gases in terms of the motion of their molecules is said to be a kinetic explanation, and the theory which ascribes such motion to them is called the kinetic theory of gases.

Let us see if an experiment may be devised whereby we can test the truth of the statement that the increase of pressure upon a gas by twice its former value renders the volume of the gas half what it was. A long tube, about 4-in. internal bore, closed at one end, is bent as shown in Fig. 9. The long limb should be

PRESSURE OF GASES

about 40 inches, the short one about 12 inches, long. A little mercury is poured in the open limb and adjusted until the level in both tubes is identical. The pressure of air in the closed limb then balances the pressure of

the air on the mercury in the open one. We will suppose this value to be equal to 30 inches of mercury. Note the length of the closed column of air, and take this as representing its volume, for the area of cross section of the tube will be fairly uniform. Now pour mercury into the open limb until the difference in the heights of mercury columns from the bench top is 30 inches. The volume of gas will then have been halved, and its molecules are withstanding twice the pressure to which they were originally subjected. The apparatus may be varied to ensure greater accuracy; but there is nowadays a prevalent desire to make ' the apparatus rather than the experimenter responsible for accuracy—a desire to be deplored in the case of beginners, as a crude apparatus only necessitates Fig. 9.—Boyle's the concentration of the faculties essential



to successful operations; those, namely, which lead to accuracy by the elimination of as many sources of error as can be found; and to the evolution, in the student's own mind, from the imperfect apparatus to one of greater perfection. The law which the experiment described illustrates was first given to the world by Robert Boyle during the prosecution of the researches to which we have previously referred;

it is known as Boyle's Law, and has led to results of far-reaching importance in the study of gases.

VI.—EFFECT OF HEAT AND COLD ON AIR

"The production of cold is a thing very worthy of the inquisition, both for the use and disclosure of causes. For heat and cold are Nature's two hands

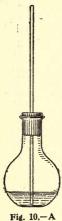


Fig. 10.—A simple "air-thermometer."

whereby she chiefly worketh." [Thus wrote Francis Bacon, who met his death from a cold caught while studying the process of refrigeration. Evidently he realised justly the importance of these great physical agents, an importance until his time greatly overlooked. The results of following up his suggestions have very far surpassed the imagination of the creator of the "New Atlantis." As the air has played a great part in the march of progress; it will be profitable to follow in outline the effect of heat and cold upon it. Galileo and Boyle were among the earliest students of the phenomena. Galileo constructed an air-

thermometer, and Boyle found that air, subjected to the freezing mixtures then at his disposal, had not its spring weakened "anything near so considerable as one would expect "—only, in fact, from 10 volumes to 9. A deeper range of cold has, as we shall see, weakened the "spring" far beyond his conceptions.

The expansion of air may be shown by the construction of a simple "air-thermometer," such as is shown in Fig. 10. The air is confined between the cork and the level of the coloured water which is contained in the flask and the long straight tube. On

THE AIR-THERMOMETER

gently warming the flask by means of the heat of the hands, sufficient expansion is obtained to be rendered visible by the ascent of the liquid in the vertical tube.

The consequences of this easy and quite considerable expansion are numerous. The fire in a grate, heating and expanding the air above it, causes the air to rise on account of its lightness; cooler and heavier air must come in to fill its place; and thus a draught is established over and towards a fire. Fires were formerly kindled at the base of the shaft in a coalmine, so that an upward draught of foul air was established, and fresh air drawn into the mine from other shafts. The rising of warm, expanded air sets the surrounding air in motion as winds; and ventilators are constructed primarily with the same principle in view, the inlet for fresh air being kept low down, and the outlet discharging the hotter foul air being placed near the roof.

Thermometers for common use are based upon the principle of expansion by heat; but the substances used in them are liquids. Air expands much more than either liquid or solid substances; its expansion is therefore easier to measure accurately; and consequently it should furnish a suitable expanding substance for accurate scientific thermometers. It has been very largely so used in recent times, and our liquid-in-glass thermometers are generally tested by reference to air as a standard substance. Air-thermometers can be used for very high and for low temperatures; the air expands very uniformly, as well as largely. For these purposes it is therefore an invaluable substance. For very accurate work, nitrogen

gas (p. 80) is even more valuable, because its expansion is more uniform.

In actual practice the air is not allowed to expand, but is confined to a constant volume by an increase of pressure. For high temperatures the air is enclosed in a porcelain vessel, which is placed in the substance or bath to be tested. The tube connected with the air has a mercury gauge similar to that in our Boyle's tube described on p. 51. The tendency of the air to expand is balanced by an increased supply of mercury in the open limb; it is easy to measure how much mercury is required to keep the air at its original volume; and, since the law of increase of pressure is the same as the law of expansion, it is easy to calculate the temperature of the air in the vessel from our measurements. No experiments have been conducted more carefully than these on the expansion and the increase of pressure of air when heated; the increase of pressure takes place always when the expansion is prevented, and thus provides an exceedingly accurate measure of temperature.

The level of the liquid in our simple air-thermometer (Fig. 10) will gradually return to its former level when the heat is withdrawn. If the air is still further cooled, the level will fall; air contracts on cooling at the same rate as it expanded under heat. Very careful measurements of this rate have been many times made by very able and skilled experimenters, and the result is given in the statement that a given volume of air at 0° C. will change by $2\frac{1}{13}$ of itself for every rise or fall of a degree Centigrade.* A little thought, however, will persuade

^{*} On the Centigrade thermometric scale, always employed in scientific work, there are 100 degrees between the freezing-point (0°) and the boiling point (100°) of water.

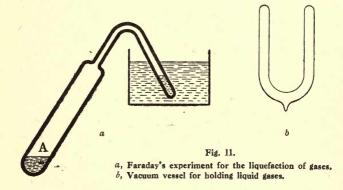
THE COOLING OF GASES

us that, if this rate of contraction is continuously maintained to any degree of cold, peculiar and intensely interesting results will follow. As one volume of air, when cooled from o° C. to $- 1^{\circ}$ C. will contract to $\frac{272}{573}$ of this volume, it follows that, if cooled to - 273° C., it should vanish altogether. At this temperature we could cool it no further; so we arrive at an absolute zero of temperature, or the temperature of the greatest degree of cold that could possibly be applied. Many investigators had varied beliefs in regard to this absolute zero temperature in the bygone days. John Dalton, a man revered by chemists, speculated -3,000° C., whilst Lavoisier essayed -600° C., and not until the expansion and contraction of gases was studied quantitatively was the real value found. We may here say that the temperature of -273° C. as the absolute zero has been confirmed by Lord Kelvin from theoretical considerations, and no doubt at present exists about its accuracy.

Although this temperature of -273° C. has not yet been in practice reached, we have experimental evidence that, before it can be attained, a gas no longer obeys gas laws, owing to the fact that it will have assumed the liquid state. The contraction suffered by a gas when cooled to a great extent is sufficient to bring the molecules of the gas into such close proximity that their attractive forces can come into play, and this ultimately results in the gas becoming liquid.

Experiments on the cooling of gases with a view to liquefaction were commenced by Michael Faraday in 1823. As early as 1805 chlorine and sulphur dioxide had been liquefied by Northmore; but Fara-

day was the real pioneer of determined experimental work on the subject. This investigator, who, beginning life as a newsagent's boy, lived to lay the foundations upon which many branches of physics are built, subjected gases, such as ammonia, chlorine, cyanogen, to a low temperature, and also to assist the reduction in volume and bring the molecules closer together, to a great pressure. The beautiful device he used for com-



bining the pressure and cold is shown in Fig. 11a. The substance yielding the gas was placed in a stout tube at A; the narrow end of the tube was sealed, and placed in a freezing mixture of ice and calcium chloride. The gas, being generated by heat at A, accumulated, and a great pressure was thus set up; combined with the cold, this caused the liquefaction of many gases. Thus the real "airs," or some of them, became "water." But a few gases resisted all Faraday's attempts to change their "element," and these he was led to describe as permanent gases. In 1835 a step further was taken by a French physicist named Thilorier, who succeeded in liquefying carbon dioxide

LIQUEFACTION OF GASES

gas (p. 87) in large quantities, by generating the gas in a cast-iron cylinder and leading it under great pressure into a second similar vessel. The great pressure alone was sufficient for him. The liquid thus produced was a very great boon to investigators, as it enabled them to obtain very much lower temperatures than hitherto. By the rapid evaporation of the new-found liquid, great cold is produced. Ever ready to seize an opportunity, Faraday used this liquid and succeeded in bringing other gases into the liquid state; but still air, hydrogen, and one or two other gases refused to submit and remained permanent gases, showing no sign of liquefaction.

In science there is always something new to learn, and the clue to the mystery which baffled Faraday was published in 1869. It was shown that cold, rather than pressure, is the more important factor in the liquefaction of gases. Dr. Andrews, of Belfast, experimenting on carbon dioxide, discovered, to his astonishment, that, above a temperature of 32° C., no amount of pressure would cause that gas to liquefy, whereas it could be easily liquefied at 31° or any temperature below it. Between 31° and 32°, therefore, we have a temperature which determines whether carbon dioxide can exist as a gas or a liquid, a temperature critical to the substance, and hence known as its critical temperature. Above this temperature the substance cannot exist in the liquid form: it is a perfect gas. Below, a suitable pressure will liquefy it. If, then, we wish to make air liquid, we must reduce it below the critical temperature; otherwise it is useless to employ the mightiest pressures obtainable. As the critical temperature of air is about - 150° C., and that

of hydrogen gas is about — 243° C., it is easy to see that the problem to be solved is that of evolving some process for obtaining the intense cold revealed by these temperatures.

Oxygen was the first of the refractory gases to yield to the apparatus of M. Raoul Pictet at Geneva in 1877. The gas was submitted to a pressure of 500 atmospheres (about 3½ tons per square inch); at the same time it was cooled by the evaporation of liquid carbon dioxide, which itself was surrounded and cooled by liquid sulphur dioxide, made to boil rapidly. Air soon yielded also, put off its aery nature, became liquid, and was ultimately frozen; but hydrogen remained obtusely gaseous until a new principle was brought into operation. Sir James Dewar then liquefied hydrogen in 1897, and concluded the splendid work begun by Faraday at the Royal Institution by liquefying helium. In Dewar's experiments the highly cooled hydrogenstill, however, above its critical temperature—was kept under great pressure, and then allowed to expand suddenly through a small orifice. The expanding gas needs energy for its expansion; this it supplies for itself from its own store; consequently it becomes very cold, and a cloud of liquid (and even solid) hydrogen is produced. The expanding gas, made to circulate round the spiral containing the compressed hydrogen, further cools the latter, until it becomes liquid. It may be collected in a vessel with a vacuum jacket (Fig. II b), kept, and examined.

Experiments with these liquid gases have been both difficult and dangerous; and the reader will doubtless have been struck by the fact that, while it

LIQUID AIR

is easy to heat a substance 273°, it has cost so much skilful and expensive work to cool it a like amount. Even now the absolute zero has not yet been reached. At least six degrees, and perhaps more, remain unconquered. One thing has been satisfactorily established, nevertheless; all gases, reduced below their critical temperature, become vapours, and can be liquefied; and even in the most "aery" substances, like helium and hydrogen, the air-element does not survive a suitable degree of cold.

Nor are these liquid gases of merely speculative interest. The extension of the principle of free expansion and consequent cooling has led to the invention, by Herr Linde in Germany, and Dr. Hampson in England, of apparatus by means of which liquid air can be obtained in industrial quantities; it is now a useful article of commerce. Many curious scientific results have been obtained by its use. The effect of very low temperatures upon chemical changes and upon such physical properties as elasticity and magnetism can now be thoroughly studied; so, too, it has been observed that, while 120° above freezing-point is destructive of all life, many seeds and bacteria can survive — 240°.

If any of these liquid gases are contained in an open tube, they are in much the same condition as a drop of water in a red-hot fire. They boil away with great rapidity. A little liquid hydrogen produces so much cold in this way that the air around it is liquefied and frozen; the manner in which this may be employed to produce a perfect vacuum will occur to the reader readily. It is the cold produced by the boiling of hydrogen under reduced pressure, aided by

the effect of free expansion, that has caused the liquefaction of helium; and we now await the discovery of a new gas, more "permanent" than helium, in order to reach that absolute zero of temperature at which the substance contains no heat at all. Liquid helium seems to boil about 6° above it.

VII.—THE RELATION OF AIR TO COMBUSTION, AND THE COMPOSITION OF THE AIR

We have hitherto been dealing with air merely as a material gaseous substance. So important a part does it play, however, in the life of man and beast; so vital is it to plant life; and so necessary to combustion, that we must turn to a consideration of the part it plays in these phenomena—a part which changes its characters even more deeply. And seeing that its composition has been ascertained primarily by studying its share in combustion, and that its composition is necessary in interpreting its many functions, we must see how this has been arrived at.

The phenomena of fire must always have attracted attention. So striking was this invaluable, but mysterious, servant of mankind that it was considered of sufficient importance to be incorporated among the four elements of the ancients. For many years taken as a "property" of the particular burning substance, no attempts were made to explain its cause, and not until about 1700 was any theory presented that was presumed to account for it. About that time Stahl, a Swedish physician, put forth the view that substances burnt because they burnt—a theory surely simple, but which nevertheless attracted

COMBUSTION

numerous supporters and left its mark upon chemistry as late as the dawn of the past century. Stahl attributed two great principles to every burning substance, one remaining when the substance was burnt, the other disappearing. The latter was the burning principle, or principle of inflammability, the *phlogiston* contained by the substance; the incombustible residue was termed the *calx*. Substances which had the power of burning brightly were supposed to be rich in phlogiston; and varying degrees of inflammability were ascribed to varying proportions of this immaterial essence.

This theory, at its best but a mere refuge in words when considered as an explanation of combustion, yet attracted many scientists in its day; and we shall presently see how, contrary to all expectation, epochmaking men clung to it with great tenacity. It is surprising that the theory, born in Sweden, should have found its chief adherents in France and England, inasmuch as Boyle and Hooke in this country, and Rey in France, had previously conducted experiments which should have shown them clearly that without air combustion cannot take place. Boyle found, using his air pump, that a candle refused to burn in an exhausted space; and heating lead in contact with air, he found that it increased in weight. Hooke, at one time an assistant of Boyle's, also stated that something in air, like the "fixed air" in saltpetre, helps substances to burn. Mayow found that air which had been used to support the burning of a candle refused to allow another lighted candle to burn in it, and Rey also confirmed Boyle's observation that lead increases in weight on being heated in the

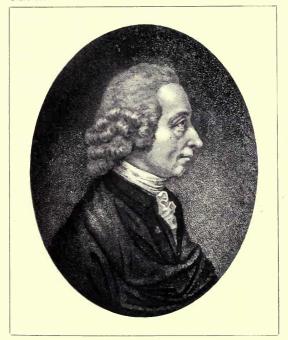
air. Rey also found that tin behaved similarly. In the light of such evidence, culled from true inductive methods, it is truly remarkable that room should ever have been found in the scientific world for such a theory as that of phlogiston. Like all theories which are incapable of explaining facts, however, it was destined to fall; and it is somewhat significant that its fall was completed by the introduction of a new theory of combustion, which may be said to have been also the dawn of a new chemistry.



Fig. 12.— Priestley's experiment.

The new ideas obtained and the truths brought to light during this period have had a far-reaching effect on subsequent research and discovery. The experiments of Boyle, Mayow, Hooke, and Rey were conducted between 1660 and 1680. Stahl was born in 1660 and died in 1734; and the theory of phlogiston still held sway in the latter half of the eighteenth century! During the latter period—in 1774

—Dr. Joseph Priestley submitted a preparation known as "mercurius calcinatus" to the action of heat. This substance, which had been made by slowly roasting (or calcining) mercury in the open air, he placed at the focus of a large lens and concentrated the sun's rays upon it. To his astonishment he found an "air" evolved which possessed "vital" properties to an extent hitherto undreamt of. The substance was contained in a small phial filled with quicksilver and inverted in the latter (Fig. 12), the pressure of the evolved "air" displacing the quicksilver from the bottle to the basin. Having collected about "three or four times as much"



JOSEPH PRIESTLEY
1733-1804



VITAL AIR

as the bulk of his materials, Priestley examined the gas with a view to finding its properties, and found it to be a very active "air." To use his own words, "what surprised me more than I can well express was that a candle burned in this air with a remarkably vigorous flame," a fact he was "utterly at a loss to account for."

At the same time that Priestley made the above experiment, he conducted a similar one, using "red precipitate," a substance produced by the ignition of a nitrate of mercury. He succeeded in isolating the same "air," and surmised that it was possible for the red precipitate to have yielded a substance which it had obtained from the nitric acid used in its manufacture; he also thought it possible that the mercurius calcinatus with which he was supplied had not been made by calcining mercury, and that he had really been supplied with red precipitate. Obtaining, however, a pure sample of the mercurius calcinatus, he again obtained the lively "air," and mentioned the fact to Lavoisier during a visit to Paris; he subsequently obtained the same gas from red lead. After the latter experiment he came to the conclusion that the gas he obtained came first from the air and was taken up from the air by the mercury during its calcination. The comparison of the properties of this new air with those of atmospheric air convinced Priestley that air was not an element; such a view was only confirmatory of others which he must previously have formed during experiments on respiration and plant growth-experiments which we shall consider a little more in detail later on.

But, although this was the case, and although it

may be said that he held the key to the chemistry of the air in his hands, Priestley came to altogether erroneous conclusions about its composition, the result chiefly of the fact that he remained a firm adherent of the phlogiston theory and tried to state the composition of the air in terms of its impossible conceptions. The communications that Priestley made to Lavoisier,

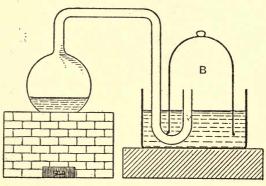


Fig. 13.-Lavoisier's experiment.

however, fell upon fertile soil. Lavoisier quickly recognised that Priestley's gas was a constituent of our atmosphere, and that it had been taken up by the mercury during calcination. As it was so much more active than ordinary air, he rightly inferred that the air must contain some other constituent which dilutes its action. He therefore promptly designed an experiment which conclusively showed that the air was not an element; that as such its reign must end, and that it contained at least two constituents. The constituent which Priestley had found, and had named vital air, Lavoisier called oxygen, and as such we shall henceforth speak of it. The properties of

OXYGEN IN THE AIR

the gas were remarkably well demonstrated by Priestley, who showed experimentally its great activity as a supporter of combustion and of life. He studied its effect upon mice and upon the human body, and he also showed that it was not imbibed by water.

The classical experiment by which Lavoisier showed for the first time that air was not an element was conducted as follows:

Mercury in the retort (Fig. 13) was calcined in the confined space indicated. As the oxygen of the enclosed air was absorbed by the mercury-upon the surface of which a red tarnish appeared—a loss in volume naturally occurred, and this was shown by the liquid rising in B. In the course of the experiment a stage was reached when no further diminution in the volume of the air took place. The gas remaining was the second constituent of our atmosphere, and obviously it will not support the calcination of mercury. It was found to be an inactive gas, almost incapable of chemical activity, and was for this reason called azote. (We ought to mention that at high temperatures it is more energetic.) It was subsequently found to be of identical properties with a gas called nitrogen that had previously been obtained from saltpetre. The atmosphere was thus shown by Lavoisier to be composed mainly of two gases-oxygen and nitrogen.

The experiments of Lavoisier showed that the air contained about four volumes of nitrogen to every one volume of oxygen, and later experiments confirm the general accuracy of this result. Henry Cavendish (1731–1810) was the most careful of these early investigators, and his papers, when compared even with

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those of Priestley or Lavoisier, show a scrupulous care and diligence in the prosecution of research, that have very rarely been surpassed. He made more than five hundred experiments in order to obtain an accurate measure of the "goodness" of the air. The vessel he used is called a eudiometer (Fig. 14), and his method is in principle that which is at present used for the same purpose. There is a gas, called nitric oxide, which unites directly with half its volume of oxygen and forms a new gas that is readily imbibed by water. By carefully serving a measured volume of air with this gas over water, the amount of oxygen consumed can be obtained. The result of his analysis given by Cavendish is, in the light of modern work, remarkable, as will be seen from the numbers following:—

Cavendish (1781) obtained 20.833 vols. oxygen per cent.

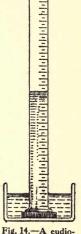
Lord Rayleigh (1894) obtained 20.61 vols. oxygen per cent.

The close agreement of these numbers is a striking testimony to the effect of personal care in the conduct of experiments. In modern analyses hydrogen gas is preferred to nitric oxide, but it plays essentially the same part. It is mixed with the air in known proportions, and the mixture exploded by an electric spark. Hydrogen and oxygen then unite in the proportion of 2: 1, and a water-mist results which takes up a negligible volume. There must therefore be contraction of volume as a result of this disappearance of hydrogen and oxygen, and one-third of that contraction will be due to the oxygen which has departed. For the sake of simplicity, suppose 30 cubic centimetres (c.c.) of dry air and 30 c.c. dry hydrogen are measured

ANALYSIS OF THE AIR

off carefully in some suitable vessel and exploded by means of the electric spark. After explosion, the volume is 42 c.c. It follows that 18 c.c. of gases have gone to produce water. Of these, one-third, or 6 c.c. is oxygen. Hence, of the 30 c.c. of air we have 6 c.c. of oxygen, or 5 vols. of air contain I vol. oxygen. The apparatus used is generally a stout glass tube of 100

c.c., closed at one end, into which two platinum wires have been sealed (Fig. 14). The tube is carefully graduated to admit of accurate measurement of the gases. It is filled with mercury and inverted in mercury; dry air is passed in, followed by hydrogen, each volume being carefully noted and corrections necessary for temperature and pressure made. The tube is then clamped securely upon a piece of india-rubber, as during explosion concussion occurs. A spark is passed, union takes place, and on cooling and releasing the tube the mercury enters to take the place of the departed gases. The final readings and corrections being Fig. 14.-A eudiomade, the analysis is complete.



Analyses have also been conducted with a view to finding the composition of the atmosphere by weight, the principle being to allow air to pass over hot copper into a previously weighed and exhausted globe. The hot copper has the power to unite with the oxygen. The increase in weight of the globe gives the nitrogen, and the increase in the copper gives the weight of oxgven in the same quantity of air.

VIII.—THE RARE ELEMENTS OF THE AIR

Many such experiments on the composition of atmospheric air have been made since the days of Cavendish and Lavoisier, all approximating more or less closely, and none seeming in any way to vitiate the accuracy of Lavoisier's conclusions in regard to the elements present. Imagine, therefore, the consternation among grave men of science when Rayleigh and Ramsay announced to the world in 1894 their discovery of a new constituent of our atmosphere! For over 100 years the air had been treated as a mixture of oxygen and nitrogen, and was then found to contain a third element that had escaped so many observers! The story is too fascinating to leave untold, and serves as an illustration of the scientific truism that, accuracy being the first essential in scientific work, fact will stand before authority or theory. In order to obtain the density of nitrogen gas, Lord Rayleigh had obtained nitrogen in a pure condition from many sources, and naturally expected to obtain uniform results in his determinations. The nitrogen from the air, however, persisted in being heavier than that derived from other sources. It is obvious that. if one determination only had been made, and that with nitrogen obtained from some chemical, this fact would have been overlooked. The heaviness of the nitrogen in the air, however, could only be caused by the presence of some hitherto unknown gas, a substance itself heavier than nitrogen, or by some change whereby the nitrogen molecules condensed to give heavier ones. This latter idea had no support in experimental fact, and the isolation of the unknown gas settled the question.

DETECTION OF ARGON

This has been accomplished in two ways. If a mixture of air with an excess of oxygen is exploded in the eudiometer over water or alkalis, the nitrogen and oxygen will enter into combination to form a gas which is readily absorbed by the liquid. By using sufficient oxygen, all the nitrogen can thus be withdrawn from the air, and the excess of oxygen can afterwards be absorbed by a small quantity of pyrogallic acid. When this was done several times it was found that a small quantity of gas remained unchanged and unabsorbed. It was, however, so small that great difficulty was experienced in examining it. Professor (now Sir William) Ramsay, therefore, sought a substance that would absorb nitrogen, just as so many substances absorb oxygen. He found it in the metal magnesium. When nitrogen is continually passed over hot magnesium turnings, it combines with the metal to form magnesium nitride; this is the basis of the method finally adopted. Air. freed from oxygen by being passed over hot copper, is then freed from nitrogen by means of hot magnesium, an arrangement being devised by which the gas could be repeatedly brought into contact with the metal. The resulting gas was sparked with oxygen to withdraw the last traces of nitrogen; then there remained the new element, named argon because it would not do any work. During the severe treatment to which the air had been subjected it survived, independent and uncombined. This is the cardinal characteristic of the gas: it refuses to enter into chemical combination with even the most active of other elements. For this reason it had so long escaped detection, although it forms about I per cent. of that

part of the air which had been supposed to be nitrogen.

It is interesting to note, however, that Cavendish, during his experiments upon air, really made the observation that might have led him to argon. After repeated sparking he found that about 120th part of the air used would not enter into union with oxygen. This, doubtless, was argon; but the significance of his observation did not strike anyone until argon was definitely known. This is very singular when we recollect that Cavendish had actually designed his experiment to ascertain whether any part of the dephlogisticated air (nitrogen) was different from the rest. And he concludes: "If there is any part of the dephlogisticated 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 1120th of the whole." This ought to have been a stimulating observation, but more than a century elapsed before the nature of the inactive residue was unfolded.

By the principles previously explained, argon, subjected to a low temperature and a high pressure, was liquefied. In boiling the liquid argon, however, it was soon found that it was not a single substance. The first vapours given off contained, besides argon, appreciable quantities of two other elements, helium and neon. The former element had been previously found to exist in the sun and in certain rare minerals; it has received much attention from its connection with radio-activity (Chapter VII.); and of all known gases it is the last to become liquid. Neon occurs in the air in very minute quantities. Like helium, it

THE RARE GASES IN THE AIR

does not condense when surrounded with boiling liquid air; but it yields to the intense cold of boiling hydrogen, when helium does not. Two other gases, krypton and xenon, heavier and less volatile than these, have been extracted in very minute quantities from the liquid argon. Their discovery and identification indicate the possibilities of chemical research at very low temperatures. Xenon exists in the air in the proportion of one part in 20,000,000; krypton and neon perhaps form one part out of every million. Yet their atomic weights are known. We know also that the five elements which remain untouched by the process of Sir W. Ramsay are totally inert, and exist in the universe apparently always in isolation.

We thus realise that air is not one element, as ancient philosophers thought, but a mixture containing at least seven. It shares with many other substances the properties of a gas—its elasticity, compressibility, power to mix or diffuse into other gases, ready expansion under heat. But these properties are general to all gases. Air is, however, a mixture of two particular gases, nitrogen and oxygen, with traces of five others. In the chemical sense its behaviour is that of oxygen, hampered and diluted by the nitrogen which is mixed, and not chemically combined, with it. It is important, therefore, to review the salient qualities of these two gases.

IX.—OXYGEN

This gas, the most abundant element on the earth, may now be prepared by methods other than that adopted by Priestley to obtain it from the air. It is a constituent of many substances, one of which, in

particular, will readily yield the oxygen it contains. This substance, potassium chlorate, white and crystalline, need only be cautiously heated in a test-tube to teach one that it contains a large amount of oxygen gas. After crackling and melting, the liquid begins to effervesce, and on introducing a glowing splinter into the mouth of the tube, it is at once rekindled, and the rekindling will take place many times. Since potassium chlorate is easy to obtain, and cheap, it

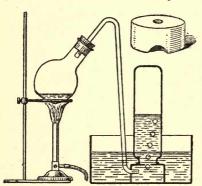


Fig. 15.—The preparation of oxygen.
(Inset is the beehive shelf.)

will suitably serve for the preparation of the gas in large quantities. To facilitate the production of the gas, it is usual to mix with the chlorate a little manganese dioxide, which must be pure. On gently heating the mixture in the flask, as shown in Fig. 15, and neglecting the few

bubbles of air at first produced, oxygen may be collected in jars, inverted and full of water, over the beehive shelf placed in the pneumatic trough. This shelf and trough, of the utmost service in the preparation of gases, were invented by Priestley, the trough being any suitable vessel containing water and the shelf shaped like a cylindrical box, with a hole in the side and in the top. The hole at the side admits the end of the delivery tube; the top one allows the gas to pass into the inverted jar above, thus displacing the water in the latter and ultimately

OXYGEN

filling it. In this way three or four jars full of oxygen may be obtained.

The gas is without colour, taste, or smell, and when breathed produces feelings of "life"; it is, in fact, the life-giving gas, and the conjecture of Priestley that it would probably, in the future, be used for patients suffering from shortage of breath, has been realized. A few experiments will convince

us of its activity. A candle may be burnt in the first jar. A piece of wire, bent round the candle, and carrying the lid of a canister, serves as an easy means of introducing substances into the gas. The candle is consumed very rapidly, and a brilliant light results; were the air composed of oxygen only, wax candles would not last long. The candle is finally extinguished, and refuses to burn in the same gas jar again. It has, therefore, consumed the oxygen, and a portion of the candle has also disappeared, the candle and oxygen evidently having produced something entirely unlike oxygen in properties and evidently unlike the candle also. The candle

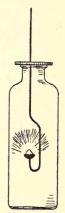


Fig. 16.— Burning sulphur in oxygen.

and oxygen are said to have undergone a chemical change. Such a change is evidently not a mere mixing of the candle and oxygen, but brings them into far closer contact, such contact resulting in chemical combination. When such actions take place, a mere change in appearance is not the only change; the products of the action are different in themselves from the original substances. If the oxygen used in the experiment is dry, water is, never-

theless, seen to be deposited upon the sides of the jar in a mist, and if a little clear lime water be poured into the jar after the burning it is turned milky. Neither the candle nor the oxygen is like water; nor does either of them turn lime water milky. Hence a wonderful change has occurred, a type of change met only during the process of a chemical operation. The gas turning the lime water milky is carbon-oxygenstuff, made by the oxygen combining with the carbon which is a constituent of the wax of the candle. is generally spoken of as carbon dioxide. Water may be chemically described as hydrogen-oxygen-stuff, and can be made by the combination of those elements. The hydrogen must also have been supplied, along with the carbon, by the wax, as the only substance present, in addition to the oxygen, was the burning wax candle. We may express the whole change by a statement, thus:

As a second experiment, a little sulphur may be ignited and gently lowered into a jar of the gas (Fig. 16). The change will be quickly observed. Instantly the sulphur bursts into a beautiful blue flame; evidently its combustion is greatly helped by the oxygen. On removing the spoon after the sulphur has been consumed as far as possible, the jar will be observed to be full of choking fumes, with the well-known penetrating smell of burning sulphur. On being shaken up with a little water, these fumes will be seen to dissolve, and on adding a solution of the vegetable colouring matter known as blue litmus, the latter is instantly turned red, owing to the acid nature of the resulting

CHARACTERS OF OXYGEN

liquid, acids having this common property. Reason tells us that the gas must contain sulphur and oxygen, and that a mere mixture of sulphur and oxygen would possess no such properties. It must, therefore, be a *compound* of the two substances, and may be called sulphur-oxygen-stuff. It is commonly known as sulphur dioxide.

Sulphur + Oxygen = Sulphur-oxygen-stuff. (Sulphur dioxide)

Lavoisier himself found that many products formed by the combination of other substances with oxygen, when dissolved in water, rendered the latter acid; and hence the name "oxygen" (or acid-producer) was given to the gas which seemed to cause the acidity. Lavoisier believed oxygen to be contained in all acids, and this is true in the great majority of cases; an exception is the solution of hydrogen chloride in water (commonly called hydrochloric acid). In Lavoisier's day, however, this was thought to contain oxygen (see page 100), and some chemists argue even at the present time that this is by no means improbable.

In a third jar of oxygen drop upon a piece of thin aluminium foil a little charcoal which has been made red hot. The aluminium at once burns brilliantly, and the inside of the jar is coated with a white incrustation of aluminium-oxygen-stuff, or aluminium oxide. This oxide, in distinction to the two previous ones, is a white powder.

When oxygen combines with substances, a class of bodies known as *oxides* is produced; mercurius calcinatus is evidently one of these, and the "red precipitate" used by Priestley is really the same substance,

mercuric oxide, which has obtained its oxygen from nitric acid. This acid, like saltpetre, chlorate of potash, and other solid or liquid substances, contains much oxygen in its molecules; and is often commercially used for the quick preparation of metallic oxides.

Just as oxygen supports life and combustion in its free state, so it does in its diluted condition in our atmosphere. Substances burn in the air because they unite with oxygen, and when the oxygen in a confined space is removed, the combustion ceases. Many other changes may be likened to slow combustion—changes all depending upon the oxygen in our air. The rusting of iron, necessitating an enormous expenditure yearly upon paints, is in its final state a union of iron with oxygen, iron rust being chiefly a compound of iron and oxygen, or iron oxide. The rusting is facilitated by the presence of water and carbon dioxide, two substances always present in our air to some extent; these form intermediate compounds which end finally in the iron oxide. Pure iron will not rust in pure oxygen, and it may here be stated that no substance in a pure, dry condition, even though it ordinarily manifests a strong liking for oxygen, can be made to unite with it; it may be said, indeed, that no chemical change can take place by the action of two pure substances upon each other. Some third substance is necessary to help on the action. The conditions prevailing in our atmosphere, however, always ensure the presence of water-vapour and carbon dioxide, so that iron can readily rust. In spite of third parties, the rusting process is a slow oxidation, or a slow burning; and heat is produced just the same as when the

RUSTING OF IRON

iron is burned rapidly. Iron in a finely divided state may, in fact, rust so quickly as to take fire in the air, and a piece of watch-spring will burn brilliantly in oxygen. The "firing" of iron in the air may be shown as follows:

A little jeweller's rouge (an oxide of iron) is placed in a glass tube, and hydrogen gas (see Chapter III.), generated in the flask, is robbed of any water by the Utube containing calcium chloride, and passes through

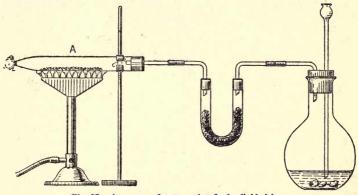


Fig. 17.—Apparatus for preparing finely divided iron.

the straight tube in a dry state. After passing for some time, it may be ignited at the end of the apparatus. A may then be safely heated for fifteen minutes, the hydrogen passing meanwhile. The lamp may then be withdrawn and the tube allowed to cool in the stream of hydrogen. We have then present in the tube metallic iron, formed by the reduction of the iron oxide by the hydrogen, the latter taking away the oxygen which the oxide previously contained. On opening the tube and throwing the filings into the air, they immediately take fire, so quick is the union

between them and the oxygen. Such quick union with the oxygen in the air, whereby substances of themselves ignite without the application of external heat, is spoken of as *spontaneous combustion*. Stacks of hay, oily rags, and heaps of coal have been known to "fire" owing to the operation of a similar process.

X.—Action of Animals and Plants on the Air

Is there any difference in composition between the air we inhale and that we exhale? We know that oxygen and nitrogen are inhaled. What gases do we send back in place of them? Procure a dry tumbler and breathe into it; a mist is quickly noted around the sides, which on analysis can be shown to be water. On pouring a little clear lime water into the tumbler, it at once becomes turbid, teaching us that carbon dioxide is also produced (p. 88). Hence we find two products which can be detected quite easily, and on submitting the exhaled air to analysis we find it to contain about as much nitrogen as, but less oxygen than, ordinary air, and, in addition, an appreciable quantity of carbon dioxide and water. The action of animals is, therefore, to use some of the oxygen, producing thereby substances identical with those formed when combustible substances such as wood and wool burn in the air. The true nature of the changes occurring during the vital process cannot be discussed here, but it may be stated that it is these chemical changes that give us our animal heat; the energy of the body is as much dependent upon the oxygen supply as is that of a railway locomotive.

That air once breathed is unfit to breathe again may clearly be shown by the following experi-

EXHALED AIR

ment: A confined volume of air stands over water, as shown in Fig. 18. The bell-jar is fitted with cork, bent glass tube, and indiarubber tube. On taking the amount of air into the lungs by suction at the end of the rubber until the water almost reaches the cork, and then returning the air, the bell-jar space becomes occupied by breathed air. On introducing a lighted candle, the latter refuses to burn, showing that the

exhaled air is incapable of supporting the combustion of a candle. It is equally injurious to human life.

Suppose, now, that into the exhaled air thus produced a sprig of mint be introduced, and the rubber tied in order to prevent the entrance of the pure air outside. If the apparatus is left in ordinary sunlight for a few days, it will be found that a candle will continue to burn in the

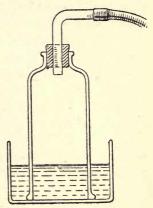


Fig. 18.—Inhaling and exhaling air.

enclosed air, as if this were pure. So if the air had originally been vitiated by the burning of a candle, the healthy growth of green plants in the sunlight would have restored its vital properties. The carbon dioxide is withdrawn and utilised by the plants which return oxygen to the air by way of compensation; and the oxygen returned is exactly that which was contained in the carbon dioxide—that is to say, it is the equivalent in amount of the oxygen originally consumed in breathing or in burning. It is well to ponder over this

very remarkable fact. Coal, wood, petrol, coal-gas are continually undergoing combustion and producing carbon dioxide and water; * animals are continually breathing and producing the same gases; and, we must remember, one ton of coal produces at least three tons of carbon dioxide. This vast accumulation of carbon dioxide is, by a process exactly the reverse of that of combustion—a process demanding energy in the form of sunlight instead of yielding it in the form of heat -gradually taken from the air and used as one of the raw materials in the architecture of plants. Otherwise the air would soon become entirely "dephlogisticated "-unable to yield fires or support life. The fate of the water that also passes into the air in large quantities, it is needless—in Great Britain—to describe in detail. We pass, therefore, to a brief consideration of the nitrogen of the air, which is always apt to be kept in the background by its more active but much less plentiful companion.

XI.-NITROGEN

Many substances are fond of oxygen or, in more dignified language, have a strong chemical affinity for that element; such can readily be used to abstract the oxygen from the air and leave the nitrogen. Thus, air passed over hot copper loses its oxygen owing to the formation of copper oxide; the rest of the air, chiefly nitrogen, can be collected with the pneumatic trough. Phosphorus burnt in a confined space of air has the same effect as hot copper; if the air has been confined over water, the oxide of phosphorus

^{*} Soot and smoke only when the combustion is incomplete and unscientific.

NITROGEN

formed—a cloud of snowy fumes—quickly dissolves, and leaves the nitrogen in the confined space free. But probably the easiest way to collect a few jars of the gas is a more indirect one. Some strong solution of sal-ammoniac (ammonium chloride) should be poured upon a little sodium nitrite in a flask, fitted like that used for the preparation of oxygen (p. 72). On gently heating this mixture several jars of nitrogen can be quickly obtained.

Apparently the most noteworthy characteristic of this gas is its masterly inactivity. It seems to prefer to exist alone, and does not readily enter into combination with other elements. It will, under compulsion, as it were, form compounds with hydrogen, oxygen, and other substances, but for the most part such compounds are easily decomposed, so that the nitrogen becomes free. Most familiar, and many unfamiliar, explosives contain nitrogen, whose atoms seem to confer upon the molecules into which they enter a certain instability. Even the molecules of living substance possibly owe their unstable character to the exceptional amount of the unsociable nitrogen they contain.

At ordinary temperatures nitrogen will extinguish a burning candle; with some difficulty magnesium may be burnt in the gas, but all other ordinary combustibles refuse to burn. Yet nitrogen is not absolutely inert, like argon and its companions. At higher temperatures it becomes decidedly more active; under the influence of a strong electric spark, for example, it will enter into union with both oxygen and hydrogen. Still, its comparative sluggishness is, for animal life, its most valuable property; if the air were entirely

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composed of oxygen, all combustion would be five times as rapid as it is, and life would be livelier, indeed.

It has been said that nitrogen enters into the living substance of animals and plants as one of the essential elements. It follows, therefore, that it must form one constituent of their food-stuffs. Our nitrogenous food-stuffs, mainly derived from the animal world, are members of a class of exceedingly complex bodies called proteins. The animal economy does not rise to the manufacture of proteins from simpler sources, all that our digestive processes enable us to accomplish is the transformation of proteins into more useful or more available kinds. The animal world is therefore dependent upon the vegetable world for its ultimate supply of the all-necessary proteins. It is the plant alone that can manufacture proteins from simpler materials.

What are these simpler materials? The element nitrogen must be obtained somehow. If a plant is cut off entirely from all sources of nitrogen, it does not make proteins-it dies of starvation. But the nitrogen in the air, vast as its quantity is, cannot be used by the plant as such; and so we have the ironical position of the plant, growing in a great sea of nitrogen, vitally needing this nitrogen, and yet unable to avail itself of it. Chemistry is now helping the plant along lines which it is not difficult to follow

Manures and other fertilisers of the soil exist mainly for the purpose of supplying plants with nitrogen in a suitable form. By its decay all animal and vegetable refuse passes through a series of changes,

NITROGEN AND LIFE

aided by the air and by certain bacteria in the soil, the final stage of which, so far as nitrogen is concerned, is a *nitrate*.

Now, a nitrate is a compound containing nitrogen in combination with much oxygen and a metal; the best-known is saltpetre or potassium nitrate (KNO₃), and it is in this form of nitrate that plants seem to prefer their nitrogen. The effect of adding a nitrate to the soil around growing plants is always to stimulate vitality, to increase the weight, and enhance the healthy appearance of the crop. Hence the problem before chemists is that of finding some source of nitrate which shall be cheap and permanent as well as efficient.

Nitrate of soda (NaNO₃) occurs in fair quantity native in Chili; but the demand for this is increasing annually, and the supply is limited. Sir William Crookes drew attention to the matter in 1898, and made us realise that, if a new source of nitrates cannot be found, a shortage of wheat would inevitably arise. Nitrogen the air contains in abundance; it is natural that we should look to this inexhaustible store of the essential element as the possible source of the nitrates of the future. Can the nitrogen of the atmosphere be "fixed" in nitrates by any workable process? That is our problem.

We have previously explained (p. 69) that, when the nitrogen and oxygen of the air are submitted to the action of strong electric sparks over water, the two gases do combine; the fact was known to Cavendish, and has been utilised for the preparation of argon. The water is then found to contain nitric

acid, which is easily converted into a nitrate by an alkali. We thus have:—

Nitrogen + Oxygen Under electric spark + Alkali give Nitrate

Why should not this process be attempted on a large scale? After several unsuccessful attempts a factory has been started at Notodden in Norway (1905) to manufacture a nitrate by the electric method, the particular nitrate produced being calcium nitrate, in which the alkali is lime. There is every present indication that this product can compete, commercially and scientifically, with the nitrate of soda that had been in universal use. The method is that of Cavendish, conducted on a tremendous scale and with the most up-to-date electrical installation. A powerful electric arc-light is produced which, situate between the poles of a powerful magnet, is caused to rotate, and is known as a "rotary arc." This arc is enclosed in a fire-brick furnace and air is gently blown through the flame by a Roots blower at the rate of about 75,000 litres a minute. On leaving the chamber the air contains about I per cent. of a simple compound of nitrogen and oxygen, called nitric oxide (NO), and is at a temperature of about 700° C. This gas is cooled by being passed through steam boilers and by other means, and is then led into "oxidisers"—chambers which contain oxygen. Here the nitric oxide becomes nitrogen peroxide (NO₂) by simple combination with more oxygen; this peroxide is absorbed by milk of lime, and the resulting liquid converted into solid nitrate of lime by evaporation. Thus, a fact discovered first in the course of a purely scientific re-

FIXATION OF NITROGEN

search is now the basis of a commercial process fraught with possibilities of enormous benefit to mankind.

Another method of "fixing" the nitrogen of the atmosphere for the use of plants is due to observations made by Drs. Traube and Caro. Calcium carbide, which is largely made nowadays for the purpose of obtaining acetylene, when heated in nitrogen gas, absorbs some of it and is converted into an unstable compound known as calcium cyanamide (CaCN2). This compound, when added to the soil, is decomposed by the water it meets there, forming ammonia and calcium carbonate. Both these substances are serviceable to the soil, the latter by preventing it from becoming acid and the ammonia by supplying the "nutrient" nitrogen necessary to plants. The ammonia is a compound of nitrogen and hydrogen (NH₃), and is readily made available for use by the plant by the action of the soil itself. So that in this process also it is nitrogen from the air that ultimately finds its way to the plants; in fact, in commerce it is by the distillation of liquid air that the nitrogen is obtained. The calcium cyanamide (known commercially as "nitrolim") is produced by heating the carbide in fireproof retorts to 800° C. and passing the nitrogen distilled from liquid air over it. Its action towards water may be thus represented:

We have said that plants cannot use nitrogen as such; and this is true of green plants. But certain bacteria which grow on the roots of some members of the pea family (Leguminosæ) seem to have the power of making direct use of the nitrogen, incorporating

it into living material and passing it on to the plants upon which they grow. This additional source of nitrogen is of great advantage to vetches, clover, lucerne, etc., which yield a much more handsome crop when the soil is infected with the bacteria. How the bacteria accomplish their unique work is a secret hidden at present from the insight of the chemist; but it is sufficient to show us once again that the nitrogen of the air is not the inert and uninteresting gas that we were at first inclined to name it. It is gradually being compelled to contribute its part to the development of living Nature.

Here it is profitable to pause and survey our position. We have seen how air has been gradually brought from the vague realm of shadows into the clear light of science; how it is no "element," but a mixture of gases of different and individual characteristics; how it has been shown to be as truly a material substance as wood or water; how our more exact knowledge has been self-productive of still more knowledge; and how all this has in many ways enlarged our intellectual vision and served our practical ends. The story of the air element is, indeed, a magnificent object-lesson in the methods of science. Laborious experimental inquiries have in little more than a century dissipated the philosophical mists which obscured the path of truth during so many generations.

CHAPTER III

OTHER AIRS

I.—FIXED AIR (CARBON DIOXIDE)

HALES, Black, Cavendish and Priestley were the four great English pneumatic chemists of the eighteenth century. With the researches of Cavendish and Priestley we have already become, to some extent, familiar, but Hales and Black we have as yet had no occasion to mention. The merit of the former consists, not in the preparation of any new substance, nor in the propounding of any new theory, but in pointing out the fact that many substances not hitherto investigated contained locked in them certain airs. He, however, in common with other investigators of his time, connoted them all as air, recognising fundamentally no difference between them and ordinary atmospheric air. Any investigation into their individual nature and their difference from atmospheric air did not appeal to him.

Black, on the other hand, snowed that one substance, magnesia alba (carbonate of magnesium), contained, locked in its solid consistency, a gas, or "air," entirely different from atmospheric air; and in 1755 he published his "Essay on Magnesia Alba." Herein he showed that a gas existed, different in properties from atmospheric air, the gas being obtained by the action of heat upon the substance. It was subsequently obtained in a similar manner from other solid substances, and became recognised as a gas fixed in these

bodies. Therefore the name "Fixed Air" was applied to it, and it was thus learnt that all "airs" were not made of the same stuff. As time advanced, still other "airs" were discovered, and each was distinguished by a name signifying either its source or some particular striking property of the gas. We shall briefly outline the preparation and properties of these new "airs," and show in some instances how their true composition may be obtained.

To study the gas discovered by Black, let us imitate him by heating a few of these carbonates we have spoken of. An interesting one is copper carbonate, a green substance in the powdered condition. If a little be heated in a dry test-tube, a visible change is immediately noticed, the substance darkening in colour. This change is accompanied by a change in the composition of the substance; and if the original substance and the final product be each weighed, a marked diminution in weight would be noted. Thus some gas has escaped from the carbonate. If, during the experiment, we had gently tilted our tube so that the gas could be poured downwards, and placed a tube containing clear lime water underneath, the lime water would have become turbid when the gas came into contact with it. Now, we have previously shown that the gas obtained by burning carbon in oxygen (carbon dioxide) possessed the property of turning lime water milky; hence these two gases have at least one property in common. Further comparison would show that the gases are identical, and hence we find that the gas fixed in copper carbonate is really carbon dioxide. The black substance left in our test-tube used for heating the carbonate

FIXED AIR

is called copper oxide. Somewhat similar results would be obtained by heating the carbonates of lead, zinc, and (at a higher temperature) naturally occurring forms of calcium carbonate, such as marble, chalk, or limestone. The gas would be evolved, and the oxides of the metals would remain behind, colour changes in some cases accompanying the decomposition.

If, again, these carbonates are separately treated with dilute hydrochloric acid, in each case a brisk effervescence occurs, and the gas, when subjected to experiment, is again found to be carbon dioxide. That the gas comes from the carbonate, and not from the acid, may be seen when the loss in weight suffered by one gram of the particular carbonate (say, marble) when strongly heated is compared with the loss in weight suffered by treatment with acid. In each case the loss will be found to be the same.

The gas has also been mentioned as a product of decay; and it is also formed during alcoholic fermentation; indeed, some of the properties of the gas were investigated by Priestley, who obtained his supply from a brewery.

To study the properties of the gas, we must provide some easy means of preparation in bulk, and the easiest way is to decompose some carbonate with dilute hydrochloric acid. For this purpose an apparatus is prepared as shown in Fig. 19; the flask contains marble chippings covered with water and hydrochloric acid is poured down the funnel. As

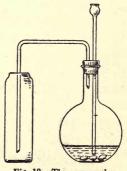


Fig. 19.—The preparation of carbon dioxide.

the gas is evolved, it streams down the delivery tube, and may be collected in the gas jar indicated. It is a heavy gas, and its ascent in the jar may be followed by introducing a lighted candle on a deflagrating spoon. As it will not easily support combustion, the candle is extinguished. A few of the properties of this most interesting gas may be studied when a few jars have been thus filled. By pouring the gas downwards into a jar filled with air, it displaces the air, and the jar ultimately fills with carbon dioxide, as may be noticed when a lighted candle is introduced. Thus it is heavier than ordinary air. If a large glass vessel similar to those used for the storing of gold fish be filled with the gas, and a soap-bubble carefully dropped into it, the bubble floats; being full of air, it is buoyed up by the heavier, but invisible, "air" in the vessel.

We have said that carbon dioxide does not support combustion, yet if some substance which is very fond of oxygen be heated in the gas, that substance may have the power of consuming the oxygen in it and liberating the carbon. Such substances are potassium and magnesium; and if either of these metals

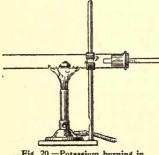


Fig. 20.—Potassium burning in carbon dioxide.

be heated strongly in a stream of the gas, they unite with the oxygen it contains. Magnesium may be set alight in the air and then plunged into carbon dioxide, when it continues to burn with difficulty; and potassium may be placed in a hard glass tube (Fig. 20)

CARBON DIOXIDE

and heated by means of a Bunsen burner while the gas is being passed. When a sufficiently high temperature has been attained to start union, the metal burns with a beautiful violet flame; potassium oxide and black carbon are liberated.

Carbon dioxide is soluble in water. If a small quantity of distilled water be tinted with blue litmus and carbon dioxide passed into it, the solution turns red, owing to the formation of an acid named carbonic acid (H₂CO₃). Its formation may be thus expressed in symbols:—

 $CO_2 + H_2O = H_2CO_3$ Carbon dioxide + Water = Carbonic acid.

If this solution be now boiled, we note with astonishment that the blue colour reappears, the water evidently losing its acidic properties. Thus, carbonic acid is a most unstable acid. It is very interesting to note that water has the power of dissolving its own volume of carbon dioxide, no matter what the pressure of the latter. It is evident, therefore, that by having the gas under great pressure a considerable amount of it may be taken into solution by the water; but when the pressure is released the gas will, to a great extent, escape. This is the principle used in the manufacture of effervescing drinks; soda water is merely water highly charged with carbon dioxide, and the properties of "fixed air" can be quite well examined in the gas that escapes from a bottle of sodawater. It is of interest to note that a paper on this subject marked the first of Priestley's contributions to pneumatic chemistry (1772).

This air, fixed in combination with the oxides of metals in the wide range of solid substances called

carbonates, is thus shown to be identical with the gas breathed into the air during the respiration of animals, during the processes of decay, and in the act of combustion of coal, wood, petrol, coal-gas, and other combustible substances containing carbon. is itself a compound, with the atoms of the solid carbon incorporated within its molecules so firmly that these molecules are difficult to break up. But it is an air which must be taken from the atmosphere as fast as it is sent into it; and this it is the special work of green plants to do. Ordinary air contains normally about 4 parts in every 10,000 of carbon dioxide; when this proportion rises to 9 in 10,000 the air is injurious to health. And this small quantity is all-important to plants as their first article of diet. Under the influence of sufficient sunlight, the chlorophyll, or green stuff of leaves, has the power to decompose carbon dioxide, retaining the carbon for the use of the plant and returning the oxygen into the atmosphere. The carbon can easily be recognised in an active leaf, because it is at once compounded with water to form starch (C₆H₁₀O₅). This action is the beginning of the plant's vital processes; it is the indispensable first step for the existence of life on the earth. We cannot, therefore, exaggerate the importance of Black's "fixed air" in nature; but it was not until the nineteenth century was well on its way that the point just referred to was elucidated.

II.—INFLAMMABLE AIR (HYDROGEN)

When metals, such as zinc and iron, are treated with dilute hydrochloric or sulphuric acid, an "air" is evolved which has the property of inflammability,

INFLAMMABLE AIR

unlike any "air" we have as yet considered. It can scarcely be questioned that the alchemists, during their random gropings, had met with this "air"; yet the real discovery of it seems wrapped in obscurity. Certain it is that Boyle encountered it; and equally certain that Cavendish established its chief properties, showing it to be, along with "fixed air," a gas entirely different in nature from atmospheric air.

Cavendish obtained the gas by the solution in dilute sulphuric acid or muriatic acid (hydrochloric acid) of the metals zinc, iron, and tin. Believing, however, that these metals contained phlogiston (the inflammable principle), he naturally thought that the acid turned the inflammable air out of the metals. These he supposed to contain the gas locked in them in a similar manner to that in which carbonates contain their gas. We now know that zinc, iron, and tin contain no gas, and that the gas Cavendish obtained arose from the killing of the acid, the latter yielding the inflammable air they contain under such conditions, and losing their acidic properties at the same time. We now call inflammable air hydrogen, and it is known to be a constituent of all the commonly occurring acids.

It also exists in water (p. 142).

To prepare the gas, the method we have briefly outlined is followed. Zinc in a granulated condition is placed in the flask (Fig. 21), covered

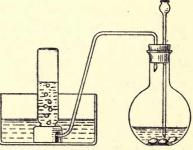


Fig. 21.-Apparatus for preparing hydrogen.

with water, and sulphuric or hydrochloric acid poured down the thistle funnel. The dilute acid sets up a brisk effervescence, and the ensuing gas may be collected over water in the pneumatic trough. The gas is colourless, and on bringing the first jar collected near a light, an explosion follows. The second jar, however, will be found to contain a gas that burns quietly at the mouth of the jar. This difference is evidently due to the fact that the gas in the first jar was mixed with air, which was ultimately cleared out of the flask by the stream of hydrogen. Thus admixture with air causes the explosion. Like ordinary coal-gas, pure hydrogen burns quietly at the mouth of a tube or jar. The gas in the air that promotes combustion is, as we know, oxygen; and the question may arise, does hydrogen explode more violently when mixed with oxygen than when mixed with air? In order to test this point we fill a stout soda-water bottle approximately two-thirds with hydrogen and the remaining one-third with oxygen; if this mixture be presented to a flame, it explodes violently, owing to the rapid union of the two elements. So violent is the explosion that a duster should be wrapped round the bottle to diminish the danger from its possible bursting.

As we shall see in our chapter on water, the union of hydrogen with oxygen is most fascinating, in consequence of the production of pure water by the combination, a matter which we must abstain from discussing until then. We simply note now that if a jar of pure hydrogen be ignited in the air, it burns quietly at the mouth of the jar, only being capable of combustion when the air is present; but when the air and the hydrogen are well mixed, the molecules of

COMBUSTION OF HYDROGEN

the various gases are in such close proximity that the hydrogen molecules can burn all at once, giving suddenly so much heat and producing such a sudden change of volume that explosion results. The pure gas may easily be burnt at a jet just as coal-gas may; but before applying a light at any such jet leading from a hydrogen generator, a sample of the issuing gas should be tested by collecting a little in a small test-tube and presenting it to a flame. If the gas burns quietly, the light may be brought to the jet; but if explosion occurs, it is safer to wait a short time.

The flame of hydrogen, although commonly spoken of as pale blue, is really invisible when the gas is pure. It quickly attains a yellow tint, however, but emits

no luminosity. It is intensely hot. Seeing that hydrogen is a combustible body, the question may be asked: Will it support combustion? If we collect a jar of the gas, invert it, and gently push into it a lighted candle on the end of a glass rod (Fig. 22), the gas will be ignited at the mouth of the jar, but the candle at the same time will be extinguished. Thus the hydrogen does not support the combustion of a candle. is interesting to note, however, that hydrogen supports the combustion of oxygen; for if a jet of oxygen be introduced into a jar of burning hydrogen, the oxygen will be ignited and continue to burn. The flame produced by thus burning oxygen in hydro-



Fig. 22.—
Diagram
showing that
hydrogen will
not support
the combustion of a
candle.

gen (or vice versa) is intensely hot; and the oxy-hydrogen flame thus obtained is used to supply the great heat necessary to obtain the glow of the limelight.

The great use of hydrogen to the chemist arises from the fact that it is extremely fond of oxygen; and when substances such as oxides of metals are roasted in a stream of hydrogen, the latter is capable of abstracting the oxygen by uniting with it, and thus leaving the metal in its pure condition. Such a withdrawal of oxygen from oxides is a simple case of what is called reduction; and in countless instances hydrogen is of great service to the chemist as a reducing agent. We may recall the reader's attention, for example, to the reduction of rouge to metallic iron mentioned at p. 77.

In addition to the foregoing interesting properties of hydrogen, its extreme lightness renders it an attractive gas. Thus it may be poured upwards from one jar to another; it may be poured into a tumbler that has been counterpoised in an inverted position on a balance, when at once the tumbler is found to be lighter, because the hydrogen has taken the place of the air that was inside it. It may be siphoned upwards from one jar to another; and soap-bubbles blown with it rise rapidly. On account of its extreme lightness it is used in filling balloons. It is more than fourteen times lighter than air.

III.—MARINE ACID AIR (HYDROGEN CHLORIDE)

Although "spirits of salt" (hydrochloric acid) had been used for many years, it had not, until Priestley's time, been recognised as containing a specific "air" in solution. Examining the action of copper upon spirits of salts, Priestley found an acid air evolved, and subsequently found that it could be obtained by merely warming the liquid. This gas

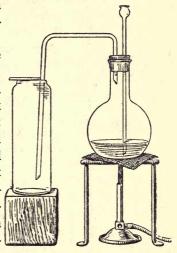
MARINE ACID AIR

he called marine acid air, and it was subsequently made by the process still adopted: that of the action of sulphuric acid (oil of vitriol) upon salt. The gas is so interesting that we intend briefly to study the

method of its preparation and investigate its pro-

perties.

To prepare the gas, the apparatus shown in Fig. 23 may be used. Common salt is placed in the flask and sulphuric acid (about 2 volumes of strong acid to I of water) poured down the funnel. A great effervescence at once occurs: this afterwards subsides; but the application of gentle heat is sufficient to produce a steady Fig. 23.—The preparation of hydrogen chloride. stream of the gas. This can



best be collected over mercury; but as mercury is expensive, we generally collect it as indicated, by allowing it to displace the air in an open gas jar. The gas is colourless, but forms abundant fumes in the air, and possesses a sharp, penetrating smell. On placing a lighted candle in the gas, the candle is extinguished: it will not support combustion.

One of its most interesting properties is its extreme solubility in water. Thus, if a jar containing the gas be inverted, mouth downwards, in water, the water rises to the top of the jar, indicating that all the gas in the jar has passed into the water. The liquid

formed turns blue litmus solution red; hence it belongs to the class of bodies we call acids. It is, in fact, a solution of hydrochloric acid, commonly known as spirits of salts.

Its extreme solubility may be shown by filling a round-bottomed flask with the gas, and corking up

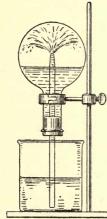


Fig. 24.—Diagram illustrating the solubility of hydrogen chloride in water.

the flask with a rubber bung through which passes a glass tube with a jet at one end (Fig. 24). The other end dips into water. On causing the gas in the flask to contract by pouring over it a little ether, which rapidly evaporates and produces cold, the water enters the flask. As soon as a few drops enter they absorb the whole of the gas, and thus produce a vacuum. More water then enters as a fountain, and ultimately fills the flask.

During the solution of this "marine acid air" in water, a considerable evolution of heat occurs.

Thus, if an air-thermometer be wetted with water and placed in a jar of the gas, so much heat is produced by the absorption of the gas that the liquid in the tube shows a considerable rise. And if the gas be passed for a long time through water a tremendous absorption takes place, considerable heat is produced, and a strong solution of hydrochloric acid obtained.

It may be instructive if we endeavour to find, by adopting the experimental method, what this "marine acid air" contains. Is it an element? And if a compound, what are its constituent elements? In

HYDROCHLORIC ACID

the first place we may note, as Priestley did, that a strong solution in water attacks iron filings most violently, and that a considerable amount of hydrogen is at the same time evolved. As we know that iron has no such power of rapidly evolving hydrogen from water, we must conclude that the gas has been obtained from the "marine acid air." Hence it contains hydrogen. All its properties, however, tell us that it is not merely hydrogen; hence some other substance must be combined with the hydrogen. The question naturally follows: How may we discover what this other substance is? and the answer is as readily given: Take the hydrogen away. To do this means that we must bring the "marine acid air" into contact with some substance capable of taking away the hydrogen. Now it happens that there are certain substances that contain in their molecules oxygen which may be looked upon as loosely attached. Thus, in hydrogen peroxide (H₂O₂) we have in the molecule two atoms of oxygen combined with two atoms of hydrogen, whereas in stable chemical combination one atom of oxygen is the maximum amount that two atoms are capable of holding. The additional oxygen atom present in hydrogen peroxide can therefore be given up to substances which are capable of taking oxygen, and these are then said to be oxidised. Can we, we may ask, oxidise the hydrogen in "marine acid air" by such a process? We will try by using for this purpose a convenient solid substance of the same class as the hydrogen peroxide-namely manganese peroxide, which occurs native in the mineral pyrolusite. If a little of this black substance is placed in a glass tube open at both ends and "marine acid air"

passed over it, on warming the manganese peroxide in the tube, a gas with a greenish colour will be seen coming from the remote end of the tube; and, on placing there a piece of moistened blue litmus paper, we find that the gas no longer turns the blue litmus red, but bleaches it. Thus a second gas is obtained from "marine acid air," a gas of a greenish yellow colour, which possesses the power of bleaching, and is also entirely different in chemical properties from the original "air." Hence the latter contains at least two distinct gases, chemically combined; and further experiments have shown that these are its only constituents. The greenish-yellow gas is called chlorine, and thus we see that the acid air is a compound of hydrogen and chlorine. For this reason it is now referred to as hydrogen chloride; its solution in water is still universally known as hydrochloric acid, or (by metal workers) as spirits of salts.

IV.—Dephlogisticated "Marine Acid Air" (Chlorine)

A study of the properties and uses of the second constituent of "marine acid air" must now be considered. Probably no gas has so interesting a history. Its exact nature was the subject of much controversy among many scientists of repute at the time of its discovery, and almost all had different ideas regarding it. It was very commonly held to contain oxygen, but the most far-sighted thinkers perceived its elementary character. The gas owed its discovery to Scheele; a great Swedish chemist, who in 1774 discovered it by heating together a mixture of marine acid and braunstein, a native variety of manganese

CHLORINE

peroxide. Even when left in the cold, this mixture gave off a wonderful green gas, fraught with many astonishing properties, and Scheele, a thorough-going follower of Stahl, and hence an ardent phlogistonist; regarded it as the substance remaining when the phlogiston had departed from the marine acid. many of its properties, Scheele had come to regard braunstein as a dephlogisticator (a substance capable of removing phlogiston), and interpreted the part it played in this change by supposing that the phlogiston was removed by it. This, as we know, is in the main, what really does occur; but Scheele's interpretation is now stated in a different chemical language. The braunstein does not take phlogiston away, but supplies oxygen. Acting up to his theory, Scheele named the gas dephlogisticated marine acid. Subsequently Lavoisier and his French contemporaries, arguing that when substances become dephlogisticated they really become oxidised, called it oxymuriatic acid (muriatic acid being another name for spirits of salts). It was left, however, for Humphry Davy to show the true nature of the substance. After exhaustively studying the gas experimentally, he came to the conclusion that it contained no oxygen, and that the name oxymuriatic acid was therefore unsuitable. Further, he convinced himself that the gas was simple in nature; that all experiments made with a view to decomposing it were failures; that, in short, it was an element. In 1810 he suggested the name chlorine for the gas-a name which was only adopted after some controversy. It is still retained; and, though certain facts tempt us to doubt its elementary character, those facts do not

include any sign of its decomposition into simpler elements.

To prepare the gas, we still adopt the method of Scheele—that of warming manganese peroxide with hydrochloric acid. A little of the former substance is placed in a flask and hydrochloric acid poured on it, the apparatus used being similar to that in which we made hydrogen chloride. As the gas collects in the jar, it is found to have a greenish-yellow appearance, not easily perceptible by gaslight, but easily seen in daylight or by the light of burning magnesium. It possesses a characteristic smell, and if taken in quantity is poisonous. Even in small quantities it is very irritating to the throat and nose. Its general properties are most interesting. It shows no fondness for oxygen; indeed, it resembles oxygen in its very strong partiality for hydrogen and for metals.

In a jar of chlorine a lighted candle may be placed, when it will be observed that it continues to burn with a very smoky flame, emitting dense, sooty fumes of carbon, and producing at the same time fuming clouds of hydrogen chloride. As these are the only products formed, we see that candle wax consists of carbon and hydrogen; and that the chlorine acts towards it very much as oxygen did.

A little powdered antimony, sprinkled in a jar of the chlorine, burns spontaneously, forming a white substance called chloride of antimony; and a thin leaf of Dutch metal (an alloy of copper and zinc) also ignites spontaneously in the gas. Thus it is a very active gas, uniting with many metals vigorously without any external application of heat, and yielding *chlorides*. A jet of hydrogen may be burned in chlorine gas, when fumes

CHARACTERS OF CHLORINE

of hydrogen chloride are again synthesised. If a mixture of these gases in equal volumes is sealed up in a glass bulb and exposed to direct sunlight, a vigorous explosion occurs as the two gases unite. Hence hydrogen and chlorine are proved to have a strong affinity for each other.

One of the most useful properties of chlorine is its power to bleach natural colouring matters and to strip away the colours from ordinary dyed articles. If a dyed piece of calico be placed in moist chlorine, the latter oxidises the colouring matter, and produces a colourless compound. The colour of ordinary writing ink may similarly be removed from paper, and numerous other substances can be decolorised by the chlorine. It is of interest to note, however, that chlorine in a dry condition, with a dry fabric, has but little activity: and is thus robbed of its bleaching properties. The water is an essential factor in the bleaching action; and it is supposed that the hydrogen in it unites with the chlorine and that oxygen is thus liberated from the water. Set free in this manner, right in the midst of matter they can attack, the oxygen atoms have not the opportunity to combine together and so form oxygen molecules, but at once attack the unoxidised substance with which the fabric is dyed, and bleach it. Oxygen, or any element in this condition, is said to be nascent, or fresh; it is much more active in this condition, because the oxygen molecules have not to be split up as a preliminary to the activity of the element. Thus the bleaching activity of chlorine depends upon its fondness for hydrogen, and the actual bleaching work is done by the nascent atoms of oxygen.

Chlorine as a bleaching agent is not universally employed, on account of its great tendency, not only to bleach, but to impoverish the fibre of the material used. When it is used, however, the portable form in which it is supplied is *bleaching powder*, or "chloride of lime," made by passing chlorine into slaked lime. The latter substance has the power of absorbing chlorine, as may be seen by shaking a little with chlorine in a gas jar, when the colour of the gas disappears. Quicklime, on the other hand, does not absorb chlorine.

Bleaching powder, which smells of chlorine, is generally used in dilute aqueous solution, though often it is mixed with sodium carbonate solution and filtered from the precipitate that forms. The clear solution then contains sodium hypochlorite, and this is much used as a laundry agent.

If the lime is well incorporated with the water, and the chlorine passed through the milky fluid while it is hot, we do not obtain bleaching powder, but a solution containing calcium *chlorate*, which is afterwards used for the production of the well-known chlorate of potash, which has no bleaching powers.

We may conclude our remarks upon this gas by mentioning that it is now made industrially by passing strong currents of electricity through brine or fused salt. In each case chlorine is produced along with other products, and the method is cheap and economical in those places where electric energy is easily obtained. In this country, owing chiefly to lack of water power and the high initial cost of coal, electric energy is expensive; consequently the old method used by Scheele is still in vogue. For a few

USES OF CHLORINE

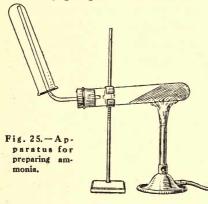
other industrial preparations that have been used in this country, the student is referred to some higher text-book on industrial chemistry.

V.—ALKALINE AIR (AMMONIA)

Our tale of Priestley's researches on "airs" is not yet ended, and once more we have to chronicle a discovery made by this indefatigable worker. Judging from the fact that sal-ammoniac was well known to the alchemists, we might have expected them to have recognised this alkaline air; especially when, by heating sal-ammoniac with slaked lime, they had really obtained it and passed it into water, forming for themselves a solution with alkaline properties, which they called the volatile spirit of sal-ammoniac. It was from this liquid that Priestley obtained his first sample of "alkaline air." Arguing from analogy with the case of "marine acid air," he heated a little of the volatile spirit in a phial by the flame of a candle. He found a torrent of vapour to be discharged from it, and he collected it over mercury. He afterwards collected some of the air by heating the mixture of salammoniac and slaked lime. He named the gas "alkaline air," because of its most striking property: it restores the blue colour to reddened litmus, and is able to neutralise acids—that is, destroy their acid properties-and convert them into salts. The gas is now known as ammonia, and the salts made by it with the various acids are called ammonium compounds.

In order to make the gas most conveniently, we still use a mixture similar to Priestley's—I part of salammoniac with 3 parts of slaked lime. Being lighter

than air, the ammonia formed must be collected by upward displacement (Fig. 25). It has a characteristic and very pungent odour, and when a jar full of the gas



is placed, mouth downwards, in water, the water almost instantly rises to the top of the jar, showing that the whole of the gas has been dissolved. It is, in fact, extremely soluble in water: one pint of water will hold something like 1,150 times

as much ammonia gas in solution. Its solubility can be demonstrated by the same striking method as we described for hydrogen chloride (Fig. 24). The liquor ammonia of commerce is a very strong solution of the gas, with a specific gravity of 0.880; it is known to chemists as ammonium hydroxide, and enters into the composition of many cleansing agents.

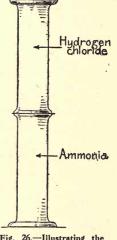
Ammonia gas will not burn in air; but if it is liberally supplied with oxygen combustion takes place, and the products of such combustion are found to be nitrogen and water. Hence ammonia is a compound "air," containing at least nitrogen and hydrogen (the latter of which, of course, gave the water). That it contains nothing else we may prove by attempting to synthesise it from nitrogen and hydrogen alone. Under the influence of powerful electric sparks, a very small quantity of ammonia is produced—enough, however, to show that it can be made from the two elements. It is,

ALKALINE AIR

however, much easier to decompose ammonia than to make it up again. In presence of chlorine gas, the ammonia gives up its hydrogen very readily, and nitrogen alone is left. It cannot be said that ammonia is a very unstable gas; still, the atoms of nitrogen in its molecules are easily liberated when any element. like oxygen or chlorine, which is fond of hydrogen is given its opportunity. Fairly simple experiments only are required further to settle the proportion of the

two constituents and to give to the alkaline air the formula NH3.

If a jar of ammonia be brought into contact with a jar of hydrogen chloride (Fig. 26), immediate combination takes place. Dense white clouds are formed, which settle as a fine powder on the sides of the jars, and are found on examination to consist of sal-ammoniac, or ammonium chloride. Thus the function of the slaked lime in the preparation of ammonia was the withdrawal of the acid from the salammoniac, leaving the ammonia Fig. 26.—Illustrating the free. Ammonia is a volatile alkali, combination of hydrogen and can easily be removed from its



chloride and ammonia.

salts by any of the "fixed" alkalis, like lime, soda, or potash. If ammonia be introduced into sulphuric acid a violent combination, with great evolution of heat, follows; and there results the sulphate of ammonia now largely used as a manure. From this sulphate any alkali will liberate the ammonia if gently heated with it, just as lime sets the gas free from sal-ammoniac.

Ammonia is produced when many organic substances, such as horn, glue, etc., are subjected to destructive distillation—that is, heated away from communication with the open air. It is a common product of the decay of vegetation, and slowly forms in stagnant urine, which accounts for its common presence in stables. Much of the liquor ammonia of commerce is obtained as a by-product in the manufacture of coal-gas. Coal is submitted to destructive distillation in large retorts, and ammonia is one of the vapours given off. These vapours, during the process of purification, are led through water, when the very soluble ammonia is retained, along with a few other compounds. This liquid is the liquor ammonia, and if heated with lime it yields a copious supply of ammonia gas. Led into dilute sulphuric or hydrochloric acid, the gas gives the sulphate or chloride of ammonia. The latter substance finds a commercial use in electrical work as an ingredient of many dry cells and of the Leclanché cell.

VI.—VITRIOLIC ACID AIR (SULPHUR DIOXIDE)

Oil of vitriol was a liquid Priestley also subjected to the action of heat with the object of testing whether it would yield an air when thus treated. Mixing it with olive oil, and subsequently heating, he collected an air over mercury in a manner similar to that adopted when collecting "marine acid air." Priestley concluded that olive oil, being, as he put it, rich in phlogiston, gave the latter to the vitriol; and he determined to try other substances which were similarly rich in the inflammable principle. He accordingly heated the vitriol with charcoal, and again

VITRIOLIC ACID AIR

obtained a supply of the same gas; and finally, when trying to disengage the air by the mere application of heat to the acid, the mercury in his collecting vessel accidentally sucked back into the hot acid, and a tremendous evolution of the gas took place. This at once opened up the whole field of the action of metals upon vitriol, and it was found that if such metals as copper, mercury, and zinc are heated with oil of vitriol a gas with a suffocating odour is evolved—the gas called by Priestley vitriolic acid air.

Let us endeavour to study a few of the properties of this air. For a supply of the gas we might conveniently use the apparatus of Fig. 23, copper being placed in the flask and sulphuric acid (oil of vitriol) poured down the funnel. On the gentle application of heat, the contents of the flask darken in colour (owing to the formation of a compound of copper and sulphur, Cu₂S), and presently a brisk effervescence occurs. The heavy gas collects in the gas-jar and may be subsequently examined.

The new air has a choking smell, and may at once be recognised as similar in this respect to the gas obtained by burning sulphur in oxygen, previously referred to as sulphur-oxygen-stuff or sulphur dioxide. If a jar containing the gas be inverted in water, the gas is found to be very soluble, and to change a solution of blue litmus red, exactly as our sulphur dioxide did. If further accurate comparisons were made, this vitriolic acid air would be found identical in all respects with sulphur dioxide; hence this name is given to it. We have, then, a new method for its preparation; but it may be at once said that the method invariably used for

making sulphur dioxide in large quantity is that of burning sulphur (or some compound of sulphur in which the element is present in a combustible condition) in a stream of air.

A solution of this gas in water is known as sulphurous acid, and it has a large application as a bleaching agent. If the gas be led into solutions of the alkalis potash or soda, salts known as sulphites are obtained, which are sold as "sulphite liquors" for bleaching purposes. Chemically speaking, both sulphur dioxide and the sulphites are good reducing agents (p. 96); the gas is also a useful disinfectant, and its solution a fairly powerful antiseptic.

Sulphur dioxide itself can easily be liquefied; it is sufficient to pass some of it through a tube immersed in a mixture of ice and salt. The liquid sulphur dioxide is indeed an article of commerce, and serves as a convenient supply for the gas when a large quantity of it is required for experimental work.

We have previously seen that hydrogen gas is contained in sulphuric acid, since zinc is capable of displacing it from the diluted acid. We now see that it must also contain sulphur and oxygen, inasmuch as the sulphur dioxide, which we have made from it, contains these two elements. Other experiments that we might make with the acid would fail to reveal the presence of any other element in it; and we may safely conclude that oil of vitriol is made up of hydrogen, sulphur, and oxygen as its fundamental elements. It is natural for the scientific mind now to seek a process for the synthesis of sulphuric acid from these three elements. If sulphur dioxide is dissolved in water, however, we do not obtain sulphuric, but sul-

SULPHUR DIOXIDE

phurous, acid; the sulphurous acid smells strongly of burning sulphur (sulphur dioxide), but if left in contact with the air gradually loses this or any smell; the oxygen of the air slowly oxidises it, in fact, into dilute sulphuric acid. This may be carefully concentrated by evaporation, and pure oil of vitriol obtained. We may represent the two steps of this action in symbols, thus:—

 $SO_2 + H_2O = H_2SO_3$ (Sulphurous Acid) $H_2SO_3 + O = H_2SO_4$ (Sulphuric Acid)

We thus arrive at the principle of the method for the manufacture of the acid which, on account of its immense utility, Liebig described as the "key to chemistry." Its manufacture is one of the largest and most important chemical industries; the student will find it a most instructive lesson in applied chemistry, if he will consult in a larger work the methods by which the principle we have outlined has become practically operative.

From the airs that we have briefly studied in this chapter, it will be easy to gather that the air-element is as varied in its appearances and characteristics as its companion "elements," water and earth. Some of the airs here dealt with must literally have stunk in the nostrils of the early workers in chemistry, but, hampered by ill-founded speculations, they failed to recognise their individual differences. All airs or gases—and there are hundreds known to us—are now material stuffs, and not spirits. When this step had been gained the course of science was cleared of a great obstacle; and the rush of discovery during the time of Priestley, Lavoisier, and Scheele was the consequence.

CHAPTER IV

FIRE

I.—Some Early Theories and Simple Experiments

Fire raised man from the savage state and placed him on the upward road to civilisation. Its obvious powers we need not dwell upon here, except to ask what man would be now if he could not work in metals or stone, cook his food, and provide himself with artificial warmth. Little wonder that the myths of the nations have their Prometheus, the fire-stealer, for their first benefactor, giver of arts, intelligence, and learning. From heaven, from the sun, it came; but how, except through a demi-god, a Titan defying a jealous Zeus?

But the Greeks advanced early from the ruts of superstition, and inoculated the world with the germ of science. What is Fire? Surely it is one of the fundamental formative essences—one of the primordial elements? It can scarcely be otherwise, in the infancy of science. And the philosophical mind, eager to reduce these four elements to one, the primitive principle or Urstoff, whence all the others arise, names, first, water, then air, later fire, as the finest, irreducible first cause. It was Heraclitus (c. 535–475 B.C.) who gave the honour to fire, mainly because he saw that fire—by which he meant heat—was the main cause of motion or change—the cardinal phenomenon of the universe. Heat the cause of motion! The step is not a long one into the great physical dis-

covery of the nineteenth century. Yet fire was not regarded, any more than air, as a stuff, but as a principle combining the properties of hotness and dryness. Verbiage like this crossed the dark ages and the middle ages without criticism, though the root of the matter was near at hand all the time.

Heat does not imply flame, though flame is always accompanied by heat. We may have a substance hot without being able to perceive it with the eye; when we can so perceive it, the substance is described as *incandescent*. Incandescence is the consequence of exceptionally intense heating, and always means a very high temperature or degree of heat. We do not get incandescence or flame without heat, so that our first real inquiry concerning the fire-element must be directed to the heat which is its basis.

First, what can heat do? It can flow from one body to another like a fluid, always from bodies at a high temperature to others at a lower, until the two temperatures are the same. It can set up motion, as when we boil water. It can cause expansion. can travel from the sun or stars across empty space. These and many other characteristics have been known very many centuries. And further: it is old knowledge that heat is produced, i.e. becomes perceptible in an increased degree, when certain chemical changes, such as combustion, take place; and that it always arises from somewhere whenever there is friction. When a savage obtains fire by rubbing two sticks together; when a schoolboy makes a brass button painfully hot by rubbing it briskly on his coat; when the red-hot spark flies off the wheel of a railway carriage when the brakes are sharply applied; when

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a match is rubbed along a rough surface—these, and many similar cases, remind us of the connection between heat and friction.

Now, the salient point about friction is that it always leads to the destruction of motion: in modern language, energy disappears. Energy is a something which bodies in motion possess, and by virtue of which they are able to do work—to overcome resistances, exert force, and communicate motion to other bodies. If the speed of a train is reduced, it has less energy than it had before. Now, is the energy lost in friction really destroyed, or is it merely transformed? In other words, does the heat which is produced when motion is destroyed by friction represent the energy that has disappeared? That is to say: is it energy? Is heat a kind of motion?

Think of two other simple experiments. Strike an iron nail a few times sharply with a hammer. Does it not become hot? Whence comes the heat? Assuredly it must be the equivalent of the energy which you have expended; for, the more you hammer the hotter the nail becomes. And again, take the case of the fire syringe. This is an accurately bored glass cylinder in which an air-tight piston can move; if a piece of phosphorus be placed at the bottom of it and the piston pushed down, the phosphorus will ignite. Again we are struck by the coincidence that energy expended develops heat; again we are driven to the thought that energy and heat are but different forms of one thing.

What is the alternative? Heat may be a substance, like air—it may be a real element; and this idea was prevalent among men of science in the eighteenth cen-

THE NATURE OF HEAT

tury. A hot body was held to possess a certain highly subtle and penetrating fluid called caloric; this could move freely through the densest matter, and out of it through the air into space or elsewhere. This caloric is not so obnoxious to modern science as phlogiston, because it was exceedingly difficult to decide by experiment whether heat per se made any difference to the weight of a body. But in cases of friction the apparently limitless reservoir of caloric that must be presupposed is an insuperable difficulty. This was present to the mind of Count Rumford when he made his decisive experiments in 1798. He bored a hollow gun-metal cylinder with a steel borer, and found that 837 grains (troy) of filings were produced; but that, during the operation, the temperature of the barrel had risen to 70° F. Enough heat had been produced to raise 5 lb. of ice-cold water up to the boilingpoint. "Is it possible," he asked, "that such a quantity of heat . . . could have been furnished by so inconsiderable a quantity of metallic dust merely in consequence of a change in its capacity for heat?"
The believers in caloric would have explained the appearance of the heat by the supposition that the powdered metal could not hold so much caloric as the original solid, so that the caloric was, as it were, squeezed out in the process of powdering. But even this explanation cannot be applied to the experiment in which Sir Humphry Davy melted large quantities of ice by merely rubbing two pieces together.

We are, then, left with the theory that heat is a form of energy; and careful measurements by Joule (begun in 1840) established beyond doubt that the heat produced is in all cases proportional to the work

wasted in producing it. Joule measured also the connection between the two, and found that the energy spent when I lb. falls 772 feet would, if all turned into heat, raise the temperature of I lb. of water by I° Fahrenheit. The converse process of turning heat into motion is, we need not remind our readers, carried out—imperfectly, it is true—in the steam engine.

If the molecules of a hot body are conceived to be in motion, we can explain all the facts known about heat as a physical agent. The molecules may be actually moving or merely in vibration, or both. The vibrations of the molecules will be communicated to the ether (Chapter VII.) surrounding them, and carried off as waves. The waves which produce heat only are longer and less rapid than those which produce light; but they are of the same nature. As waves through the ether comes then the energy of the sun to us. The sun's heat is one form of motion: the waves in the ether are another form. When these waves fall upon any substance on the earth they may be absorbed and transformed into heat again. Thus does our theory of heat link itself up with other branches of physics, and thus do we find further cause to admire the intuition of the Greeks in contemplating their opinion that Fire is motion.

II.—HEAT AND COMBUSTION

Let us now briefly reconnoitre our position. We know by experiment that energy and heat are closely related: that when energy is wasted heat is produced, and in many instances the heat produced is sufficient to cause the ignition and consequent burning of some

HEAT AND MOTION

particular substance. Now from our chapter on air we know that burning is a chemical change, and the energy we waste in the production of heat thus gives rise to chemical energy. Where, we may ask, has this energy its origin? To answer this question, we must take the reader once again to those coarse grains of which matter is supposed to be built: those ultimate molecules which are accountable in modern belief for many kinds of phenomena. We have evidence that, in the solid, liquid, and gaseous conditions of matter, these molecules are possessed of motion. If an iron ball be heated in a fire to a dull red heat and then removed, no visible external signs on the ball may manifest themselves; but a little above it we may see the quivering of objects, showing that the air has been disturbed: it is in motion, and obviously has received its energy by communication from the ball. If the ball be made hotter, its molecules vibrate at a still greater rate; and the greater rapidity of the waves they generate in the ether is revealed by an effect on the retina of the eye: we perceive the ball in a red-hot and finally white-hot condition. That in the dull red, red and white-hot states it starts waves of different length may also be beautifully shown by means of the spectroscope, an instrument by the help of which the wave-lengths may be compared. It is then seen that these undulations, started by the vibration of the molecules, are of long length when the ball is dull red, but that as a white heat is obtained they are produced more and more quickly, finally issuing at an unimaginable rate—something like 500 billions per second. So thoroughly does theory adjust itself to facts that we may safely conclude, in the words of

Davy, that "heat is a mode of motion," and that the motions of the molecules of a body may be revealed by their heat effect.

Continuing our consideration of the iron ball, we may imagine that the ball is made white-hot and then plunged in oxygen gas. The heat energy possessed by the iron now renders it capable of quick union with the oxygen; this is impossible in the air owing to the diluted condition of the oxygen, the molecules of the iron and oxygen not being in close enough proximity. This quick union shows itself in combustion; the iron commences to burn. In burning, we have a chemical change, and such changes involve atomic considerations. On the one hand, we have atoms of iron and atoms of oxygen, each possessed of energy. This energy is of a complex nature. Some of it is doubtless due to motion or to vibration, but some of it is also due to the nature of the atom itself. The atoms have affinities-loves or hates, as Empedocles styled them; the atom of iron has a chemical attraction for the atoms of oxygen, and this attraction, possibly of an electrical character in its essence, is responsible for their union into molecules when they can get into one another's sphere of action. When the union takes place, a substance, black oxide of iron, is produced, which possesses far less intrinsic energy than the atoms forming it possessed when free or uncombined. Hence the production of oxide of iron is accompanied by a change in the energy of the system, and it is this change in energy which results in the liberation of a large amount of heat, this heat being sufficient to keep up the combustion of the iron. The change here in the energies of the constituent atoms

THE HEAT OF COMBUSTION

results in combustion, and is really a transformation of atomic energy into heat.

In a similar manner, we may consider the burning of carbon in oxygen. Both the atoms of carbon and oxygen possess intrinsic energy, and the intrinsic energy of carbon dioxide is less than the total intrinsic energy contained in the atoms of carbon and oxygen producing it. This excess energy is transformed into heat during combustion, and sufficient heat is produced by completely burning I lb. of wood charcoal to carbon dioxide to raise the temperature of 80 lb. of water from freezing-point to boiling-point.

The consideration of many problems of combustion such as these leads us to state that mechanical work transformed into heat may raise the temperature of some bodies sufficiently to ignite them. Combustion is produced by such ignition, and during combustion some of the intrinsic energy of the constituent atoms of the reacting substances is converted into heat. Thus first mechanical energy, and secondly chemical energy, are transformed into heat.

In our chapter on air we had many instances of combustion, but we must pause a few moments in our consideration of this phenomenon. Combustion is really chemical change accompanied by heat and light, and too often is it assumed that only in air and in oxygen can combustion take place. We have, however, many other instances where the chemical union between two substances is so violent as to liberate enough energy in the form of heat to start spontaneously the combustion of one of them. Thus a piece of phosphorus, held in chlorine on a deflagrating spoon, first melts and then fires, the combustion continuing

until one of the reacting substances is exhausted. A piece of dry phosphorus, placed by the side of a few flakes of iodine, also bursts into flame. Powdered antimony thrown in chlorine instantly flashes and burns, and copper is at once ignited if thrown into sulphur vapour. These are instances of combustion where clearly oxygen plays no part; and there are many others. In our subsequent work, however, unless stated to the contrary, we shall consider combustion as referring to the burning of substances in air, i.e. in oxygen.

In observing the combustion of various substances, equally various phenomena are observed. Thus charcoal burns slowly in air, or smoulders, generally without the emission of any flame. But when coals burn flame is produced, and this is due to the production of vaporous compounds of carbon and hydrogen, which continue to burn and emit the flame. When the hydrocarbons, as these compounds are called, have been driven from the coal, the carbonaceous matter that remains burns without any further flame-formation. In short, if the combustible solid substance does not in any way yield a vapour, we shall find that no flame is produced; but if vapours are found, the combustion is attended by flame. In all cases of flame formation the combustible substance is first converted into a gas or yields some vapour which is inflammable.

It will also be evident that the temperature of the combustible body is an important consideration. Some substances will ignite at a low temperature; others need to be strongly heated before visible burning begins. The heat energy given to the combustible substances in a match-head by friction is sufficient to cause

FORMATION OF FLAME

ignition. The vapour of carbon disulphide may be ignited by introducing into it a warm glass rod; yet carbon requires a very high temperature before it can ignite. This temperature at which ignition takes place is generally referred to as the *ignition temperature* of the substance. Nothing can more impressively illustrate the mysterious character of the process of chemical combination than the fact that, whereas carbon and sulphur have a comparatively high ignition temperature, the flashing-point of their compound (CS₂) is so dangerously low. The same oxides are produced whether the atoms are burned singly or in the compound form.

III.—PRODUCTION AND NATURE OF FLAME

It will be interesting now to consider in greater detail the production of flames, as these are, generally speaking, the most noticeable attendants of the process of combustion. They are, as we have said, produced by the combustion of gases; and it at once follows that the conditions of any system of reacting gases should be capable of being reversed. Thus, if coal-gas unites with oxygen in air, and the combustion of the coal-gas is due to union between these bodies. then air should be capable of being burnt in coal-gas. Similarly, a jet of oxygen should burn in hydrogen, and chlorine should also burn in hydrogen. By leading a little chlorine through a jet and introducing the jet into a jar of hydrogen-which has been ignited at the mouth of the jar-the chlorine will continue to burn, showing that the positions of combustible body and supporter of combustion can be reversed. A similar experiment may be conducted, using oxygen

in place of chlorine; the oxygen burns in the hydrogen with a very hot flame as freely as the hydrogen itself burns in oxygen. The following experiment may also be performed to show that air is capable of burning in coal-gas.

A lamp-glass chimney is provided with a cork at

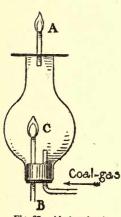


Fig. 27.—Air burning in coal-gas.

its base, two tubes passing through the cork as shown in Fig. 27. At the top the chimney has a sheet of asbestos placed over, through which passes a straight glass tube. By leading in coalgas through the right-angled tube, and closing A, coal-gas may be ignited in a few seconds' time at B. If now the finger be released at A, the flame ascends the tube B c and sits on the tube at c. Air is now being dragged up B C, and continues to burn as shown. The excess of coal-gas may be

ignited at the end of A.

It was at one time thought that combustion immediately antecedent to flame-formation started suddenly at the ignition temperature of the gas, and that this temperature must be attained before combustion can take place. This, however, seems to imply that the transformation is sudden; but careful experiments have shown that the transition from hot gas to flame is gradual, not sudden. And, although an ignition temperature must first be reached before full combustion can proceed, the actual process is a very gradual one, the heat effect as it gradually increases being

SLOW COMBUSTION

attended by certain changes immediately before ignition takes place.

In some cases the preliminary effects of heat may be noticed. If a little ether, for instance, be dropped on to a hot plate in a dark room, it is seen to emit a light, although it is not ignited. In short, it phosphoresces; and only if it is raised to a higher temperature does it burst into flame. The phosphorescence of the ether vapour precedes the ignition. The vapour of turpentine and that of carbon disulphide have also been obtained in a phosphorescent condition before yielding a true flame. In the case of one substance, yellow phosphorus to wit, this phosphorescence is manifested at ordinary temperatures, owing to the extremely low ignition temperature of phosphorus (about 44° C.); and common experience, in the case of this substance, tells us that the phosphorescence is an effect immediately preceding combustion. It is, in fact, a slow combustion of the substance; but the substance is in such a condition that it is losing heat to its environment by conduction, etc., more quickly than it is generating heat; and full combustion cannot take place. Immediately the production of heat by the phosphorus-oxygen system is greater than that lost by conduction, etc., the ignition temperature is reached and full combustion begins and proceeds. In many other instances it can be shown that phosphorescence is antecedent to full combustion, and probably in all instances of flame production the combustible substance first passes through the phosphorescent state. Thus then, if, by some means -mechanical, chemical, electrical, or by heat-we can supply a combustible with energy, we ultimately get

it at a temperature when full combustion can take place. If vaporisation takes place, or if the combustible body is itself a gas, such combustion is attended by flame formation; flame is the final stage of a series of gradual changes.

On closely observing the flame of an ordinary gasburner, or of a burning candle, it at once becomes evident that the flame has a definite structure. In the study of such structure, it will obviously be the simplest method to commence with some simple flame, and gradually work up to the more complex. Now, if a flame is produced by the combustion of some simple substance which can yield only one possible product of combustion, we should expect such a flame to be of the simplest type. Such, indeed, is the case. The flames of hydrogen and carbon monoxide, where only one product of combustion can possibly be produced, are beautiful shells of blue; although pure hydrogen has a colourless flame, the gas is generally admixed with some slight impurity, which imparts the tint. Carbon monoxide (CO) is really carbon imperfectly oxidised; given the opportunity, it will readily pass into carbon dioxide, with the blue flame often seen flickering above a very red coal fire. Now, in each of these instances the burning substance is oxidised straight away, the hydrogen to water and the carbon monoxide to carbon dioxide. If, however, a more complex compound, say cyanogen (C2N2), be burnt, a gas which may be oxidised in two separate stages, the flame obtained shows two cones very distinctly. The inner cone is of a roseate or purple hue; the outer cone pale blue. When cyanogen burns in this way, the carbon it contains can be supposed to burn

SIMPLE FLAMES

first to the halfway stage of oxidation, to carbon monoxide, the nitrogen being simply liberated unchanged. This change is accomplished in the inner cone of the flame, and the carbon monoxide and nitrogen then pass to the outer cone, the former then burning more completely to produce carbon dioxide. The blue outer cone is thus due to the carbon monoxide burning in air to produce carbon dioxide. We thus learn from this case the very important truth that the two-coned structure of the flame is dependent upon the fact that the oxidation can take place in two stages.

We will now extend our considerations to the flames of still more complex substances. Compounds are known which contain only the two combustible elements, carbon and hydrogen, and are called hydrocarbons. Many of these, such as petroleum, marshgas, etc., occur naturally, whilst some are produced by destructively distilling certain natural substances rich in carbon and hydrogen. Thus when coal is heated out of contact with the air, as in the retorts of the gas manufacturers, many volatile products are obtained, chiefly hydrocarbons and free hydrogen. Of the hydrocarbons, we may mention marsh-gas (CH₄), ethylene (C₂H₄), benzene (C₆H₆), toluene (C₇H₈), and naphthalene (C₁₀H₈). Of these, the marsh-gas and ethylene, along with hydrogen and a little benzene vapour, escape condensation when the volatile products are cooled, and pass along to gasometers, from which they are supplied as coal-gas. Our common illuminating gas, then, may be looked upon as a mixture of hydrogen with light hydrocarbons. The major portion of the benzene, along with the toluene, naph-

thalene, and other hydrocarbons, is condensed and afterwards obtained by distillation from the tar. The benzene and toluene are liquids; naphthalene is a solid. The hydrocarbons as a class can easily be converted into vapour, and burn with characteristic luminously sooty flames, the carbon in them burning finally to carbon dioxide and the hydrogen to water. Composed of such a substance is the wax of which ordinary candles are made, and the products of the

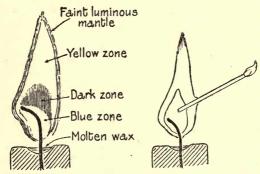


Fig. 28.-Candle flame.

Fig. 29.—Conducting gases from dark zone.

combustion of a candle are carbon dioxide and water. This combustion, however, is not so simple as the mere expression implies, and the study of the flames of hydrocarbons, commencing with that of a candle, is brimful of interest.

A burning candle shows wonderfully well the change from solid to vapour undergone by a substance burning to produce flame. The heat supplied by the match melts and vaporises a little wax, and this burns. The heat produced melts the wax at the immediate base of the flame, which then rises in the wick by capillary

THE CANDLE FLAME

attraction, is vaporised by the heat of the flame, and afterwards takes fire. Careful observation of a burning candle shows that the flame formed by the combustion of the wax may be divided into four portions and reference to Fig. 28 may serve somewhat to make these portions clear.

We have the wick surrounded by a blue portion, which gradually merges into a darker region; and this region, at about one-third the height of the flame, shades off fairly abruptly into a yellow portion, the region of greatest luminosity. A close observation also reveals a faintly luminous mantle surmounting the whole flame, although this is often missed in a casual glance. It is quite natural to suppose, therefore, that these different appearances arise from definite causes, and it is our desire to find these causes for the varying effects. Let us introduce one end of an open straight glass tube into the dark portion (Fig. 29). If care be exercised, a light may be obtained at the other end of the tube; combustion proceeds, showing that gases still capable of being burnt exist in this portion of the flame. In all probability, this dark portion is a zone where no true combustion is proceeding, the hollow space being filled by vapours formed by the mere effect of heat upon the wax-gases whose combustible portions will be burnt on their ascent up the flame.

Let us now examine the yellow or luminous portion of the flame. On introducing into the flame a piece of white porcelain, it is at once coated with soot, which is really carbon in very fine powder. Hence on momentarily cooling the luminous area of the flame, carbon is deposited. It is now generally supposed that the luminosity is due to particles of this carbon, dis-

seminated in a free and hot condition in the flame. They shine because they are very hot—so hot as to be incandescent. It was suggested, some years ago, that the luminosity was due to the vapours of dense hydrocarbons in an incandescent state; but we may take it now as more likely that the incandescence of free particles of solid carbon is the cause of the brightness. The question of the origin of this carbon is one which has, from time to time, aroused most interesting controversies among investigators. The simplest suggestion is that the hydrocarbons decompose under the action of the heat into carbon and hydrogen; and, relying upon this suggestion, it has been supposed, and believed for many years, that the hydrogen in the hydrocarbon obtains preferential treatment over the carbon, the oxygen uniting with the hydrogen first and producing an intensely hot flame, in which the particles of liberated carbon become incandescent.

This theory is, however, hard to reconcile with many known facts. The gas methane (CH₄) burns with a blue flame, with little luminosity. Admixture with chlorine greatly increases the luminosity of the flame by virtue of the fact that chlorine is very fond of hydrogen. Thus preferential treatment, as it were, occurs, and the liberated carbon becomes incandescent in the flame produced. But admixture of the methane with oxygen (which we might expect to behave similarly to the chlorine) has the reverse effect, even diminishing the luminosity. Again, the hydrocarbon ethylene (C₂H₄), when served with its own volume of oxygen and exploded, has all the hydrogen it contains set free, whilst all the carbon it contains is found to be burnt (incompletely) to carbon monoxide.

LUMINOSITY OF FLAMES

These facts, we say, have been urged against the theory that the hydrogen is preferentially burnt at the expense of the carbon. Within recent years certain compounds, intermediate between the hydrocarbon and its final products of combustion, have been shown to be produced by certain gradual stages of union of the carbon, hydrogen, and oxygen; and it is probable that these in some way interact among themselves and with the hydrocarbons to produce the liberation of carbon. Any idea of preferential treatment, either for the carbon or the hydrogen, has had to be abandoned.

The blue region at the base of the candle flame is probably due to the burning of carbon monoxide and hydrogen, and hence is a zone beneath which partial oxidation is proceeding; whilst the faint luminous mantle surmounting the whole flame is the place where, air being in greatest abundance, the carbon monoxide, and any hydrogen and hydrocarbons, passing from the blue region, undergo complete combustion. That the complex structure of a candle flame is due to the possibility of partial combustion is certain, but precisely how the various gases are distributed throughout the flame it would be hazardous at present to say.

IV.—THE BUNSEN FLAME

A stream of coal-gas, issuing from the open end of a glass tube, presents a flame very similar to that of a candle; but if a supply of air is fed into the flame, the luminosity begins to decrease, and the greater the amount the less the luminosity and the more complete the combustion. As gas names are in great

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demand for heating purposes, and as luminosity in such cases is an undoubted disadvantage, it was long ago felt that a burner producing a good hot nonflickering flame would be an advantage. The first really successful one was due to Bunsen, and the burner which bears his name has been adopted universally. The burner, as generally met with, has an

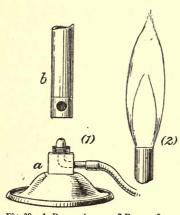


Fig. 30.—1. Bunsen burner. 2. Bunsen flame.

iron base (Fig. 30 a), upon which screws a cylindrical chimney b, containing at the base two holes, which are capable of being closed or shut by a ring slipping round the tube. The gas escapes through a fine orifice in the base; it comes out under pressure, and is ignited at the top of the chimney. When the holes at the

base are open, a current of air is dragged up the tube, and the coal-gas and air are so far mixed that the gas can undergo more rapid and complete combustion than before. Under these circumstances the flame is non-luminous. If, however, the holes in the base be partially or completely closed, the air is shut off, and once more a luminous flame is produced, the luminosity depending on the extent to which the air-holes are closed. The burner used with the Welsbach mantle is one of this type.

If one observes the non-luminous flame, it is easy to see that two distinct cones are present. Lower a

NON-LUMINOUS FLAMES

piece of paper over the flame and quickly pull it away. It will be found to be scorched where the flattened outer cone has come in contact with it, but to be unaffected where it met the inner cone, This gives us, as it were, a section across the flame. The inner cone evidently contains cool and unburnt gas, which is afterwards consumed in the outer cone. A match head may be held in the inner cone for some considerable time without ignition, on account of its hollow nature; and on drawing out a sample of the gas in the inner cone, and burning it at the end of a straight glass tube, it will be found to be combustible.

When the air-holes at the base are open, the flame generally burns quietly, revealing markedly its twoconed structure. If, however, the air comes in a little too rapidly, the flame "roars," and the conal portions are even more distinctly developed. There seems, under these conditions, to be a tendency on the part of the inner cone to move in a downward direction. If now we could still further increase the supply of air, what would happen? We may answer this by allowing the supply of coal-gas to diminish, the air supply remaining somewhat the same. We then ultimately arrive at a condition where the air and coal-gas are mixed in such proportions that quick union can occur between them. In other words, we have an explosive mixture, and this ignites all at once, producing an explosion which passes down the tube at a rate depending on the proportions of the constituents in the mixture. The gas is then said to "suck back," which often happens in the Welsbach burner if the light is applied too soon. This phenomenon may be more completely studied by burning a mixture of coal-gas and air at

the end of a long glass tube. With a particular admixture of air we may have the coal-gas burning with a non-luminous flame. If the air current be then increased, we ultimately arrive at the condition when the air and coal-gas are in proportions favourable to explosion, with the result that the flame travels down the tube, and with care it can be induced to travel so slowly that its velocity can easily be measured. Hence admixture with air has greatly affected the flame, and the experiment may with truth be said to bear out Sir Humphry Davy's remark that "flame is a tethered explosion."

If, in the glass tube referred to, we get at any point a condition of stability, with the flame at rest and, as it were, balanced in the tube, what would be the cause? For even when the mixture is explosive by reason of its composition, the flame need not travel down the tube; it all depends on the rate of influx of the explosive mixture, as compared with the rate at which the explosion would pass down the tube. If now the velocity of the ascending current of coal-gas and air at a particular place in the tube just overcomes the descending flame produced by explosion at the top, the flame will stop; easily able to go thus far, it can go no farther. Hence we should see a flame at that point, in addition to the flame at the top of the tube. The lower flame would then correspond to the inner cone of a Bunsen burner, the outer flame to the outer cone, and the space between would furnish us with the inter-conal gases.

This interesting state of things may be obtained experimentally in several ways. We may have the glass tube constricted at some point A (Fig. 31). The air

DECOMPOSITION OF FLAMES

and gas are supposed mixed in an explosive state. On applying a light at the top of the tube; the flame travels downward till it reaches the constriction at A, and

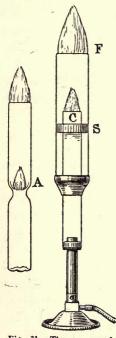


Fig. 31.—The two-coned structure of flames.

there it burns with a steady cone of blue flame. The effect of the constriction is to increase the speed of the uprushing gas at that point, this increase producing an opposing current to that of the explosive mixture too great to allow the latter to progress any further downwards.

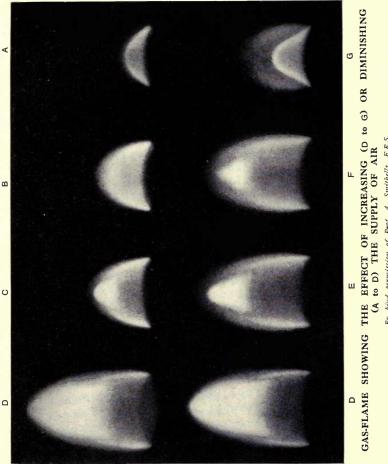
The method adopted by Professor Smithells in his beautiful experiment is also illustrated in Fig. 31. The Bunsen burner is fitted to the glass tube by means of a perforated cork, and a wider outer tube slides over it, acting as a sheath. A little asbestos at s keeps the tubes coaxial. Quoting from the paper in the "Journal of the Chemical Society" for March, 1892, we find that "if the apparatus be arranged so that

the mouth of the inner tube is about 10 c.m. below that of the outer one, and the gas be lighted, an ordinary Bunsen flame is obtained at the mouth of the latter. If, now, the gas supply be gradually diminished, the flame becomes smaller and the two-coned structure more evident until the inner cone, having become very small and very green in colour, shows a tendency to enter the tube. As the gas supply is

further cut off, the inner cone will probably descend and reascend a few centimetres, until finally it descends as far as the orifice of the inner tube at c, on which it will then suddenly settle and remain. This point is equivalent to a constriction in the tube, and the consequent increase in the velocity of ascending gases determines the sudden arrest of the receding flames. While this is going on a feeble flame, consisting of a single hollow cone of pale lilac colour, remains at the orifice of the outer tube F. The two conical areas are thus widely separated, and the gases coming from the lower one can be easily aspirated by introducing one limb of a bent tube at F."

This separating apparatus also gives us the means of analysing the inter-conal gases. These are found to consist of carbon-monoxide, hydrogen, carbon dioxide and water, with excess of nitrogen. Hence the main chemical change in the inner cone consists in the imperfect combustion of the hydrocarbons to form carbon monoxide and water, with smaller quantities of carbon dioxide and unoxidised hydrogen. In the outer cone the unburnt gases are burnt, and the oxidation is complete. It will thus appear that. in the inner cone, owing to the limited supply of air, we have imperfect combustion, both of the carbon and of the hydrogen proceeding at once. There is no preferential treatment of the hydrogen; imperfect combustion of hydrogen simply means that some of it remains unburnt, while imperfect combustion of the carbon gives us a different oxide—carbon monoxide, instead of the dioxide produced when it is fully burnt.

Plate IV., which we owe to the courtesy of Professor



By kind permission of Prof. A. Smithells, F.R.S.



HYDROCARBON FLAMES

Smithells, illustrates beautifully the effect of increasing the supply of coal-gas or of air to an ordinary gas-flame. From a to d, we see the effect of increasing the supply of gas; from d to g we have the influence of an increased air-supply to the same flame. Of course, the blue portions of the flame appear too bright in the photographs because of their exceptionally strong effect upon the plates; nevertheless the connection between the luminous zone and the supply of gas is clear. The appearance of the special luminous zone in c and its disappearance in f should be especially noted.

V.—FLAMES FOR LIGHT

The Bunsen flame is used entirely as a source of heat. For many years the candle and ordinary coalgas flames served for lighting man's darkness; but in the advance of time we have had a corresponding advance in science, and the science of lighting has added its quota in the forward march. For many years it has been known that three great factors influence the luminosity of a flame: first, the density of the flame gases; secondly, their temperature; and, thirdly, the presence in the flame of some infusible substance which, being rendered incandescent, continued to glow as the carbon particles glow in the candle flame. The denser hydrocarbons yield more luminous flames than the lighter ones when burnt under similar conditions, and increased pressure upon a combustible gas increases its luminosity. If, also, a stream of combustible gas be burnt at the end of a platinum tube, and the tube be then made red hot as the gas is passing through, the increased luminosity is

clearly seen. It is in the third factor, however, that the chief advances along industrial lines have been made. Welsbach, in pursuing investigations on certain rare earths, thoria and ceria, found that their infusible nature rendered them incandescent when subjected to a high flame temperature, and that the incandescence contained a larger proportion of light-waves than is usual. Adapting this knowledge in practice, he prepared his well-known mantle to surround the flame of a Bunsen burner. This mantle consists merely of a framework of some fabric dipped in "milk of thoria," to which is added a little "milk of ceria." The framework is then dried, and a film of the oxides is deposited all round. On placing in position for use, the fabric is first burnt away, leaving the thin film of oxide, which, being made incandescent by suspension over the flame of the Bunsen burner, emits the beautiful white light known as the incandescent light. It seems to be the small percentage of ceria used that is responsible for the brilliant light effect.

In incandescent lights a substance, white hot, emits the light; consequently the incandescent body must be given a considerable amount of heat to maintain it at a glowing temperature. Hence, although such lights may be used for illuminating purposes, they nevertheless are not of maximum efficiency owing to the large amount of heat given out along with the light. For light production, therefore, it seems hardly sound to do as we are doing at the present day with gas; namely, to waste a considerable amount of its energy of combustion as heat. There are some lights, however, that are produced without heat, although

THE INCANDESCENT LIGHT

such lights are not, unfortunately, producible in practice. Substances like calcium sulphide, for instance, after exposure to the sun's rays, have the power of absorbing a certain amount of solar energy, by virtue of which they possess the property of glowing in the dark and of emitting light without heat. Such glowing bodies are said to be luminescent, as distinct from incandescent; and a light-producing body, giving light by luminescence only, converting some form of energy into light without heat, is badly wanted. The mercury vapour lamp partly fulfils this purpose, converting electrical energy into light, and we may hope it is but the precursor of better things in the future.

VI.—ULTIMATE NATURE OF THE FIRE ELEMENT

In our brief glance at the properties of fire and flame we thus leave many mysteries unsolved, enchanting and tantalising. Have we not indicated that the old fire-element does indeed open to us a thousand avenues of knowledge and thought? We have shown some of the probes which have exposed the ignorance of the past and revealed the truth of the present; yet much remains also for the future. We have not penetrated quite to the root of the matter.

Heraclitus, we remember, claimed that fire was the beginning of motion, and that this motion was the cause of the endless metamorphoses which are the chief acts in the great spectacle of the universe. And when we remember what fire is, what a remarkable intuition was this of the old philosopher! We see an electric tramcar speeding along the streets: what is its motion but fire transformed? It begins with the combustion of coal; the heat generated thus

causes water to boil and expand into steam; this expansion drives the machinery which in its turn drives the dynamo, and this sets free the electrical energy which, transformed again, appears in the motion of the car. But the fire itself is not in existence ab initio. It is not as such locked up in the coal. It is, as we have previously explained, itself but a transformation of the energy inherent in the atoms of the coal and of the oxygen in which it is burned. So that we have to consider fire and change to spring from what is called the intra-atomic energy of the atoms of matter. That the atoms of coal derived some at least of their energy from the sun does not solve the difficulty which confronts us now that we have reached the ultimate roots of speculation on this question. For we have still to ask for the origin of the stupendous amount of atomic energy that exists in the sun. Fire, whether we mean by it incandescence or flame, is but the evidence of a transformation—its concomitant but not its cause. Fire is a motion transmuted from antecedent motion; and when we inquire whence arose this motion that is locked up in such inconceivable quantities in the atoms we are groping among the "first Causes," the prima philosophia which lies beyond the ken of science.

CHAPTER V

WATER

I.—EARLY VIEWS ABOUT WATER

"WATER-water everywhere!" might well be the exclamation of the ancient mariner of Nature who would explore the inner secrets of the composition of the earth. We look around us and see it in river, lake or sea; look above and read it in the clouds, in mists and in rain. We can watch it disappear and reappear; put on the invisible garb of vapour, and clothe itself in the palpable form of mist; evaporate, and condense again according to circumstances. The countless metamorphoses of the clouds are matched by the subtle beauty of the snowflake and the grandeur of the glacier; and little more need be said to emphasise the value of water as a contributor to the varied beauties of Nature. Without it our skies would be an intolerable glare of unbroken light, and the earth itself a monotonous and lifeless desert.

Its universality must strike the least observant of us. It is literally everywhere; and even where it is not now seen, there is evidence that it once spread as a sea over our present continents, whose rocks bear within them the unmistakable sign-manual of their aqueous origin. The dry land rose from the bosom of the deep, carrying with it the remains of the living millions which once flourished there. Water is indeed a necessity of life, and doubtless the earliest organisms had their home in it. Thus in the present, as in the

past, water is a substance which is essential to the system of Nature as we see it—to its skies and storms and seas, to its land and its life.

And the uses which man must make of it give it still further claim to our attention. To enumerate them would be impossible; they enter every phase of our daily life. It cleanses our homes, our cities, and ourselves; it is food for man, beast and plant; even our solid foods contain very much water. Through its transformation into steam it drives our machinery; in falling streams it supplies energy to innumerable millwheels; while it bears across its ocean depths the Dreadnoughts and Mauretanias which make the future of the nations. To deal well with one aspect of this fascinating element would require a large volumemuch larger than any man could write. It is not remarkable that, from the very earliest times, the thoughtful philosopher should have pondered over its nature and wrought theories of its meaning.

In the dawning days of Greek philosophy, when men first strove to interpret the universe in the light of certain fundamental "causes," Thales, a pioneer of the Ionian school in the sixth century B.C., found the first Cause of all things in water. Wrapped, as it were, like an envelope round the land, the latter peeping through here and there, and breaking the unending expanse, water was naturally regarded as the birth-place and original source of the land. This notion seemed to be supported by the fact that water was found by digging in the earth; and, as water came from the clouds to fertilise the land and cause man's food to spring therefrom, it is easy to understand how the untrained, but still thoughtful, mind came to

THE LIQUID ELEMENT

regard water as the element—the great Invariable out of which sprang the many Variables met with in Nature. Water became to Thales what air was subsequently in the speculations of Anaximenes—the First Cause, the life-giver, the ultimate basis of the material universe.

But as philosophy expanded and knowledge grew, this place of honour was seen to be unsuitable, and water became the liquid element par excellence. It was regarded as the chief property of those substances which existed or could exist in the liquid form. Substances like sulphur, gold, or metals generally, which became liquid under suitable treatment, were held to contain water; that is to say, in modern language, they possessed the property which water was held to have in its unmixed form. Water conferred the liquid character upon earthy things, just as air conferred the gaseous character. In this way water came to be regarded as one of the four elements, and took its place alongside air, fire and earth as one of the four properties which by their interaction gave birth to the many things of the universe.

For many centuries this view prevailed; and even after Boyle had given to the word "element" its true meaning, water was considered to be still one of the simple stuffs; out of water, no one expected that anything but water would ever be obtained. The fate, however, that attended the similar views held about air fell also upon the water. Its reign as an element lasted only a little longer than that of air, and in fact ended during the period that the air was receiving systematic examination. While engaged in his researches on the air, Cavendish was led to explode

hydrogen gas with air in a specially constructed eudiometer, expecting that the hydrogen would phlogisticate the air, i.e. rid it of the oxygen it contained. Whenever he performed this experiment he found that a dew was produced; and although for a time he believed this dew to be nitric acid, he finally demonstrated it to be water. Cavendish's own account of the matter is brimful of interest; it shows his observation of the dew and the inference he drew from it. His mind was critical and scientific; though hampered by a fallacious theory of combustion, his observation and his explanation were alike accurate and acute; and he pointed out the nature of the further experimental work needed before the belief that the dew was in reality water could be accepted.

"From the fourth experiment it appears that 423 measures of inflammable air are nearly sufficient to phlogisticate completely 1,000 of common air; and that the bulk of air remaining after explosion is then very little more than four-fifths of the common air employed; so that as common air cannot be reduced to a much less bulk than that by any known method of phlogistication, we may safely conclude that when they are mixed in this proportion and exploded, almost all the inflammable air, and about one-fifth part of common air, lose their elasticity, and are converted into the dew which lines the glass."

Hence hydrogen and oxygen disappeared to form the dew. But what was this dew? Cavendish, as we have stated, thought it at first to be nitric acid; but experiment dispossessed him of this belief. He obtained more of the dew by burning "500,000 grain measures of inflammable air in 2½ times that quantity of ordinary

EXPERIMENT OF CAVENDISH

air, and collected 135 grains of the dew." He found that it had neither taste nor smell; it yielded no residue on evaporation; nor did it give any offensive or pungent smell during the process. In short, "it seemed pure water."

It was thus that Cavendish, in 1781, gave to the world the true composition of water. Its position among the elements had to be abandoned; and we hope to show in the present chapter how a fuller chemical knowledge has merely served to confirm the views of the original investigator.

II.—THE EFFECT OF WATER ON METALS

The rusting of iron or steel objects is one of the most familiar of everyday phenomena, and everyone knows that the rusting process is facilitated by, if not actually dependent upon, the presence of moisture. Iron utensils, if they are to be preserved for any length of time, must be kept in a dry condition and in a dry place. Now iron-rust, in its final condition, is essentially an oxide of iron—that is to say, a compound of iron and oxygen. A more thorough examination shows that the oxide of iron exists in rust in the form of a compound with water, forming a hydrated oxide, to which the formula Fe₂O₃.H₂O is generally given. The rusting of iron, therefore, takes place in two steps: first, the iron is oxidised by combination with oxygen; secondly, we have the more complicated hydrated oxide formed. Water is evidently essential to the second step; it may fairly become a subject of inquiry whether it also enters into the first. And if water is what Cavendish supposed it-a compound of hydrogen and oxy-

gen—it is clear that the necessary oxygen is present in it and that iron may be completely rusted by it. The possibility is the fact; at ordinary temperatures iron has the power of slowly abstracting oxygen from water and becoming rusty. It is interesting, however, to notice that this statement is not in the strictest sense truthful, because in absolutely pure water iron may be kept for a very long time without showing the least tendency to rust. The commencement of the rusting seems to be dependent on the presence of a trace of carbon dioxide in the water, a carbonate of iron being first formed. This is converted into the hydrated oxide by the joint action of air and water. Chemists are not unanimous about the exact mechanism of the process; but, whatever this may be, the essential facts are the formation of the oxide and that water yields some of the oxygen needed.

If, now, iron is found slowly to abstract oxygen from water at ordinary temperatures, will it abstract it more quickly if the temperature is raised? In numerous cases we have evidence to show that an elevated temperature of the reacting bodies promotes chemical change. Let us then raise water to its boiling point and pass steam over red-hot iron. A suitable apparatus to use is shown in Fig. 32. The iron (preferably iron tacks) is loosely packed in the iron tube A, which is heated in a furnace or by several Bunsen burners, and steam passed over from the boiling water in the flask B. If the end of the delivery tube be placed under the bee-hive shelf in the pneumatic trough, bubbles of gas may be collected in the jar as shown. On examining the gas it will be found to burn easily, to be very light, and not to support the com-

EFFECT OF WATER ON IRON

bustion of a candle. In short, the gas has all the properties of hydrogen. It is evident, therefore, that when oxygen is absorbed from steam by red-hot iron,

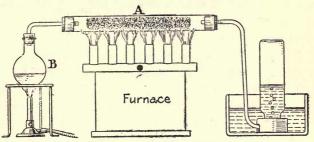


Fig. 32.-Decomposition of steam by red-hot iron.

hydrogen gas is formed. The oxide of iron produced may be noticed on the surface of the tacks on their

removal from the furnace; but in this case the compound formed varies slightly in composition from the previous iron rust; it is a different oxide of iron, with rather less oxygen than the latter contains. The action of iron on water, therefore, serves to show us the compound nature of the water.

Iron is not the only metal which has the power of decomposing steam. Magne-

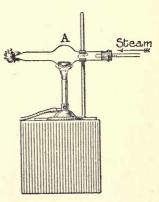


Fig. 33.—Decomposition of steam by magnesium.

sium, a metal which burns with a brilliant flame when heated in presence of oxygen, may also be used by slightly varying the conditions of the experiment. The metal is placed in the glass tube A (Fig. 33), and steam

is blown over as the metal is being strongly heated. So energetically does magnesium decompose the steam that it burns brilliantly and the issuing gas may be ignited. This is a beautiful experiment, as the combustion of the magnesium in the steam is little less bright than its combustion in the air.

Far more vigorous, however, in their actions on water are the metals potassium, sodium, and calcium. Even at ordinary temperatures these metals possess the power of abstracting the oxygen and turning out the hydrogen from water. If a small piece of the former metal be thrown upon water a most vigorous reaction ensues, the metal uniting with the oxygen so violently that sufficient heat is produced to ignite the liberated hydrogen; and the latter burns, the colour of the flame being violet, owing to the vapour of potassium disseminated through it. During the reaction white fumes of oxide of potassium may be observed rising from the water, but the greater portion of these dissolves in the water and confers upon it a soapy feel. If a little red litmus solution be added to the water, the solution is turned blue, as the water now possesses the properties of an alkali. It is a solution of potassium hydroxide, more commonly known as caustic potash.

If a fragment of sodium be thrown upon water, the reaction is less violent than in the case of potassium; and in this instance the liberated hydrogen does not burn, because a temperature high enough to ignite it is not produced. Hence, if due caution is manifested, a little of the gas may be collected. For this purpose a piece of stout wire should be bent in a large loop at the lower end and a piece of wire gauze wrapped

EFFECT OF WATER ON METALS

round it, the gauze being a little larger than the loop and the overlapping portion being bent underneath. This is to serve as a "trap" for the sodium. If a fragment of the latter be placed on the water and the

gauze gently lowered over it, a growling noise is heard, and the collected gas bubbles through the meshes of the gauze into the jar above (Fig. 34). The process may be repeated with very small pieces of sodium, and the gas finally tested.

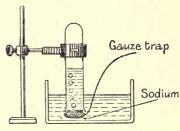


Fig. 34.—Decomposition of water by sodium.

It is hydrogen. The liquid again has alkaline properties; the sodium oxide produced by the union of the sodium and oxygen dissolves in the water, forming a solution of sodium hydroxide or caustic soda. The indiscriminate use of these metals, however, is attended with some danger, and numerous explosions have followed their rash use. Hence they should only be used by the reader if he is under the guidance of a qualified teacher.

A safe metal to use is calcium, now cheap and easily obtained. If a few small pieces be placed in a flask containing a little water, hydrogen is gently evolved, and in a few minutes a jar full of gas may be collected (Fig. 35). This is probably the easiest method of procuring hydrogen by the decomposition of water. The water in the flask has once more alkaline properties, containing as it does a solution of calcium hydroxide, which we shall later see to be merely an accurate name for slaked lime. If, however, much

calcium be used, a heavy white precipitate of calcium hydroxide, i.e. slaked lime, begins to make its appearance: the experiment furnishes a beautiful example of chemical change, a shining metal and water produc-

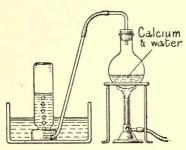


Fig. 35.—Decomposition of water by calcium.

ing an inflammable gas and a copious deposit, or precipitate, of a white solid.

Five metals have thus been separately used to decompose water. But no chemical change is so simple as it seems at first sight, and it is noteworthy that whereas iron

and magnesium possess the power of completely decomposing water, potassium, sodium and calcium can only partially do so. Let us, therefore, push our experimental work a little further.

If pieces of sodium be gradually added to water in a small porcelain basin, we arrive at a point when the action of the metal seems to be retarded, the retardation being accompanied by the formation of a thick syrupy liquid. Finally, the sodium refuses to react, and we have then in the basin a semi-solid mass of sodium hydroxide, which is strongly caustic. If this be dissolved in some more water and a piece of aluminium foil added, the whole being then gently heated, a great effervescence occurs, and considerable quantities of gas may be collected, which gas is on examination found to be hydrogen. Now water and aluminium do not yield hydrogen when boiled; hence the water used to dissolve the sodium

HYDROGEN FROM WATER

hydroxide has not yielded the hydrogen obtained in our experiment. It must, therefore, have come from the sodium hydroxide, showing that the latter still retained hydrogen from the original waterhydrogen which the sodium was incapable of turning out. Thus the hydrogen in water is displaceable in two steps, and accurate measurements would show that the volume of gas first evolved by the action of the sodium is equal to that evolved by the subsequent action of the aluminium. At each step, therefore, equal amounts of hydrogen are displaced. Assuming now we could start with one molecule of water, we could divide its hydrogen into two portions, but never into more than two. We may, therefore, say that the molecule yields two atoms of hydrogen, and thus contains two. Similar changes would occur if we used potassium or calcium, and it may be inferred from our action of metals on water that the latter contains hydrogen and oxygen, and that it contains to its molecule two atoms of the former gas.

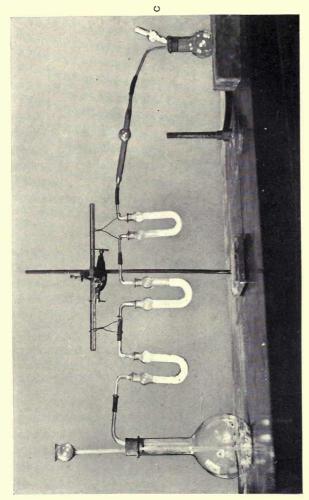
III.—THE COMPOSITION OF WATER BY WEIGHT

Seeing that we have found the nature of the substances which go to make up the compound water, can we not now arrive at some method whereby the water may be accurately synthesised and the quantities of the reacting substances weighed carefully? This would make the general knowledge that we have obtained exact and accurate; synthesis will clinch the results of analysis.

To accomplish this, it is obvious that we must have some substance capable of yielding us oxygen, and must have our hydrogen in a very pure condi-

tion. Now we have previously found that hydrogen is a good reducing agent (i.e. it possesses the power of abstracting oxygen from certain substances), and we can suitably make use of this property. A convenient material for reduction is copper oxide, the black substance formed by roasting copper in the air or in oxygen. Some of this compound, in a dry condition, is placed in a bulb tube A (Plate 5) and very accurately weighed. Hydrogen gas, made by pouring dilute sulphuric acid upon zinc, is generated in a flask B, purified and dried by passing through tubes containing lead nitrate and calcium chloride respectively. At the farther end of A is a small flask, and attached to it we have a calcium chloride tube. The flask and calcium chloride tube we will call c. These are also carefully weighed. The tubes are then joined together and hydrogen allowed to sweep out all the air until a sample collected at the end of the apparatus burns quietly. The copper oxide is then heated, and as the hydrogen continues to pass it abstracts oxygen from the oxide to form water, most of which condenses in the flask, the remainder being absorbed by the calcium chloride tube. Meanwhile the copper oxide continues to glow. After continuing the action for a few minutes, the flame is removed and the apparatus allowed to cool, while the current of hydrogen is still being passed through. When cold, we detach and re-weigh A and c. The loss in weight of A gives us the oxygen which has departed; the increase in weight in c gives the water formed.

Hence the amount of hydrogen is got by subtracting the weight of oxygen from the weight of water produced. In this manner the percentage



APPARATUS FOR SHOWING THE COMPOSITION OF WATER BY WEIGHT



COMPOSITION OF WATER

composition may be found; and, in rough numbers, accurate for our purpose, we find that—

100 parts of water contain \begin{cases} 88.88 & parts of oxygen. \\ 11.11 & ,, & hydrogen. \end{cases}

Using much more elaborate apparatus, yet adopting the same principle, Dumas first found the gravimetric composition of water.

In our first chapter we briefly outlined the Atomic Theory, according to which compounds are expressed by formulæ representing their composition, this system being far better than constantly writing down clumsy percentages.

Now as each molecule, or smallest indivisible particle, of water must contain oxygen and hydrogen in the same proportions, it follows that the numbers 88-88 and II·II respectively must represent in each case the weights of exact numbers of atoms. The weight of the atom of oxygen is 16; that of the atom of hydrogen is I; and the atoms in the molecule of water, of course, bear these weights. We can therefore find the relative numbers of each kind of atom in the molecule of water thus:—

 $\frac{\text{No. of Atoms of Oxygen}}{\text{No. of Atoms of Hydrogen}} = \frac{88.88 \div 16}{11.11 \div 1} = \frac{5.55}{11.11} = \frac{1}{2}$

Hence, in its simplest form the molecule of water would contain two atoms of hydrogen and one atom of oxygen, and its formula would be H_2O . But, obviously, formulæ like H_4O_2 , H_6O_3 , etc., maintain the same proportional number of atoms, and we ought, perhaps, to give a hint of the method of reasoning by means of which the simpler formula, H_2O , is chosen.

In 1811 an Italian scientist, named Avogadro, helped the atomic theory out of a real difficulty by

the hypothesis that, under similar conditions of temperature and pressure, equal volumes of gases and vapours contain an equal number of molecules; in other words, the molecules of all gases under the same conditions take up the same space. Thus, if we weigh equal volumes of hydrogen and steam, we shall obtain the ratio of the molecular weights of the two gases. This can be accomplished with a considerable degree of accuracy, and we find that a given volume of steam is nine times as heavy as the same volume of hydrogen at the same temperature and pressure. Now, the molecular weight of hydrogen is found to be 2, and hence the molecular weight of steam is 18. This corresponds to the formula H₂O, and not to H₄O₂, H₆O₃ etc. The formula of water—in the state of vapour, at all events—is H₂O; and the sure establishment of this truth was one of the earliest triumphs of the atomic theory. But the assumption of Avogadro, it must be remembered, was necessary to this; and it is, of course, by its very nature unproved, though by no means unverified.

IV.—THE VOLUMETRIC COMPOSITION OF WATER

Chemical theory, supported by experiment, gives us the information that both hydrogen and oxygen contain two atoms to their molecules. As the molecules of these gases occupy equal spaces, it follows that their atoms do likewise; and when hydrogen and oxygen are united to form water, we should therefore expect two volumes of hydrogen and one volume of oxygen to disappear in such union if our formula for water is correct.

The determination of the volumetric composition

COMPOSITION OF WATER

of water was first made by Cavendish; and his method is, except for improvements in the apparatus, that which is in use at the present day. For the purpose we use the eudiometer previously described, following the method laid down there, and exploding oxygen with excess of hydrogen. Suppose 30 c.c. of oxygen were bubbled in, followed by 30 c.c. of hydrogen, and that after explosion 15 c.c. of a gas, found to be wholly oxygen, remained. This would clearly show that two volumes of hydrogen and one volume of oxygen had been used. Figures giving this information are obtained by the use of the eudiometer, and the whole of the experimental evidence at our command indicates that the composition of water is accurately expressed by the formula we have arrived at. Thus it is known, not as an element in the sense that it was known to the early philosophers, nor yet as it was known to the chemists in more enlightened times, but as a compound, compounded of two gases, each differing markedly in properties, these characteristics disappearing, however, when union occurs and the glistening dew is formed.

V.—NATURAL WATERS

Naturally occurring waters are never pure. Rainwater, caught in country places before reaching the ground, approximates very closely to pure water; but even this contains air in solution, the air having been collected during the passage of the water through it. Any other gaseous impurities in the atmosphere are also dissolved to some extent by the water, and these are carried by the water wherever it goes. As our drinking waters have all been rain water in the

first instance, these dissolved gases will still be present in all waters. By boiling the water they are expelled, and the loss of air leaves the water insipid. The dissolved air is thus useful in imparting a taste to the water, and also in supporting the lives of aquatic animals.

As soon as rain water comes in contact with the ground, it meets with impurities, some of which the water can dissolve, while others resist its solvent action. The former are spoken of as dissolved impurities, the latter are described as suspended, and the nature of such impurities depends upon the path along which the water passes. If it passes, say, through beds of chalk, the water, charged with a little carbon dioxide, has the power of dissolving the chalk, and hence chalk becomes the dissolved impurity. Salt would likewise be dissolved, while mud, sand, clay, etc., would remain suspended in the water; and, if their particles were fine enough, might be carried off with it. The study of these impurities is most interesting, and furnishes useful information respecting the suitability of water for drinking, domestic and other purposes.

The suspended impurities, as we have stated above, chiefly consist of sand, mud and dirt, and to purify the water containing only suspended matter it is necessary to allow the water to stand, when, in course of time, the solid matter sinks and the clear liquid can be decanted off. As this settling process takes some considerable time, it is more usual to pass the water through some porous substance, the holes in which are small enough to arrest the particles of solid matter, while the clear water percolates through. The process is referred to as filtration, and the porous substances

IMPURITIES IN WATER

in use are many and varied. Charcoal, sponge, very fine gauze, and unglazed earthenware are each used in domestic filters. In the Pasteur-Chamberland filters the water is passed through fine unglazed porcelain; and this substance is so efficacious that it stops the passage of micro-organisms, as well as the mechanically suspended particles of mud. With domestic supplies, however, it is rare to find any large quantity of suspended matter, and when the water is heavily charged with such, it should be first passed through canvas, coke, or some such substance. It may afterwards be deprived of the small amount these fail to arrest by passing through the finer substances enumerated. The efficiency of filtration in removing suspended impurities may be demonstrated by pouring the impure water through unglazed paper. This paper, similar to blotting paper, is generally met with in circular pieces, which admit of such folding as to fit easily in a funnel. On pouring the water through such a paper the solid matter is removed. This is the process used by the student for removing suspended matter and, although simple, it is remarkably efficacious.

On the very large scale where water must be filtered for industrial uses, sand, charcoal, or coke is used, and in some cases the porous ashes from the furnaces are packed together and the water passed through. Barrels filled with shavings are also much in use.

The dissolved impurities are by far the most important, however, and upon their presence depends, to a great extent, the value of the water as an article of food. Perfectly pure water would not possess the value it would have if it contained dissolved matter

helpful in building up the system, and a water containing slight amounts of salt, Epsom salts, and lime or chalk is of great value to the community. On the other hand, dissolved matter may be of a poisonous nature. As the dissolved impurities cannot be seen in water it is evident that, by mere appearance, a water may be judged quite wrongly, and many times indeed water absolutely unfit to drink has been consumed because it looked bright and pure. A few simple experiments will give us a fund of information about water, and we shall briefly mention a few to indicate how the presence of the commoner soluble impurities may be detected.

The presence of dissolved matter in general may be ascertained by boiling a pint or two of water to dryness in some clean vessel, when the impurity would be left dry at the bottom. In some towns it is a matter of common occurrence to find this kind of impurity around the sides of vessels, such as saucepans and kettles, that are in constant use, and "furrs" are due to this cause. Having ascertained that dissolved matter is present, we may endeavour to ascertain roughly its nature. Such impurities generally consist of chlorides, sulphates, and carbonates of sodium, magnesium and calcium. We may roughly say salt, Epsom salts, and chalk or gypsum. To ascertain if salt is present, we must fill a clean glass jar with a sample of the water and add a little nitric acid and a solution of nitrate of silver. The presence of salt is indicated by an opalescence in the water. Epsom salts may be detected by adding barium chloride solution and hydrochloric acid to a fresh sample, when a white cloudiness comes over the liquid; and to test

IMPURE WATERS

for chalk or gypsum we add a solution of ammonium oxalate. A white precipitate, faint or strong, indicates the presence of chalk or gypsum.

These impurities, in moderate amounts, confer upon the water useful properties; but frequently it happens that when a water contains none of these impurities, it is very liable to dissolve lead from the pipes through which it passes. Waters containing little dissolved matter are said to be soft, since they easily lather with soap; those containing much dissolved matter are said to be hard. Now, soft waters have been found to have an appreciable action on lead, since they form inside the pipe a compound called lead hydroxide, which is soluble in water; and further, moorland waters, possessed of acidic properties, can dissolve lead by virtue of their acidity. In towns supplied, therefore, with such waters, the standing of the water in the leaden pipes throughout the night greatly facilitates the action, since the water remains a long time in contact with the lead; and the first runnings on a morning contain an appreciable quantity of the metal in solution. Continual drinking of such waters brings about lead poisoning. In towns supplied by such water it is imperative that a sufficient quantity be first discarded to clear out the water which has been standing in the pipes, as, during the day, owing to constant service, it does not get the opportunity provided during the night. The presence of lead in water may be detected by adding to the water a little solution of sulphuretted hydrogen, when a light brown colour is produced if the metal be present. A water containing chalk in solution does not exert an action upon lead, as continual passage through the pipe causes

a slight deposition of chalk on the interior, which serves as a protector to the lead.

Of all the impurities met with in water, those due to the operation of micro-organisms are the most injurious. The waters commonly referred to as polluted waters owe their pollution to such causes, the microorganisms present being of a species which the human body is incapable of easily rejecting. Such a statement must not be construed as meaning that water containing micro-organisms is necessarily injurious; all waters contain armies of them, and the majority are friends, not foes, to mankind. But certain species do exist, which, when present in water, produce cholera, typhoid fever, etc., when the water is consumed; and water so polluted may poison a whole community, so virile are these foes. Rarely does it happen, however, that a good source of supply ever suffers contamination; but frequently it happens that a water badly chosen may be contaminated. The waters of shallow wells may very easily become polluted by decaying vegetable and animal refuse from above; the drainage easily percolates through the soil and subsoil, and finds a way to the water. In all cases the water from shallow wells must be avoided, and in boring wells the deep water, and not surface water, must be used. Very often such waters smell, and when this is the case they must on all accounts be rejected. In other cases an odour is manifested when the water is warmed, and again it should be avoided; in fact, such a water may be said to be unfit for drinking purposes. Filtration has been known to remove a certain amount of bacteria from water; but where a water is found to be polluted it must be rejected and advice sought. A

POLLUTED WATERS

water may generally be said to be dangerous when it possesses the power of destroying the purple colour of a permanganate solution, although exceptions are met with. Such exceptions are waters containing sulphuretted hydrogen at our health resorts; but then people do not habitually resort to such, and they are taken under medical guidance. Only a comparatively short time ago polluted waters were responsible for epidemics of disease, particularly for cholera; but the onward march of science has, happily, done much to alter that state of things, and almost every town has now a source of supply that is beyond suspicion.

VI.—Solution and Crystallisation

It is common knowledge that, when many substances are added to water, they mix with the liquid, and some of their characteristics disappear. Thus a piece of sugar when immersed in water gradually loses the properties characterising it as a solid, and disappears into the water to form a solution. This act of solution is not confined to solids, as we have previously seen that gases dissolve in water; nor is the property in any wise restricted to water. In fact, many liquids are often used commercially solvents, particularly petrol, alcohol, carbon tetrachloride, etc.; and we have many instances on record in which one metal dissolves in another to form a solid solution. In the first instance, however, we will confine our study to the solvent properties of water and to the solution of solids in the same.

If a little potassium nitrate (saltpetre) be finely powdered and added to water in successive small

quantities, the saltpetre dissolves to the accompaniment of an absorption of heat. The liquid becomes cooled, heat having been taken from it by the solid as it dissolves. In some cases of solution, however, heat is developed, and the liquid becomes warmer. Waiving for the present the difficulty thus created, and returning to the saltpetre, we find that, as we continue slowly to add the solid, more and more is taken into solution until a point is reached when the water will dissolve no more; this point is marked by the presence of undissolved solid at the bottom of the liquid. Under these circumstances we say the solution is saturated in regard to the given solute (the saltpetre). The question now arises, since heat is evidently used up in the act of solution, will the saltpetre dissolve to a greater extent if we give heat to the liquid? On gently warming the liquid, we find that this is so, the elevated temperature helping the water to take more into solution; and on boiling the solution, we may add a considerable excess quantity of the solid. It is evident that, on allowing the solution to stand and cool gradually, this excess, when the original temperature is reached, will separate out. When such separation occurs, however, we notice that the separated solid conforms to a particular shape, and fashions itself into needle-shaped crystals. Such a process of separation is referred to as crystallisation. The more slowly the cooling takes place the more beautifully do the molecules build up these structures, and by cooling such solutions of various substances in water crystals of beautiful shapes can be made. Thus, alum separates in diamond-shaped crystals; salt in cubes; whilst the familiar crystal of sugar candy is

SOLUTION IN WATER

well known to all. The observation of the growth of these crystals forms most interesting experiments, and might well be commended to the attention of our readers. In some instances it happens that the cooling takes place so slowly that absolutely no movement occurs and no solid separates. Such a solution is said to be *super-saturated*, and rapid crystallisation is at once produced by disturbing it with a crystal of the solid which has been dissolved.

It frequently happens that crystals of various substances, when in a perfectly dry condition, yet contain, locked up in them, a large amount of water. Such water is referred to as water of crystallisation, and we generally speak of the crystals as hydrated crystals. Thus, ordinary washing soda consists of carbonate of soda crystals, containing more than 60 per cent. of water; and when this hydrated carbonate is heated the water is evolved in copious amounts, the white substance remaining being anhydrous sodium carbonate. The loss of water takes place slowly in the open air in this case, and everyone is familiar with the result of this change. Similarly, crystals of alum contain a large amount of water, also capable of expulsion by the application of heat; and it is significant that when crystals containing water are heated to the boilingpoint of water, the water they contain is gradually expelled and the crystals fall to pieces. The inference is therefore drawn that such crystals owe their structure to the water they contain. In some cases, however, all the water is not expelled at 100° C., and that remaining is referred to as water of constitution, since the affinity of the remaining water with the parent substance is evidently of a stronger nature than with

L

the greater portion of the water the crystals previously contained. A substance in which this can be well shown is the familiar blue vitriol or sulphate of copper. At the temperature of boiling water this salt loses much water, and with its water it loses its clear blue colour and its crystalline character. The pale greenish powder left behind, however, still has water in its constitution; this can be driven off at a higher temperature, and a white powder, pure anhydrous sulphate of copper, is left behind. In this case, as in so many others, both the crystalline condition and the colour of the salt are absolutely dependent upon the presence of the water of crystallisation.

VII.—PHYSICAL PROPERTIES OF SOLUTIONS

It is not easy to say offhand what happens to salt or sugar when it disappears into water; but during the past thirty years a great deal of skilful experiment and careful thought has been given to the question, and we have arrived at a satisfactory, if not absolutely final, theory which we shall endeavour in a simple way to make clear. But we must first draw attention to certain changes which may be observed in the properties of the solvent itself.

It is common to find, and the fact is well known, that the water of lakes and rivers has frozen, while the sea remains liquid; it is familiar knowledge also that salt tends cause ice to melt when added to it. Evidently water containing salt must be reduced to a much lower temperature than water itself needs before it will freeze. The effect can be studied with accuracy by surrounding a tube containing pure water with a mixture of ice and salt, and inserting a

PROPERTIES OF SOLUTIONS

delicate thermometer in the water. As this water, under the influence of the cold mixture around it, becomes cooler, it eventually arrives at the temperature marked o° on the thermometer. If it is then disturbed a little, ice begins to form, and the temperature is described as the freezing-point. If the liquid is, however, kept perfectly quiet, it may be supercooled, i.e. taken to a temperature much below its freezing-point without freezing; but it will return to this temperature and yield ice on the slightest disturbance. Having noted the freezing-point of pure water, add to it enough salt to make I per cent. of its weight, and thus form a "I per cent. solution" of salt. The liquid now freezes at a slightly lower temperature, and the depression of the freezing-point can be recorded. Increasing the amount of salt to two per cent. we shall observe that the total depression thus produced is twice as great as that produced by the one per cent. of salt. And the law thus indicated is general: the depression of the freezing-point is always proportional to the amount of substance dissolved.

If a dilute solution of potassium permanganate be frozen, the important and interesting fact may be observed that the solid ice is colourless; the ice obtained from the freezing of dilute solutions is pure. But, obviously, during the freezing of a dilute solution of salt, as more and more ice separates, the residual liquid becomes a strong and stronger solution, until it must become saturated. At that point both ice and salt would separate from the liquid; the temperature thus reached would be the lowest obtainable by the freezing of salt solution—it would be the freezing-point of a saturated solution of the salt.

This temperature is called the *eutectic temperature* of the solution, and the mixture separating is known as a *cryohydrate*. This was at one time thought to be a definite compound of ice and salt; but it has no special chemical characteristics of its own; the two constituents can be readily separated, and we now

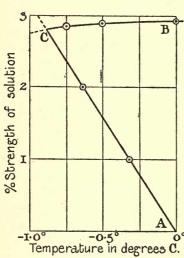


Fig. 36.—Formation of a cryohydrate.

prefer to regard it merely as a mixture of the solute and its solvent in the solid state.

The changes in the freezing-point obtained by experiment can be represented instructively on squared paper. Just as a place on the earth's surface is exactly fixed by its latitude and longitude, so the freezing-point of a solution of a definite strength can be completely indicated by a

point, as in Fig. 36. The curve joining the various points shows at a glance the whole variation of the freezing-point as the solution is strengthened. Such a curve is AC, which was constructed from experiments on a solution of potassium chlorate. On the same diagram we can also place the curve BC, which indicates the amount of the substance that can be dissolved at the various temperatures. These two curves intersect at C, and evidently C stands at the eutectic temperature. For that point is on AC, and

FREEZING OF SOLUTIONS

therefore tells us that ice is forming; it is also on BC, which is the curve of the saturated solution. In other words, C is the point at which the solution is both saturated and freezing.

Study of the boiling-point of solutions has yielded equally interesting results. It is easy to show that the boiling-point of water is raised by the presence of dissolved substances, and that the rise is proportional to the amount of substance present. The line of thought here opened up has been of great importance in the development of chemistry, both in theory and in practice.

VIII.—THE FREEZING OF ALLOYS

One of the most interesting practical applications of the freezing of solutions has thrown a great deal of light upon the nature of alloys. These useful substances are, as is well known, formed by the fusion and subsequent cooling of two or more metals together; and the question to be determined is whether the metals form a mere mixture or enter into any kind of chemical combination. Inasmuch as the behaviour of an alloy often depends upon the state in which one of the metals may be present, i.e. whether it is free or combined, it is interesting to follow out briefly one of the methods upon which a decision can be made. Several methods can be applied; but that of freezing the molten alloy and following the changes attendant upon cooling has been applied with very considerable success.

If a particular metal be taken, its freezing-point carefully obtained, and afterwards the freezing-points of the metal when successive additional quantities of a second metal have been dissolved in it, we find

that a depression curve, very similar to that obtained from solutions of salt in water, is followed for a time. In all such cases the solvent metal is the first to separate, and the microscopic examination of thin slices of the solid shows the crystals of the pure metal clearly distinguishable. Evidence such as this shows that dilute solutions of metals in metals behave in essentially the same way as dilute solutions of salts in water. Pushing the comparison a little further, we find in many simple alloys that, at a definite percentage composition, both metals separate out at the same time; they yield a mixture which is similar to a cryohydrate, at a definite eutectic temperature. Microscopic examination again confirms the reasoning process; a conglomerate mass is seen, the nature of which seems to indicate the presence of the two separate metals.

Representing this behaviour diagrammatically (Fig. 37), we will call the two metals A and B. The meltingpoints of these two metals are indicated, one on each vertical line. If now to pure A a little of B is added, the proportion added may be set off horizontally, as shown, and the corresponding freezing-point represented vertically. By making the observation with various proportions of A and B we obtain the curve A C. Supposing c to be the point where both the metals separate together, it is clear that this, being the eutectic point, will also be found on the curve Bc, obtained by starting with B and adding successive quantities of A. This case is a simple one, and in all probability the alloy formed at the eutectic point is a substance corresponding to a cryohydrate, i.e. a mixture of solvent and solute.

FREEZING OF ALLOYS

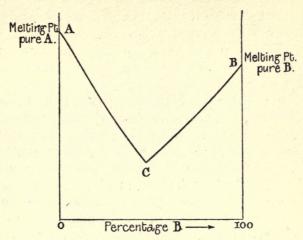


Fig. 37.—The eutectic point of an alloy.

But the case is different when our alloy is in part a definite chemical compound. Such compound metals have been isolated, and their freezing-point curves are

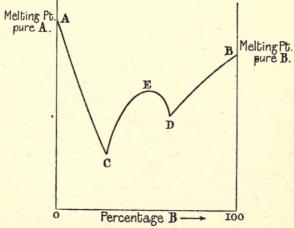


Fig. 38.—Curve of alloy forming a compound at B

of somewhat different type. Fig. 38 shows a typical one. Here A c is the curve of B dissolving in A, C being the eutectic point; and BD is similarly the curve of A dissolving in B, with D for the eutectic point. At c and D we get mixtures of the metals of different composition; but what happens between these points? If we start at c or D and add more of B or A, as the case demands, the curve takes the course CED, at the summit of which we have a composition represented that, when isolated and examined, behaves very much like a compound of the two metals; the microscope reveals in thin sections a perfectly homogeneous mass, and other methods of analysis confirm the belief. It will thus be seen how a study of the freezing-point curves can throw a much-needed light upon the nature of an alloy.

IX.—WHAT IS A SOLUTION?

We have wandered somewhat from our original question; but our vagaries have not been useless if we have succeeded in showing that the properties of solutions lead us into unexpected and interesting lines of work and thought. We come back now to the first difficulty. What is the cause of solution? What happens actually to salt and sugar when they dissolve in water? The old confusion, still rife among people who have not acquired the scientific habit of an accurate use of words, between dissolving and melting, suggests a possible explanation. Does salt really melt, i.e. become liquid, when it dissolves in water? At first sight it might seem to do so. The molecules of salt do seem to acquire the liquid condition; and in most cases heat has to be supplied for

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solution, as it always must be supplied for melting. But several considerations cut out this explanation; the mere fact that gases can dissolve in liquids is enough—in those cases, at all events; and the changes which occur both in the properties of the water and in those of the dissolved substance, make a more deep-seated explanation imperative.

The promotion of the solution of a solid in water probably depends upon the operation of forces which tend to disintegrate the solid, the resultant of which determines the extent to which the substance will dissolve. On the one hand we have the solid, made up of molecules held firmly by cohesion; on the other, the liquid, the molecules of which are free to move, their movement being accelerated by increase of temperature. Further, every evidence tends to show that in a solid the individual molecules are tending of themselves to move, but are prevented from so doing by the cohesive forces between them. It is evident that, during solution, these cohesive forces are broken down; and this breaking down must result somehow from the contact of the solid with the liquid. It may be assumed, then, that contact of the solid with the moving molecules of the liquid causes molecules of the solid to acquire sufficient energy to break down their mutual attractive forces; and these molecules pass away from the main mass along with the liquid. Thus some of the substance passes into solution; and, as increased temperature means an increased molecular motion, we should expect it to accelerate the process of solution, as indeed we find it to do in most cases. This passage of the substance into solution continues until saturation occurs; and even then it is

fair to assume that the solution of the solid still proceeds; but the process of solution is now balanced by the deposition of some solid upon the substance which remains undissolved. This fact will be rendered clear when we consider that the latter must be continually meeting with molecules of the solution, which must in their turn leave behind small amounts of the solid, even though some further amount is washed into solution. When solution is continuing, then, we must picture the liquid taking away substance and at the same time depositing a little, the amount removed being greater than that deposited. When these are equal—i.e. when as much solid is being taken away as is being brought back in a given time-it is evident that no further solid will, on the whole, pass into solution; in other words, the solution is saturated.

Having dissolved then, the substance has assumed the liquid condition. But how does it exist now it is in solution? Have we molecules of liquid salt, liquid sugar, and so forth, or has the water produced some manifest change in the substance? Now it is of great significance, and somewhat remarkable, that the particular nature of the dissolved substance determines many physical characteristics of the solution; particularly so in regard to one great property of solutions, to wit, their electrical conductivity. Pure water conducts the electric current to so slight an extent that it can, broadly speaking, be termed a non-conductor. If, therefore, two pieces of platinum foil, attached to wires leading from the poles of a cell generating a current, be dipped side by side in pure water, no current will pass through the latter. But

ELECTROLYTES—NON-ELECTROLYTES

if a dilute solution of salt in water be substituted for the vessel containing water, the current at once passes, and its passage is attended by decomposition of the salt. If a solution of sulphate of copper be used, decomposition again accompanies the passage of the current, and metallic copper is deposited upon the strip of platinum where the electric current leaves the liquid. A solution of any salt (p. 176) in water confers upon the water the property of conduction of the current.

On using now a solution of sugar instead of a solution of a salt, the current is once more refused passage; if a solution of gum be taken, again the current cannot pass. Many substances, indeed, form solutions that are non-conductors, and thus we can have, among aqueous solutions, two great classes: those which conduct the current of electricity, and those which do not. The former are called *electrolytes*, the latter are *non-electrolytes*. To the former belong saline solutions, to the latter a vast army of soluble substances which are compounds of carbon and have no saline properties.

This difference in the behaviour of the two types of solution is, as we have said, remarkable: it complicates the whole question; and our theory of solution must provide some explanation for it. What is the nature of the change which salt undergoes, and sugar does not, when it is dissolved in water? As water itself is a non-conductor and salt refuses to conduct a current of small strength—salt will conduct a strong current when in a fused condition—we must assume that the water and salt help each other in some way. We can conceive this help to be given either

by the water and salt uniting to form complex bodies which we may term *hydrates*, and which would have the power of conducting the current; or, alternatively, by the water resolving the salt into simplexes of some kind, such simplexes being the conductors. We turn to experiment for the necessary light upon these possible theories, and there is reasonable hope that such experiments will throw light also upon the nature of solutions in general.

It has been previously stated that the depression in freezing-point produced by a dissolved substance is proportional to its amount. To this we may now add the further statement that careful investigation has shown that, if quantities proportional to the molecular weights of many substances are contained in 100 parts of solution, the depression of the freezing-point would be the same for all. This depression is known as the molecular depression of the liquid used as solvent, and its value for water has been found. But electrolytes are all found to behave irregularly. Salt gives almost twice the molecular depression in water that sugar and other non-electrolytes give. Hence, in the salt solution we must have present either heavier molecules than those of the salt itself, or more molecular quantities than we bargained for. If the salt-molecules join with water-molecules to form hydrates, these hydrates might well behave on freezing as sugar does. On the other hand, if the salt-molecules were each separated into two simplexes, we should have twice as many molecular units, and thus obtain twice the molecular de-We can explain the anomalous result, therefore, either by the aid of the hydrates or by means of the simplexes, one of which we needed

THEORIES OF SOLUTION

also to explain the conducting power of the solution.

We cannot here enter into a full discussion of these theories; but the second of the two is the more generally accepted, and we may profitably explain how it can be applied to a special case. Think, then, of common salt dissolving in water. Now, common salt is on analysis found to be sodium chloride, i.e. it is a compound of the two elements sodium and chlorine, represented by the formula NaCl. The supposed simplexes formed by the influence of the water would be the atoms Na and Cl. But if, by merely dissolving the salt, we obtain atoms of sodium and chlorine, we should expect also the properties peculiar to these atoms; we should expect the sodium atoms to decompose the water (p. 146) and the chlorine to confer bleaching properties upon it. Needless to say, salt does not behave so; the simplexes cannot, therefore, be the atoms of sodium and chlorine, unless they are in an unusual condition. Now, it is well known that an electric charge endows substances with new properties and obscures or modifies their ordinary behaviour. Suppose, then, that the atoms, as they exist in the solution, are each accompanied by a definite charge of electricity. These charged atoms, or ions, need not act as the uncharged atoms would; but they would account for the easy manner in which an electric current passes through the solution. On this hypothesis, the simplexes into which salt decomposes in water would be sodium ions and chlorine ions; the ions possess equal electrical charges; that on the sodium ion will be positive, and that on the chlorine negative. We represent the ions symbolically as

Na and Cl, and the effect of water on salt will be shown in chemical language, thus—

$$NaCl \equiv Na + \overline{Cl}$$

When the terminals of the battery are fastened to strips of platinum dipped into the salt solution, we introduce, as it were, a storehouse of positive electricity on one strip and of negative electricity on the other. The chlorine ions will then migrate towards the positive strip or anode, and the sodium ions will similarly be drawn towards the cathode or negative strip. There the ions will give up their charges, and become converted into atoms of sodium and chlorine, which atoms will now exercise their normal activity. The sodium will produce hydrogen at the cathode, and the chlorine will issue as a gas from the anode. Thus we realise the difference between the atoms and the ions.

Sometimes the ions are not composed of single electrified atoms as in the case of salt. What happens to sulphate of copper (CuSO₄) when it dissolves in water? On passing the current, what we really obtain is a deposit of copper on the cathode and oxygen gas at the anode, This is explained by supposing the salt to

be decomposed into two ions, Cu and SO₄. The positive ions give up their charge and are deposited without more change; but the negative ions, having given up their charge, are unstable and readily decompose water, thus—

$$SO_4 + H_2O = H_2SO_4 + O$$

The presence of sulphuric acid (H2SO4) in the liquid

IONIC THEORY OF SOLUTION

can easily be proved, and the essential correctness of the explanation thus guaranteed.

In many cases, again, three or more ions may be produced. Analysis shows copper chloride to have the formula CuCl₂. Dissolved in water, this molecule would produce one copper ion and two chlorine ions. Since the electricity on the copper ion neutralises that on the two negative ions, the copper ion must have a double charge, as represented above. The presence of the three ions in the solution can be checked by the effect on the freezing-point of the liquid; the depression produced in this and other similar cases would be found to be almost three times that which would have occurred if no dissociation had taken place. A very great body of experimental support is thus available for what is called the ionic theory of solution. But, of course, it only applies to electrolytes: substances like sugar or gum cannot be dissociated into ions; their solutions do not conduct the electric current, and their molecules must mix intimately and unchanged with those of the solvent. And even in the case of electrolytes, the dissociation is not complete unless the solution is very dilute; in the ordinary way a good proportion of the molecules must remain unchanged.

X.—ACIDS AND BASES

The main support of the ionic theory is the fact that all electrolytes can be dissociated into positive and negative ions. Now, when hydrogen is the positive ion, the resulting solution has what are called acid properties, whatever the negative ion may be. The easiest method of showing the presence of an

acid is to take advantage of the action of the hydrogen ions on certain dyes or vegetable colours, such as blue litmus, which is turned pink by them. All the familiar acids are electrolytes and undergo the ionic dissociation in water; those which at various places we have had occasion to mention in this book are hydrochloric (HCl), nitric (HNO₃), and sulphuric (H₂SO₄) acids. We have not the space to describe the particular properties and special importance of these invaluable substances, but we must discuss them for a few lines in general terms.

An acid can be "killed," i.e. have its acidic properties destroyed, in several ways, which all imply, however, the removal of the hydrogen and its replacement by some other positive ion. The replacing ion may be a metal or an equivalent single group of atoms. In the first case, we find that the metal is often able to perform the change directly, as when zinc dissolves in dilute sulphuric acid (p. 93); hydrogen gas is then eliminated, and the acid is said to be neutralised. But frequently we find that the metals will not act directly on the acid; nevertheless the acid may be neutralised and the said metal indirectly introduced.

Zinc and zinc oxide both neutralise the common acids directly, and the final product is the same in both cases, so far as the zinc is concerned; but whereas the zinc liberates the hydrogen from the acid free, zinc oxide liberates it in the form of water. Zinc oxide is therefore described as a base, a term often vaguely used, but here defined to be a substance capable of neutralising an acid, water being produced at the same time. The neutral substance formed, which

NEUTRALISATION OF ACIDS

has neither acid nor basic properties, is called a salt. The salt is named after the acid and base contained in it; the name suggests the method of making it; thus, copper nitrate from copper or copper oxide and nitric acid; magnesium sulphate from magnesium or magnesium oxide and sulphuric acid, and so on.

A few of the oxides of the metals dissolve in water easily, and communicate to the water alkaline properties. But before doing so they change chemically into what are known as hydroxides, compounds containing both hydrogen and oxygen. The most familiar of these are sodium and potassium hydroxides, the common caustic soda (NaOH), and caustic potash (KOH). These alkalis are white solids, readily soluble in water with evolution of heat, giving solutions with soapy touch, which turn red litmus blue. In solution they change into metallic ions (Na or K) and the compound negative ion (OH), called hydroxyl. It is this dissociated condition which enables them to neutralise any acid whatever with ease. We may express the reactions which occur in two cases as follows :-

$$\begin{array}{lll} HCl &+ NaOH &= NaCl &+ H_2O \\ & Acid &+ Alkali &= Salt &+ Water \\ HNO_3 &+ KOH &= KNO_3 &+ H_2O \\ &+ Alkali &= Salt &+ Water \\ \end{array}$$

Now, as we have explained in our first chapter, the symbols above used stand for definite quantities—the molecules—of the reacting substances. If, then, we make experiments with quantities of the above acids and alkalis which are proportional to their molecular weights, we obtain the interesting results that the neutralisation is complete, and that the heat dis-

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engaged by the process is the same in each case. That is to say, when one molecule of hydrochloric acid is added to one molecule of caustic soda, approximately the same amount of energy is liberated as would be set free by a molecule of nitric acid neutralising a molecule of soda or of potash. And this is true in numerous other instances also. Searching our equations for the common factor that is responsible for this uniform behaviour, we find it in the constant amount of water produced; and the reason why this also implies a constant amount of energy is clear if we assume both acid and alkali to be dissociated into ions, but cannot be comprehended otherwise. The water is produced in each of the reactions by the combination of a positive hydrogen ion and a negative hydroxyl ion; at the same time the equal and opposite charges are neutralised, because water itself is practically undissociated. The withdrawal of these ions and their conversion into equal quantities of water may be represented on the ionic idea in the equations:-

Thus the essential process in the neutralisation of acids by alkalis is this production of water by the union of H from the acid and OH from the alkali. The ions which constitute the salt still remain dissociated, until the solution is concentrated, when they also tend to unite to form neutral molecules. When the water is all driven away the molecules of salt remain, neutral and undissociated.

FORMATION OF SALTS

This formation of salts from acids and bases is one of the most far-reaching and important of chemical processes, and it lends very strong support to the electrical theory of solution. That a solution should contain a vast number of electrified atoms moving rapidly among the molecules of the solvent it is difficult to realise. Yet such an explanation is demanded by many phenomena such as we have explained; it is contradicted by none; and it only leaves us still to ask, what becomes of those substances, like sugar, which cannot dissociate and do not conduct electricity when they are dissolved in water?

XI.—WATER AS AN INFLUENCE IN CHEMICAL CHANGES

How and why water is able to accomplish the dissociation of acids, alkalis, and salts into ions which render them capable of electric conduction, we are in a complete quandary to tell. The water molecules, themselves capable of being resolved into the ions H and OH, are not in any noticeable degree dissociated; but a small quantity of salt or of an acid is almost entirely separated into two ions, by the influence of the water present in comparatively large quantities. Almost as mysterious is the influence of mere traces of water in certain other changes.

We have referred to certain gases, like oxygen and chlorine, which, in contrast with others, like argon, are very active in the chemical sense, entering easily into combination with other elements and remaining stably in the compounds formed. It is, nevertheless, the fact that these gases are by no means active in a pure and dry condition. Thus, hydrogen

and oxygen, mixed in explosive proportions and carefully dried in sealed tubes in contact with phosphoric oxide, refuse to explode when a light is presented to them. Perfectly dry phosphorus will not burn in dry oxygen, nor will it ignite in dry chlorine. The latter gas ceases also to act upon Dutch gold, and refuses to bleach a coloured fabric, if everything concerned is perfectly dry. Ammonia and hydrogen chloride gases, when dry, remain side by side without union. In all these instances-and there are many more-the usual chemical action is at once set afoot when water, even the slightest trace of it, is introduced into the mixture. What the exact function of the water is can be stated only in a few cases. Its presence in the mixture of ammonia and hydrogen chloride gases, for example, no doubt converts them into solutions, one of which is alkaline and the other acid. The formation of a salt follows by the withdrawal of the ions, which cannot exist except in water. But we have no absolute knowledge of the part played by water in the explosion, let us say, of carbon monoxide and oxygen. Many chemists, however, consider chemical changes in general to be dependent upon the presence of a third substance which acts as a means of connection between the two reacting substances. We have sufficient data to show that in many hundreds of chemical changes water plays the part of this necessary adjunct to the action.

Thus we perceive that water is not less interesting since it has been deposed from its place among the elements and has been subjected to the scrutiny of science. The beauty of Nature is magnified a thousandfold when the intellect and the imagination yoke themselves to the chariot of wisdom which they drive

WATER IN CHEMICAL CHANGES

along the pathways of experiment and speculation in the pursuit of Truth. In a new sense through science, water is the wrecker of rocks, the builder of continents, the architect of clouds, the beginning of life. We have learnt much about the intimate nature and the powers of water; but no reader of these pages will suppose that we have done more than break the ice which covers a vast sea of mystery. The compound of hydrogen and oxygen is, just because of our greater knowledge, a more subtle and perplexing problem than the *prima materia* of Thales.

CHAPTER VI

EARTH

I.—" EARTH" AND THE OTHER ELEMENTS

While air and water are symbolic of all that is slippery and elusive, the solid earth stands firm as the emblem of stability. Terra firma is our natural support, relied upon as the unchanging and certain. Once anchored there we feel safe. Yet nothing is surer than that "earth" takes on itself as many bewildering forms as "air" or "water"; its metamorphoses are of fascinating interest, and have been turned by mankind to a thousand uses; in contact with the various airs and waters it crumbles, dissolves, and changes beneath our feet, so that its romance is no less thrilling than theirs.

The properties assigned to the "earth" element in the Greek system were coldness and dryness. Nothing could be cruder than this assignment to solid substances of these properties and no others; yet it does express a gleam of the truth. If the coldness is replaced by hotness, we were supposed to obtain the fire-element: thus the fiery fluid lava became dead, solid earth by an exchange of the principles of hot and cold, the principle of dryness being the common factor between the two. To us, after two thousand years of science, the matter is read differently; the fluid lava consists of a certain material substance infused with a large quantity of heat-energy; if this heat escapes in sufficient quantity, the lava loses its

SOLIDS AND LIQUIDS

fluid and fiery appearance, and becomes solid. The fluid does differ from the solid in the possession of more heat; and indeed all solids, if they are supplied with sufficient heat, will become liquid; and, vice versa, the liquid, when deprived of some of its heat, becomes solid. There is thus an intimate connection between "earth" and "water." If we imagine the whole earth possessed of enough heat, it would become "water," i.e. liquid; and when we recollect that the earth is constantly cooling, it is evident that in the distant past it was probably hot enough to be wholly liquid, and that the "earth" element did not then exist here.

Most "earths" have submitted to the high temperatures that we are nowadays able to produce, and yielded themselves to the liquid condition. A few solid substances are still refractory; and such substances are, of course, of great value. A cylinder of lime, raised to an intense white heat by the flame of the oxyhydrogen blow-pipe, shows no sign of melting; the small quantities of thoria and ceria used in the construction of incandescent mantles glow white-hot, but cannot be melted; and the fire-clay used for lining steel furnaces resists unchanged the temperature required to fuse steel. These are the substances in which the solid properties—the "earth" element -remain unimpaired. But there is no reason for supposing that they too would not become liquid if a sufficiently high temperature could be obtained.

Once become liquid, the originally solid substance may even go further: it may continue to receive heat until it boils, and is converted into "air," i.e. into the gaseous form. There is good reason for believing

that iron on the surface of the sun is an air or gas, and it may be boiled under terrestrial conditions in an electric furnace. To us, under everyday circumstances, it is an "earth," in which coldness and dryness are apparently the paramount properties; in our furnaces it can be made liquid and cast into any and every shape; under the very much hotter conditions of the sun it becomes a gas. These three conditions of the iron are entirely dependent upon the heat-supply. The solid earth, sufficiently heated, becomes liquid; turn further back into the earlier chapters of its history, and restore to it the heat which it has lost during its æons of cooling: it has become a fiery gas. Thus, whatever the substance may be, we may state:—

Solids + Heat become Liquids. Liquids + More Heat become Gases.

The "earth," "water" and "air" elements are linked together by heat.

II.—SULPHUR

The changes that we have dwelt upon here can be very readily studied with a little sulphur or brimstone. This very interesting substance is usually found native in the neighbourhood of volcanoes, which indicates its formation during volcanic eruptions, and suggests the interior of the earth as its origin. Its readiness to take fire, and the choking fumes that it produces when it burns, have made "fire and brimstone" a well-known and appropriate byword. Its association with metals, which we shall refer to again, made it an interesting substance to the alchemists, who regarded it as the dross to be purged from the

EFFECT OF HEAT ON SULPHUR

baser metals by the philosopher's stone. It was also looked upon as the principle of combustibility in the more confused heyday of alchemical speculation.

If a little of this yellow flowers of sulphur, such as can be purchased from a druggist's, be gently heated at the bottom of a test-tube, it can be seen to become liquid (and at the same time change colour) and ultimately to boil just as water would. These changes, produced by heat, are accompanied by changes in the appearance of the material which it is very interesting to watch. But a little careful observation will convince the experimenter that, in spite of all the changes seen, the sulphur remains essentially the same stuff. The liquid sulphur, on being allowed to cool, becomes yellow solid sulphur again, and this, if re-heated, passes through exactly the same series of changes as did the original sulphur. So the gaseous sulphur condenses on the cold upper parts of the tube into the pale yellow powder which gave rise to it. Throughout the whole process of melting and boiling the sulphur remains -in itself unchanged. It is ready, on allowing the heat given to it to escape, to go through anew the whole cycle of changes, and to do so as often as we supply or withdraw the heat.

The solid sulphur, apart from its ready inflammability, is not a particularly active substance. But, by virtue of the increase of energy which it receives when heated, it becomes much more active in the gaseous condition. A few iron or copper filings flash brightly when they are dropped into boiling sulphur, and are completely changed into blackish solids, with no lustre, while the sulphur disappears. Solid sulphur would not affect iron or copper, if they were left in

contact for years. The solid condition is far less help-ful to chemical changes than the liquid or gaseous; it has far less energy bound up in it. It would be difficult to discover a case in which two solids, placed side by side, affect each other in any appreciable degree; any apparent instance can be attributed to vapours or liquids produced by one or both of the solids. Whatever chemical property the solid may have is enhanced when it becomes liquid, and still more when it has become gaseous. Even in the combustion of sulphur, a little heat is needed to start the process; this melts and vaporises a small amount of the sulphur, and, thus making it more active, sets afoot the combination with oxygen which has been previously explained.

Much sulphur comes from Sicily, where, of course, it is found mixed with other earthy matter. In order to purify it from the useless earth the Sicilians heap the crude stuff into a large, deep hole, say 10 yards broad and 3 yards deep. Air-channels are left among the masses of earth, and the sulphur is set alight. The whole is covered with a layer of some refractory solid like plaster-of-Paris in order to limit the supply of air. When the heaps are carefully made, a slow combustion, lasting for some weeks, is set up; the heat produced by this combustion is sufficient to melt much of the sulphur without affecting its earthy companions, and the liquid sulphur runs to the bottom of the heap, from which it can be obtained when the combustion is finished. The solid sulphur is easily melted, and thus can be separated from the other solids which accompany it.

Still we have by no means a pure sulphur. In

PURIFICATION OF SULPHUR

order to obtain this the impure substance is heated in an iron retort (b, Fig. 39) until the sulphur becomes vapour. The vapour is conducted into a large brick chamber (a), on whose cold walls it returns to the

solid state. At the same time it gives up much heat — much of the heat, in fact, that had been needed to bring it into the gaseous form. The walls of a, there-

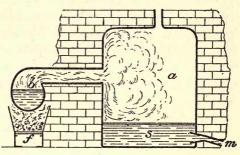


Fig. 39.-An iron retort for the refinement of sulphur.

fore, soon become hot enough to melt the sulphur on them; the liquid sulphur thus formed trickles to the floor of the chamber (s), whence it is drawn off (m) into wooden moulds, where again the liquid solidifies. The solid thus obtained is the hard sulphur sticks or brimstone of commerce; the sulphur taken from the walls before it is allowed to melt is the flowers of sulphur familiar to everybody. Clearly the only impurities that the sulphur can now contain will be such as boil at a lower temperature than itself, and such earthy substances are at best rare and not found in association with sulphur. The purification of sulphur, therefore, depends upon the fact that its "earthy" properties are more readily lost than are those of its companion earths; it easily becomes a liquid and a gas, and thus shows us that the property of solidity is not an essential characteristic of the substance, but depends entirely upon the amount of

heat it contains. Heat causes sulphur to melt and boil; more heat is the only requisite to bring all "earths" into the same conditions. And, we repeat, the processes of melting and boiling do not involve any change in the nature of the substance acted upon: sulphur is sulphur, whether the earth-element, or the fire-element, or the air-element is dominant in it. It is a true element in our modern sense of the word, not a compound of air and fire, nor playing the important part in the economy of the earth which alchemists ascribed to their sulphur-principle, but still a useful example of a real earth-element.

But although sulphur is a true element, it may be

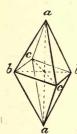


Fig. 40.—Rhombic crystal [axes of symmetry: α α, b b, c c.]

made to assume several different disguises, independent of its changes into liquid or gaseous form. If a little *roll* sulphur be powdered, it can easily be dissolved in the stinking liquid called carbon disulphide; and this liquid, being very volatile, rapidly evaporates and leaves the sulphur in the form of very well-defined *crystals*. These crystals, however much they may vary in size, do not vary at all in their general shape.

They form figures similar to Fig. 40, which has for its characteristic three unequal axes at right angles (shown in dotted lines) that divide the figure symmetrically; such a figure is said to belong to the rhombic type of crystal.

Now, if these crystals be examined under a microscope, or simply viewed by a lens, many of them will be seen to be perfect, as if they had been artificially cut according to a geometrical pattern; and those

CRYSTALS OF SULPHUR

which are not perfect will be seen to have been endeavouring to reach the same form, and this is true whether they be large or small. Let this process be attentively considered and, if possible, watched by the reader. The sulphur disappears in solution; the solvent evaporates, and the sulphur reappears, this time in definite crystalline form. The ultimate atoms of sulphur do not aggregate themselves together into haphazard masses. They never form into round balls or cubes, always into the rhombic figure; and the crystals are always found to be largest when they are able to form most slowly. Prolong the evaporation by making it take place in a cool spot, and the crystals are both larger and more perfect. Thus it is clear that, in the formation of solid sulphur, some very interesting architectural force is at work, shaping the atoms in this precise and definite way. The atoms doubtless first group themselves into molecules; these molecules exercise their attracting force on one another unequally in different directions, with the result that a small crystal forms; to this small crystal new molecules adhere, guided by the same force, and the crystal thus grows by successive invisible accretions of new molecules.

But why crystals of sulphur are necessarily rhombic, while those of sand, for example, are as consistently hexagonal, is a mystery of the molecules themselves. The study of the many different crystal-forms that "earth" can assume impresses us profoundly with the intricacy and variety of the "loves" and "hates" of the atoms. Whenever a solid forms slowly from its solution in a liquid, it takes its own special crystalline form. The reader may easily watch the process for

himself, if he will dissolve as much alum or saltpetre as he can in hot water and then leave the liquid to cool; the different shapes of these and other crystals that come across our common experience are well worthy of observation (p. 160).

To return to sulphur: if some flowers of sulphur are melted in a small earthen crucible and the liquid allowed to cool, and if as soon as a solid film begins to form on the surface the still liquid sulphur be rapidly poured out from beneath it, the solid adhering to the sides of the crucible will be found to have crystallised in the form of long needles, which are not of the rhombic form. Close examination shows them to be monoclinic, i.e. to have one of their axes of symmetry oblique to the other two. Under these special circumstances the sulphur is made to assume a new crystal form. But this form does not last; it is unstable, as we say; and if it is kept for a day or two will be found to change slowly into the rhombic form. The method of crystal formation here indicated is, it will be noticed, not the same as in the previous case. The liquid sulphur crystallises, as it solidifies or freezes; the crystals are therefore formed at a higher temperature, and, under the conditions of our experiment, in a hurried manner. The molecules of sulphur have not time to arrange themselves in their normal style of architecture; a compromise is hastily effected, and the perfect, finished crystal-edifice is completed slowly. The final result goes to show that the rhombic form is the natural habit of the sulphur molecules. When the monoclinic crystals pass into the rhombic, a little heat is liberated; this heat represents some of the energy that is required to keep

DIFFERENT FORMS OF SULPHUR

the sulphur molecules in their unstable and unusual form, just as energy is required to support any edifice that is anxious to collapse.

Roll sulphur, having been formed by the solidification of liquid sulphur, is a mass of crystals in the rhombic form; but the flowers of sulphur obtained from the walls of the refining chamber is formed from the vapour, and is amorphous. It is a powder whose particles show no trace of the geometrical forms that we see in roll sulphur. Moreover, it does not dissolve in carbon disulphide, as roll sulphur does. Yet it is sulphur, as truly as is roll sulphur; it goes through the same series of changes when it is heated, and, after being melted, crystallises into the rhombic crystals with which we have become familiar. The milk of sulphur of medicine is similarly an amorphous form of the element prepared by decomposing alkaline sulphides with dilute acids.

In order to account for the differences between the amorphous and crystalline forms of sulphur, it is necessary to go down to the atoms, and to suppose that these may group themselves in different numbers, with different results to the properties of the molecules formed. Suppose a certain number of atoms, say eight, to come together, and that one molecule results from their mutual attractions which has the power to form crystals with other similar molecules. This might then be the habit of sulphur when it is in a condition to form the rhombic crystals, i.e. when it is liquid. But we have evidence for the belief that in sulphur-vapour these complex molecules are simplified into smaller groups—into molecules which contain, say, only two atoms each. As flowers of

sulphur is formed straightway from these, its molecules may well be supposed to contain fewer atoms each than those of the rhombic crystals-to be, at all events, different in some such way, and thus to yield a variety of sulphur that is incapable of forming crystals. The differences between the two kinds of sulphur is not in their chemical actions: the atoms are the same in the two cases, but are grouped in different numbers and possibly in different ways. They may hold together in twos, in fours, in eights, maybe in larger numbers; and of the varied molecules thus formed, which are of course individually far beyond the range of the best microscopes, some will apparently group themselves anyhow in amorphous fashion, while to others belongs the special power of organising themselves into crystal-forms.

A further variety of sulphur may finally be mentioned. When molten sulphur is carefully heated, its colour will be observed to change from a light amberyellow to a deeper red, and ultimately to become almost black. At that point the liquid is more viscid than treacle. If this thick liquid be allowed to drop into cold water, it is found to set into a dark brown gummy mass known as plastic sulphur. This mass is obviously amorphous, but obviously also very different from the powdery flowers of sulphur. Clearly it shows our element in still another molecular condition. These molecules are different from those which form ordinary liquid sulphur and those which form sulphur-vapour, doubtless in containing a different number of atoms. They cannot move freely among themselves: hence the liquid is viscid; and, being suddenly cooled in this condition, they have not the power to rearrange them-

FORMS OF SULPHUR

selves into those atomic groups which yield the crystal-forming molecules. Hence arises the plastic solid. But, as this comes from an abnormal set of circumstances, we should expect it to be an unstable form; and, on being allowed to stand for a few days, it actually does become hard and yellow, like ordinary roll sulphur. Yet even while plastic it is still sulphur and sulphur only, in its atomic foundation. It shows us again how atoms of the same kind may be variously grouped into molecules which have quite different physical properties.

These transformations of sulphur, known as they were to the alchemists, may well have puzzled them greatly; and we need not wonder at the shifty disguises under which their "sulphur-principle" appeared in their speculations. But as further and even deeper mysteries, this same sulphur disappears completely into a smoky fume when it is burned, and destroys the nature of most of the metals when it is heated with them. We have already learned what the nature of the smoky fume is: it is a gas—sulphur dioxide—not an element, not an impure "fire," but a compound in which the sulphur still exists, though with its activities modified by the companionship of another element. And in regard to the metals, the case is not essentially different. The atoms of the metal unite with the atoms of sulphur, and form new molecules which contain both and are called sulphides. Thus, symbolically:

Fe + S = FeS
One iron atom One sulphur atom One molecule of iron sulphide.

These sulphides have no metallic properties, and show no sign of the sulphur they contain. Yet it is

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quite easy to prove that both are there. Indeed, many of them are to be found in the earth, and form the commonest and most easily worked ores for the metals contained in them. Thus there is galena, or lead sulphide, which has only to be roasted in the open air to yield bright beads of lead along with clouds of the choking fumes characteristic of burning sulphur and a film of the oxide of the metal. The mere roasting has revealed the metal and the sulphur in this sulphide. By the alchemists, galena seems to have been read as an impure metal. It has a dull grey metallic lustre, something like that of black-lead. The driving out of the sulphur only increased the proportion of the mercury-principle; and when, out of some lead ores, a small amount of silver could also be got, it is not difficult to account for the alchemists' belief. Silver is nearer to the pure metallic essence than lead, and lead nearer than galena. Of course really the silver is but an impurity in the lead.

Other sulphides of interest are pyrites (FeS₂); copper pyrites, containing copper, iron, and sulphur; zinc blende (zinc sulphide); orpiment (arsenic sulphide); and so on. They are found in various parts of the world, generally in older rocks, and often beautifully crystallised. Pyrites has a golden lustre, and its crystals are found in the faults and cracks of the rocks, as if they have been deposited there from infiltrating waters. Like the other sulphides, it is also found in mineral veins; that is, in larger or smaller masses intruded in other rock-masses. These mineral veins tell us a tale of prolonged water-action on the solid rocks, of the accumulation of this water in the

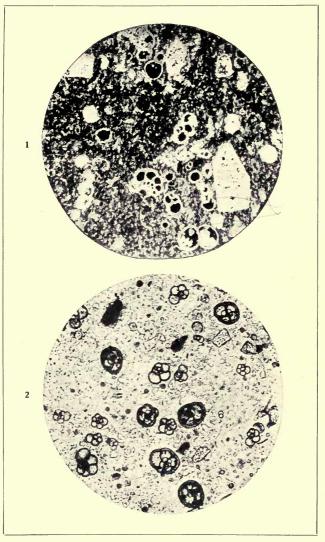
SULPHIDES

gaps and cracks underground, and of its very slow evaporation while the minerals have leisure to crystallise in their perfect forms. Many other valuable substances, besides the sulphides, are to be found in them.

We have dealt with sulphur in this rather full manner, because it is a substance in which the characteristic earth-property of solidity is well and easily exhibited. As an earth or "solid," it is capable of existence in the crystalline, amorphous, or plastic form, according to conditions. We learn from it how the mere action of heat alone is sufficient to destroy its "earth" nature, and to endow it successfully with the water and air "elements." We see how its atoms are capable of arranging themselves in different aggregations, and of forming thus its different appearances. We note finally how those atoms have a distinct liking or affinity for certain metals, as well as for oxygen and other elements; and how from this liking there arise many compounds in which sulphur is one of the partners. It illustrates well the possibilities of a solid element, an important contributor to the minerals of the earth-crust.

We might, though not so well, have told similar tales of other elements like carbon or phosphorus, or many metals. The former, for example, is well known in the various forms of charcoal, and can be proved to exist in a pure crystalline condition in diamonds; it may well give us room to ponder over the wonderful results of atomic rearrangings, when we recollect that the very atoms which compose charcoal could under changed conditions form a diamond. Charcoal dissolves in molten iron, and the liquid, if cooled

slowly and under great pressures, deposits the carbon in small crystals, which are in effect diamonds, though how diamonds have been formed in Nature we cannot yet tell. Diamond and charcoal are different enough, yet fundamentally the same; burnt in air, they produce only one gas, the same for both; their atoms prefer seemingly to be amorphous, and are refractory to deal with, yielding to the crystal-forming forces only under strong coercion. They do not take to the liquid state under any easily obtained terrestrial temperature; and only in the intensely hot electric arc are they driven into the gaseous form. But, however different among themselves the true solid elements may be-whether highly active like phosphorus, easily melted and changed like sulphur, inert and infusible like carbon, metallic and readily changed like iron, or metallic and unchanging like platinum-it must be remembered that they are the true elements of the earth, the true raw material of the old earth-element. They do not occur in any large quantity free, and we should not expect that they would. Moreover, it must not be supposed that the solid elements alone are to be found in the rocks of the earth. The elements of the air, especially oxygen, would be exceptionally active at the higher temperatures of the earth's earlier ages; elements like sulphur, phosphorus, and many of the metals would certainly be converted into their oxides; and naturally, therefore, we should expect to find many compounds containing oxygen even in the solid earth. This proves to be so strongly the fact that quite one half of the solid crust of the earth is supposed to be oxygen, combined with one or more of the other elements.



MICROSCOPIC APPEARANCE OF (1) CHALK COMPARED WITH (2) GLOBIGERINA OOZE



FORMS OF CARBON

III.—CHALK AND ITS RELATIVES

Sulphur, although an interesting and important element, in spite of its deposition from the conspicuous pedestal on which the alchemists placed it, is, nevertheless, not of any large occurrence either alone or even in compound form. Sulphides may form fairly extensive mineral veins; but they do not form any of those great rock-masses which span great areas of the earth's surface. It is obviously these—the clays, sands, granites, limestones—wherein the earth-element will be most characteristically present. We must learn how some of these stand in regard to our modern elements, and erect a finger-post to point out the road leading to a knowledge of their exact nature.

Let us take, for our first rock-substance, chalk. The first question which chemistry has to put to it is, element or compound—which? As a preliminary step, we examine its personal appearance thoroughly. This is familiar enough superficially; it seems a soft, amorphous white powder, and no more. But a microscopic study of its structure reveals the fact that it is almost entirely composed of the remains of the very small shells belonging to the lowly family of Foraminifera, the chief type present being one of spherical form called Globigerina. Very similar shells, although not quite the same, are found in some kinds of the ooze dredged from the deep sea floor, at depths from 1,500 to 2,000 fathoms. Chalk is, therefore, not a crystalline nor an amorphous rock, but clearly of organic origin; and its materials must, in the first instance, have been obtained from the sea in which the foraminifera lived.

This, however interesting it may be, does not, nevertheless, lead us much nearer our chemical goal. We therefore proceed to inquire into the changes our substance may undergo. Now, everyone who lives in a chalk district will be familiar with the process of lime-burning, in which the chalk is put into large kilns and subjected to the heat of a steady fire for some time, wherefrom it is withdrawn in a new guise: it has been changed into lime. Is this a chemical change? Is lime a new substance, or merely the chalk in slight disguise, as plastic sulphur is only another form of roll sulphur? In order to answer this, let us contrast the behaviour of the two; and we need only appeal to familiar facts.

First we note but a slight change in the appearance of the chalk, insufficient at all events to base any secure deduction upon. But if a small piece of each is soaked with water, the chalk becomes merely a slimy mass, whereas the lime grows hot and presently falls into a dry, white powder: lime can be slaked and chalk cannot. Again, if both chalk and lime are separately shaken up with some distilled water, the muddy liquids filtered, and the clear liquids that filter through evaporated to dryness, no solid residue will be left in the case of the chalk, whereas the lime water will be seen to leave a residue of lime. Hence lime does, and chalk does not, dissolve in pure water. Are these differences sufficient? In order to clinch the matter, we weigh out a quantity of chalk and heat it in a crucible. The weight of lime left is found to be less by more than 40 per cent. than that of the chalk originally taken, and this result is obtained whether the air be excluded or not. We are therefore

CHALK AND LIME

free to conclude that chalk is not a true element, and that lime is one of its constituent parts. That the other is a gaseous substance is rendered most likely by the loss of weight; simple experiments prove that it is the carbon dioxide discussed on p. 88. Thus chalk becomes a compound of lime and carbon dioxide.

The latter of these substances is itself a compound, and the nature of lime is still a problem before us. No simple process is available for its decomposition. amount of heat seems to have the least effect upon it, except to make it glow intensely, without altering its properties. The most definite of its chemical properties is its action towards water, with which it forms a new compound called slaked lime, soluble in water and giving an alkaline liquid. It is one of the most stable of substances, and it is only by indirect means that it can be shown to be the oxide of a metallic element known as calcium. Like the other alkalis, soda and potash, lime contains an exceedingly active metal, which undergoes oxidation readily. On account of its earthy nature, lime is called an alkaline earth; but, strictly speaking, only its solution in water is really alkaline, and that is not necessarily the same thing as lime itself.

We thus realise that chalk is a compound of two substances, each of which is in its turn a compound—lime and carbon dioxide; or, in symbolic language:

A considerable temperature is needed before all the carbon dioxide is driven away from the chalk; but

any diluted acid will effect this rapidly and is at the same time neutralised. Any substance which behaves in this manner-yielding carbon dioxide with a brisk effervescence when acid is poured upon it-is known as a carbonate. The pure substance which forms the basis of chalk, and becomes lime when it is heated, is therefore properly known as calcium carbonate; and many similar compounds are known in which other metals play the part of the calcium in chalk. The brown clay ironstone which is one of the most important of iron ores is mainly iron carbonate (FeCO₃); the familiar white-lead of the painters is a carbonate of lead; and the common washing-soda of everyday use is a crystalline form of sodium carbonate (Na₂CO₂). All these substances agree in their ready loss of carbon dioxide gas, with accompanying effervescence, when a dilute acid is added to them.

Returning to calcium carbonate, our readers will hardly need now to be told that limestone is another form of it. It is well known that in many districts limestone is used for the production of lime: in the chemical sense limestone and chalk are identical. Apart, however, from its occurrence in large shells, limestone is much harder than chalk; some forms of it are, in fact, hard enough to be used for buildingstone, and a very casual inspection only is needed to reveal to us its finely crystalline nature. Marble also is calcium carbonate, still harder and more compact than limestone. Microscopic examination reveals the fact that marble is made of many almost equal grains, each of which is composed of a little collection of crystals. Marble shows, indeed, every sign of having been subjected to very great pressures; it is generally

CALCIUM CARBONATE

found in the earth in the close neighbourhood of igneous rocks, i.e. of rocks that were once in the molten condition; and what seems to have happened is that a fiery lava intruded itself into a mass of limestone, subjecting the limestone near it to intense heat, while the pressure of the overlying rocks prevented the escape of carbon dioxide. The limestone was therefore brought into a fluid or semi-fluid condition, from which condition it solidified, as the intruding lava cooled, in the crystalline form; just as we saw that liquid sulphur yielded us a crystalline mass when it solidified into roll sulphur. The great pressures prevented the formation of large crystals, though the process of cooling was exceedingly slow; the pressure, too, was responsible for the granular fracture of the changed rock.

We thus see that the compound calcium carbonate, like the element sulphur, is capable of entering into various molecular arrangements or groupings, which result in the compound taking upon itself either a crystalline or an amorphous habit, according to circumstances. The crystalline habit may be assumed by large masses of rock, as in limestone or marble; but more conspicuous crystals are often found which suggest a very slow formation from solution. These crystals form the mineral called calcite, which can be easily recognised, when the crystals are well formed, by its fracture. When struck, a mass of calcite breaks up easily into fragments, which may be of very different sizes, but are all alike rhombs, i.e. figures in which every face is a parallelogram. The rhombs may vary in shape within very wide limits; but the angles at corresponding corners of the crystals are always

the same. The smallest crystals of calcite, formed by the molecular habits peculiar to calcium carbonate, fit themselves into larger crystals, very much as the individual bricks in a piled stack are arranged when they do not overlap: the whole stack will have the same angles, but only in a general sense the same shape, as the individual bricks; and what happens when a portion of the stack is broken away illustrates very well what is meant by the regular fracture of crystals. In a mass of calcite the crystals are fitted together as compactly as is possible; in ordinary limestone the crystals are heaped together haphazard, not without injury to their individuality.

Calcite, as ordinarily found, is opaque; but in Iceland the crystals are often transparent and give us the beautiful mineral called Iceland spar. has the very unusual property of double refraction, by which any object viewed through a piece of it is seen double. The crystals of Iceland spar are, however, rhombs, like those of calcite. A different crystalline form altogether is found in aragonite, another species of calcium carbonate, found in mineral veins, near geysers, and under other conditions which suggest that it has been formed by crystallisation from hot water. It is said to be less stable than calcite; if so, it bears the same sort of relation to the rhombic form as monoclinic sulphur does to its rhombic form. However this may be, we find here abundant evidence of the crystallisation of calcium carbonate from some solvent, just as sulphur crystallised from carbon disulphide.

That the solvent is in all probability water is rendered reasonable to our minds by the familiar trouble

HARDNESS OF WATER

of hardness which so often affects our natural waters. Everyone is familiar with the furr that lines kettles, boilers, etc., in which such water has been boiled. Everyone knows the simple fact that it is the waters of limestone or chalk districts that are most affected by hardness. Putting two and two together, everyone has arrived at the conclusion that water dissolved the calcium carbonate from the hills. Our chemical tests would confirm the fact that the furr is calcium carbonate; and it can all be dissolved out with a dilute acid. And yet pure water does not in any measurable degree dissolve chalk or any other form of calcium carbonate.

But natural water is, of course, ultimately rain water, and this is not necessarily pure. In passing through the air, it has the chance to dissolve any of the gases that occur in the air. Now, all the familiar gases of the air dissolve in water to some extent; and if he will attend to the teaching of the following experiment the student will learn that one of these gives to the water the power to dissolve calcium carbonate. When carbon dioxide is bubbled into lime-water a milky deposit is gradually formed, which acts, in fact, as a very ready test for the gas; but, if the gas be continued, we should notice the turbidity of the liquid disappear gradually, leaving the liquid quite clear. No further bubbling of the gas will restore the turbidity or produce any other visible change. If now the clear liquid be heated, bubbles of gas will be seen to escape, in larger numbers as the liquid becomes hotter; and when it is boiled, the whole of the dissolved gas will escape and the turbidity will be found to have returned.

Let us contemplate these results carefully. First, we attend to the turbid precipitate formed when the gas is led first into the lime-water. What is it? The simplest suggestion would undoubtedly be the correct one, namely, that it consists of calcium carbonate, produced by a synthesis of the lime and carbon dioxide, and becomes visible as a white precipitate, because of its insolubility in the water. It may be allowed to settle or be filtered from the water, and shown assuredly to be so. As long as there is any unchanged lime in the liquid, the continued passage of the gas will increase the turbidity by increasing the amount of calcium carbonate; but at last all the lime will be converted into the carbonate, and at that point the second phase of the action will commence. The excess of carbon dioxide now bubbled into the liquid evidently brings about the solution of the calcium carbonate, which just as evidently reappears when the gas is merely boiled out of the water again. If the gas forms a new compound when it is thus in excess, that compound cannot resist the temperature of boiling water; we need not here inquire into that, but content ourselves with the observation that calcium carbonate dissolves to a considerable extent in water which also contains carbon dioxide dissolved in it. Rain water which has filtered through soil will most certainly contain carbon dioxide, and will consequently have the power to dissolve some of the chalk or limestone through which it may have to percolate. Thus the water becomes hard, and is virtually a solution of calcium carbonate. This hardness can be removed by boiling, and hence is called temporary hardness, as distinguished from the permanent hardness which boiling does not remove.

TEMPORARY HARDNESS

It can also be removed by the addition of more limewater, which throws down the excess of carbon dioxide as calcium carbonate, and at the same time liberates the original chalk or limestone from its solution. Natural waters are thus partially softened for public use.

The calcium carbonate precipitated by the boiling process is a fine amorphous powder; but when the water in which it is dissolved is very slowly evaporated crystals of calcite are usually formed. In Nature this process is continually going on. Thus, for example, it is found that many fossils in very varied formations are composed of calcite crystals; the organic matter of which they were composed has decayed and the products of decay been removed by the infiltrating waters; but so slow has been the process that calcite has been deposited in its place in perfect correspondence with its original structure, and we have the whole animal, as it were, petrified in calcium carbonate. To the slow crystallisation of calcium carbonate is also due the formation of the beautiful stalactites which hang like rocky icicles from the roofs of many caverns; the flatter stalagmites which are formed opposite to the stalactites on the cavern floors have arisen from the water which dripped too soon from the hanging stalactites.

Evidence of the rate of formation of these stalagmites has been obtained from Kent's Cavern at Torquay, pointing to a growth of $\frac{1}{20}$ inch in two centuries. The increase is doubtless more rapid in the Derbyshire caverns, where the spring waters will cover any object like an open umbrella with such a deposit of limestone that it seems to be completely petrified

in a few weeks. But in that case there is a perfectly free evaporation. Under natural conditions we have to picture the solid masses of limestone or chalk being very slowly pierced and riddled by the active water: we have then to follow this water into the interstices of other rocks, into gaps, or spaces once occupied maybe by dead organisms, and there quietly forming, according to its own plans leisurely put into action, the beautiful crystals of calcite that are often found. Or possibly, the water finds its way into springs, rivers, and the sea; and the common presence of calcium carbonate in the shells of marine molluscs and other lowly organisms of the sea reminds us of a possible destination for the limestone dissolved from our mountains. A limestone rock which has to endure the rain is very clearly not terra firma when we think of it through the centuries. Every particle of it was once formed from water, and into water it will be dissolved again—but only if the water contains carbon dioxide !

Dry quicklime does not take up carbon dioxide, except under considerable pressures; and we ought not to part with it before noting that its action with water is really a chemical change, and slaked lime a different substance from quicklime. The latter, if merely moistened with water, becomes in a few minutes a dry, white powder, with evolution of heat; it has combined with the water and formed the new compound, calcium hydroxide, as thus:

$$\begin{array}{cccc} \text{CaO} & + & \text{H}_2\text{O} & = & \text{CaH}_2\text{O}_2 \\ \text{Lime} & & & \text{Slaked Lime} \\ \text{[= Calcium oxide]} & & & \text{Calcium Hydroxide]} \end{array}$$

It is this calcium hydroxide which dissolves in water

LIME

and forms lime-water, and the effect of carbon dioxide upon it may thus be represented:

$$CaH_2O_2 + CO_2 = CaCO_3 + H_2O$$

When it is mixed with sand for making the mortar of the bricklayer, lime is first slaked; and the first stage in the setting process is the production of the calcium carbonate with the carbon dioxide of the air and the simultaneous production of water. As some of the soluble slaked lime soaks into the porous bricks, we can account for its action as a cement to the different layers; and the water produced in its setting shows us why a plaster remains so long damp. A fire in the newly plastered room aids the setting process both by its heat and by the carbon dioxide which it affords.

Lime, we have said, is an exceedingly stable compound in the sense that it is difficult to separate it into its two constituents. In point of fact, this cannot be directly done at all; but indirectly it is done in an interesting process which has become commercially important. Electric currents have brought about the decomposition of a number of compounds which otherwise it is difficult to split up; but in order that electrolysis may be possible the substance must be liquid. Lime, however, shows no sign of melting before 5,400° F., and it cannot be electrolysed directly even then. If, however, it is mixed with finely divided carbon and the mixture packed in the electric furnace between two poles of carbon (Fig. 41), somewhat as in an arc-lamp, the lime appears to be decomposed when the high-tension electric current is passed through it; but both its constituents combine with the carbon imme-

diately, and no true separation of them is obtained. No decomposition at all occurs if the carbon is not there; consequently, the action is probably in part one of reduction, the carbon by its affinity for oxygen

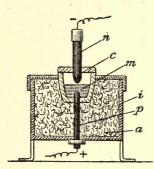


Fig. 41.—Electric furnace.
c, Crucible containing material to be

acted upon (m); β , positive electrode; n, negative electrode of carbon which can be raised or lowered. The whole is surrounded by a hollow metal jacket i, packed loosely with non-conducting material α .

helping to draw the two elements asunder. However this may be, the calcium does not appear alone, but combined with the carbon as calcium This carbide is a carbide. grevish solid with a disagreeable odour; when water is allowed to fall upon it drop by drop, it gives a gas called acetylene, which takes fire readily and burns with a very luminous flame; and for the illuminating properties of this gas calcium carbide is now

manufactured by the process above noted. The large amount of energy that is required for that process is an indication of the tenacious nature of the combination of calcium and oxygen in lime.

Lime water, a solution of calcium hydroxide, is highly alkaline; the molecules of calcium hydroxide are therefore supposed to be partly dissociated in solution into ions, the calcium ion being separated from the hydroxyl ions, as thus:

$$CaH_2O_2$$
 (in solution) = Ca^{++} + OH + OH).

Thus, in solution, the calcium is conceived as separated from its oxygen. Now, if we can find some means of keeping this ion away from the oxygen, we can at the

GALCIUM CARBIDE

same time decompose our lime. The electric current is not sufficient, because as soon as the calcium ions begin to combine into calcium molecules they proceed to act on the water and produce lime and hydrogen again. If an acid be mixed with the lime-water, however, its negative ion may so be chosen that it carries off the calcium ion with it in the form of a new compound. Like all acids, sulphuric acid has hydrogen for its positive ions, and it so happens that its negative ion forms almost insoluble molecules with the calcium ion. In these new molecules, therefore, we have the calcium, in an indirect way, parted from its original oxygen. The new molecules are those of a substance called calcium sulphate; and it is perfectly easy to produce it from lime, as well as from slaked lime, or from lime-water, by addition of sulphuric acid. In symbols, thus:

All acids will form new substances in this way with lime; only in some cases the solution must be still further concentrated before the new compound will appear. Of these compounds, calcium phosphate, as the chief mineral constituent of bones, is the most important.

The compound called calcium sulphate (CaSO₄) occurs very widely as a natural mineral; it is then known as gypsum. Usually it forms large masses of compact crystals, often fibrous in fracture, and very frequently it is found in association with rock-salt. It is soluble in water to a small extent, and is, next to

0

salt, the most common dissolved impurity in the sea and salt lakes. When the water in these latter begins to become scanty, gypsum is always deposited in a crystalline mass along their floor; but the salt, being more soluble, does not solidify until the lakes are nearly dry. If then we find, as we do, alternating strata of gypsum and salt embedded in the earth, we have very strong circumstantial evidence of the existence and drying-up of ancient salt lakes on the site; and in the present epoch such alternate layers are being formed by the drying up and refilling of the Dead Sea.

Gypsum dissolves in ordinary water, and naturally it will therefore be found scattered among any rocks that water can percolate; that is to say, it is almost everywhere. Large, isolated crystals of the compound, called selenite, also occur to give evidence of the transportal of the mineral into the hidden crannies of the rocks, where a very slow crystallisation can take place. The water which contains it has the property of permanent hardness, which can only be removed by chemical actions, and not by boiling. All kinds of hardness are caused by the presence of some calcium-containing compound in the water. It is the calcium which forms the scum, or precipitate, when soap is added to the water; all the calcium has to be chemically removed in this scum before the soap will give its lather; and the scum thus represents a large waste of soap, as well as an inconvenience. Soap softens the water, but very expensively; and for permanent hardness it is best to precipitate the calcium with common washing-soda. The soda is a carbonate, and forms insoluble calcium carbonate, thus:

GYPSUM

CaSO₄ + Na₂CO₃ = CaCO₃ + Na₂SO₄
Calcium Sulphate Soda Calcium Carbonate (Insoluble) Sulphate of Soda (Harmless)

It is useless to add lime in this case, as there is no carbon dioxide to destroy; and lime-water is itself permanently hard.

Very few springs are without gypsum in more or less degree dissolved in their waters; but, as showing the manifold variety of chemical changes that take place in our solid earth, we will mention one of its possible transformations. Water that has passed through a soil contains necessarily a considerable amount of organic matter in a state of more or less complete decomposition. Such matter makes the water a reducing agent; any substance in it that can vield oxygen will be tempted to do so, in order to further the decomposition, and will itself be reduced to a less advanced stage of oxidation. Thus gypsum, calcium sulphate (CaSO₄) will, on yielding up its oxygen, become calcium sulphide (CaS). But calcium sulphide, in the presence of even the feeblest acid, is unstable, giving a gas, known as sulphuretted hydrogen, with the fetid odour of rotten eggs. will be familiar to those who know the medicinal waters of Harrogate and other sulphurous springs. Water containing this gas, however, slowly deposits sulphur itself when it comes into contact with the air; and thus some of the sulphur found in Nature can be traced back to gypsum as its original source; but of course it existed in the compound molecules of gypsum all along.

When the calcium sulphide gave up its sulphur as sulphuretted hydrogen, an acid was required, and this is to be sought in the carbon dioxide, which is always

faintly acid when it is dissolved in water. We shall not, therefore, be surprised to see the calcium from the sulphide transformed into carbonate, in the sense of the equation:

This gives us an indication of a possible method of accounting for the production of calcium carbonate by the animals of the sea in such vast amounts. There is little carbonate present in sea-water in the ordinary way; there is much sulphate, and the transformation has to be accounted for in some way. In all probability, therefore, we are to look upon calcium sulphate as an older terrestrial substance than the carbonate; the link between gypsum and limestone being forged by the molluscs and other shell-organisms whose shells are composed of calcium carbonate. As for the origin of the gypsum itself, it is not possible to speculate profitably upon that at present.

The changes which gypsum has been thus undergoing over the long periods of time covered by the earth's history prove to be of unexpected interest; it does not diminish this interest to find it filling a little niche in the practical arts of civilised man. When it is heated carefully a little beyond the boiling-point of water, gypsum loses water and falls into a fine, heavy, white powder. This water was absolutely necessary to its assumption of the crystalline form, and shows conclusively that it was deposited from standing water, and not merely through the liquid's complete evaporation to dryness. The powder left is amorphous, and is well known as plaster of Paris. The use of plaster of Paris depends upon the fact that it will absorb

PLASTER OF PARIS

water and re-form gypsum. If the powder is thoroughly moistened and then shaped by a mould into any desired form, it will quickly harden, because every fine grain of it combines chemically with water, forming small crystals of gypsum in a very compact, fine-grained mass.

A little water still remains combined in the dry plaster of Paris, for if this is overheated the residual water is driven off and a perfectly anhydrous calcium sulphate is obtained. This is found to be quite useless for moulding; it will re-form gypsum certainly, but the resulting crystals are not consolidated into a firm and compact mass. In Nature the anhydrous substance is found where salt-lakes have been completely dried up. It is there harder and heavier than gypsum, into which it is converted, with evolution of heat, by the slow action of water. It is most interesting, however, to notice that the successful action of plaster of Paris is dependent upon so small a matter as the retention of a little water. The crystals of gypsum are supposed to contain two water-molecules, associated in loose union with one of calcium sulphate; in plaster of Paris the proportion is reversed, thus:

 $\begin{array}{lll} \text{Gypsum} & = & \text{CaSO}_4.2\text{H}_2\text{O} \\ \text{Plaster of Paris} & = & 2\text{CaSO}_4.\text{H}_2\text{O} \\ \text{Anhydrous Sulphate} & = & \text{CaSO}_4 \end{array}$

In many another preparation in chemistry, inattention to an apparently insignificant detail like this is fatal to the success of the operation.

We have thus in lime, limestone, chalk, and gypsum dealt with a group of earth-substances of wide occurrence and consequently very many interests. The element that binds them is the metal calcium, of which

we have seen nothing in our descriptions, and it is by no means easy to isolate. In fact, until quite recent electrical improvements have facilitated its preparation, it was very little more than a chemical curiosity. Is calcium, then, the earth-element? It is, at any rate, one of them; but not more than oxygen, which also enters into all these compounds, can it be regarded as the only and characteristic constituent of "earth." All and any of the elements can enter into the composition of the many varied earthmaterials. One special group is so important, and so different from our calcium group, that we must now just break the ground in preparation for a fuller study at a more advanced stage.

IV.—SILICA AND SILICATES

The calcium minerals and rocks furnish us with examples of earth-substances in the formation of which the water element has played a conspicuous part. We must spare a few pages in inquiring whether those solid rocks, which are fire-formed in the earth's interior, and anon issue from its surface in lava-streams, are of essentially different nature.

Examine, then, a piece of granite, and read the tale of its formation. When it is in the unpolished state its story can be easily read in its physical structure with the naked eye; and a careful inspection reveals clearly its threefold composition. We can see a blackish mineral which readily peals off in small flakes with a penknife; along with it is a glassy, clear substance which the knife will not scratch; and the third constituent is a dull white or pink mineral which readily gives under the knife. Further, it would seem that

THE MINERALS IN GRANITE

these three minerals form together a crystalline mass. but that each one exists quite separately and independently of the other. Granite is therefore a mixture of the dark mica, the glassy quartz, and the dull and readily-scratched felspar; a mixture in which the three constituents are in no constant proportion, but where each occurs in its own independent crystalline habit.

None of these minerals is affected by water or even by acids in the ordinary way; the crystals were probably not formed from solution, therefore, but from fusion; their size assures us of a very slow formation, and the evidence thus converges on to the supposition that granite was once a molten rock or lava, and solidified under slow-cooling conditions, probably deep down

in the earth-crust. In other words, granite is a product of earth's deeps; its minerals have stood the great temperatures of the earth's interior; its materials are of those which form the basis of the earth-crust; and it is as well to take a glance at their characteristics.

Quartz turns out to be the simplest of them. Like many other natural sub-



Fig. 42. Rock-crystal.

stances it is found in several forms: sometimes amorphous, as in flint and opal; sometimes semi-crystal-line only, as in chalcedony; sometimes in large masses of small crystals, as in sand and sandstone; sometimes beautifully crystallised in large six-sided prisms with pyramidal ends, forming then what is known as

rock-crystal. Its crystals are often found in mineral veins, and as intrusions in other rocks; they are frequent in fossils, and under such circumstances as show that it has replaced other minerals, such as calcite. Under various forms or other, therefore, it is an extremely widespread substance. The matter of which these various forms are built up is known as silica; and, as one would expect, it is an exceedingly stable substance. It has, however, been shown to be a compound—an oxide, in fact, of an element similar to carbon when it is isolated—an element which, like carbon, also returns easily to its combination with oxygen; it is known as silicon, and silica quartz and its various forms are really silicon dioxide (SiO₂).

Silica is a very obtuse substance towards chemical reagents; none of the common solvents dissolves it; acids do not affect it, except hydrofluoric, which turns it into a gaseous compound. Yet the circumstances under which flint and quartz often occur make it clear that some sort of solution of silica must be effected in Nature. Flint almost certainly is of organic origin, and if so its silica must have been obtained from sea-water; in the deep sea certain organisms are found which have siliceous shells. It seems highly probable that the other impurities of the water, especially when they are alkaline, confer on it the power to dissolve silica; but the process cannot be directly imitated with quartz or sand or other natural forms of silica.

If silica cannot, however, be directly dissolved or decomposed, we might suppose that, like lime or carbon dioxide, it would be able to enter into new combinations. That this is the case is one of the oldest pieces of chemical knowledge. When a clean white sand,

GLASS

which is nearly pure silica, is mixed with chalk and soda, and the whole heated, the mass melts and solidifies afterwards into glass. This process was in its essentials known to the ancient Egyptians; and we are well aware that mediæval church-builders had discovered, not merely how to make a good glass, but also how to colour it in several beautiful tints. A harder and altogether better glass is obtained when potash is used instead of soda; this is the Bohemian glass used for the construction of scientific apparatus. Further, the chalk (or lime) is replaceable by lead oxide (or white-lead), to give us the highly refractive flint-glass used for the best optical instruments. Whatever kind it is, the glass has the same peculiarly glass-like characters: it is brittle, transparent, amorphous; it readily melts before the blowpipe into a pasty liquid that can be moulded, blown, or worked into any shape that may be desired; it resists the action of nearly all chemical agents, except hydrofluoric acid and the strong boiling alkalis, potash and soda. It is the combination of these properties that makes it so valuable a substance.

If soda is used alone in the fusion with sand, the glass which we obtain is soluble in water; and when heated to dryness with an acid gives amorphous silica and a salt. We are thus drawn to regard the glass as a combination of soda with silica, as a kind of salt in which the acid part is played by the silica. The soluble glass will then be properly named silicate of soda; while ordinary glass is a mixture of the silicates of soda (or potash) and lime (calcium). Nothing could be less like our ordinary conception of an acid than silica is. Yet its readiness to enter into combination

with the molten alkalis, and its consequent production of a whole series of silicates, is proof enough that it acts the part. Besides, a curious gelatinous compound can be prepared which is named silicic acid, and yields when heated nothing but water and amorphous silica; by indirect means the silica has thus been compelled to combine with water and to produce the very faintly acid substance, silicic acid.

If then we grasp this fact clearly, that silica can with fused alkalis be coerced into combination as the acid constituent of a group of silicates, we shall be prepared to understand the part which it plays in mineral formation. For, think of the condition of the metallic elements in the early stages of the earth's history. How could they, themselves vapours, resist the strong affinity of the vast stores of oxygen by which they were surrounded? They would ultimately, most of them, become oxides; and in the hot, molten condition these oxides would form silicates, by union with silica, as in the process of glass manufacture. We shall not be surprised at finding, therefore, large stores of silicates among the fundamental, and especially the volcanic, rock materials of the earth. Vast quantities of silica remained uncombined, as the presence of free quartz shows; but far vaster quantities were taken up by the metallic oxides, and converted into silicates.

We have mentioned the fact that glass is corroded by boiling alkalis. This is a fact not difficult to interpret when we recollect that the lime which forms an essential constituent of glass is an alkali weaker than soda or potash. The silica, therefore, when the choice is presented under favourable conditions, will prefer

SILICA AND SILICATES

the stronger alkali; the lime will be replaced by the soda; and the glass turned into silicate of soda entirely. As this is soluble in water, it is not difficult to explain why the glass is appreciably affected by the alkali. Any natural silicate or mixture of silicates can be completely changed into silicate of soda if it is melted with the soda. Now this silicate of soda is decomposed by the weakest acids; the silica is so weak in its acid affinity for the alkali that even carbonic acid, the solution of carbon dioxide in water, is sufficient to set it free; the alkali becomes a carbonate, and the silica is liberated.

We can thus perceive the principle of the process by which silica can be released from the silicates. But does this process operate in Nature? In a slow and modified degree we may answer yes. Fused alkalis we do not meet; but an alkaline water, even when it is dilute, will, given sufficient time, attack the natural silicates forming the soluble silicate of soda; and it is in this form that the silica is dissolved in water. Almost certainly we may then assert that the silica itself is precipitated through the action of carbonic acid, or by the action of living organisms. Certain kinds of ooze dredged from the deep sea consist almost entirely of minute organisms called Radiolaria, with beautifully marked siliceous shells; and flint is often darkcoloured, to remind us of the living creature that commenced the precipitation of the silica of which it is composed. The exact conditions under which the splendid crystals of quartz are formed cannot, however, be said to be fully known; when thrown out of silicate of soda by an acid, the silica is amorphous, but possibly this uncrystalline silica can itself be

somehow dissolved and re-deposited as quartz or rock crystal.

The changes in the natural silicates which have just been explained depend upon the presence of an alkali, like soda or potash, in the water. What is the source of this alkali? In order to answer this, we will turn briefly to consider one of the other constituents of granite. The mineral felspar is, like glass, a double silicate: it contains two bases in union with much silica, viz. potash and alumina. It is in various forms one of the commonest of minerals, and, in contact with the air, it very slowly undergoes a change known as weathering. The change may be easily observed in an exposed piece of rough granite. A new piece of felspar, shown by a fresh fracture, is lustrous and obviously crystalline; an old piece is rough, and, superficially at least, not crystalline. Air and water, working persistently year by year, are responsible for this change, which is not one of appearance merely, but a true chemical change. The carbonic acid has performed the same change as we have previously explained. It has decomposed the silicate of potash into silica, which is set free, and potash, with which it forms the alkaline carbonate of potash, which is soluble in water; the silicate of alumina is not decomposed, but it becomes hydrated—that is, combined with water-and carried away in suspension as a very fine powder. Thus we see at once how a natural water may become alkaline. The massive silicates are slowly, very slowly, but quite surely, corroded-simpler silicates, silica, and an alkali being the result. We may represent it in tabular form, thus:

WEATHERING OF SILICATES

This decomposition of natural silicates by atmospheric agencies is of great and necessary importance in Nature. It is the condition precedent to the growth of a soil and to making a home for incipient vegetation. In order that mineral substances may be utilised by a plant they must first become soluble, and the formation of carbonate of potash is the first step towards this. Besides, no plant could grow on a firm, unyielding rock like granite; a superficial layer of soil at least must be formed to give anchorage to even the tiniest root-system. Once any form of vegetation has made a start, even if it be no more than some lowly alga or lichen, the process of rock-change will be speeded somewhat: the decay of the first plants will provide carbon dioxide and other soil acids, which will render the water more active; and new soil will be added to the old. How slow the whole process must have been in the first instance, when the solid earth-crust consisted almost entirely of these highly stable silicates, we can only vaguely realise. That they did ultimately yield, the living forms of plant and animal, with their age-long evolution behind them. are here to show.

The insoluble materials formed by the decomposition of felspar, the pure silica and the silicate of alumina, are either washed away or form a portion of the soil *in situ*. In the former case they are carried off by the water in suspension, and are forced to settle

as soon as the water becomes stagnant. This happens, of course, as soon as it reaches a lake or the sea: and thus we find that deposits of sand and mud are, and have been, in continual process of formation in lakes and seas. Geologists have taught us how these sands and muds have, in the course of ages, become consolidated into the sandstones and clays of the solid earth; and we should therefore expect to find these rocks containing our silica and silicate of alumina. But felspar is only one of many silicates, such as mica, hornblende, olivine, and many others; and these often contain other bases, such as iron, lime, magnesia, and soda, instead of the potash and alumina of felspar. We are therefore not unprepared to find our sands and muds impure mixtures of many derived materials. Sand is often enough red, for instance, owing to the presence of iron oxide among the quartz crystals; clay, too, is often coloured more or less by various compounds of iron, and in marl is plentifully mixed with calcium carbonate. But there are forms of clay in which almost the only mineral present is silicate of alumina; such is the pure white clay known as kaolin. Such a clay is thus composed exclusively of one of the substances set free by the weathering of granites or other rocks containing felspar.

The particles of clay are amorphous and exceedingly fine; so fine that a mass of clay holds water with stubborn tenacity. It is this water which makes a clayey soil heavy; it is that also which makes clay a valuable substance for bricks, earthenware, and porcelain. Clay in the moist state can be moulded into almost any shape; when it is baked its water is

driven off, and a hard and fire-resistent material results. The latter property is exceptionally notable in fireclay, to which some pure silica has been added; it is weakened very much if the strong alkalis are present, because their silicates are fusible. For porcelain, kaolin must be used; for earthenware a less pure clay will serve. In either case the result is porous, and the material must be glazed. This is done, either directly or indirectly, by forming a glassy silicate on the surface: soda, or lime, or lead oxide is used for this purpose; and upon the skill with which this is done depends the quality of the porcelain or pottery obtained.

When clay is steeped in strong sulphuric acid and warmed, it does not remain unaltered, as most silicates do. The silica is liberated from it, and the alumina dissolves. If the acid liquid be diluted, decanted from the silica, and some carbonate of potash also added, there can be crystallised from the resulting solution a familiar substance, much used for various purposes—alum. This was known as a natural product in very early times, and used as a mordant to fix the colours in dyed cloths. We are mentioning it here, however, in order to draw attention to a rather remarkable law. If soda had been used instead of potash in the preparation of alum, we should still have obtained what we should at once name alum; because its crystals are almost indistinguishable in shape from those of the first alum. The interchange of soda and potash produced very little change of property, and none in the crystalline habit. Two different elements can replace each other without making any real change of molecular configuration. That this must

be decidedly complex may be judged from the following formulæ:

Alums are thus known which contain no aluminium, but in which the aluminium is replaced by equivalent elements. They are all isomorphous, and form their crystals according to the same system. Let a crystal of the dark purple chrome alum be placed in a strong solution of ordinary potash alum, and it will grow by the accretion of the molecules of the latter without any alteration of shape. This fact of isomorphism shows us then that, though there are many elements, some of them have at least one common property to group them in a sort of genus by themselves.

V.—GENERAL COMPOSITION OF EARTH

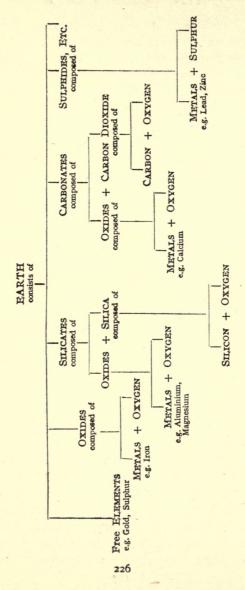
The base alumina of which we have spoken is the oxide of the metal aluminium, which therefore exists in vast quantities, wrapped up in the molecules of its silicate, in the earth's crust. The metals are true elements with whose properties we have not space to deal here. As we have seen, they are found sometimes in the form of sulphides; occasionally they are found alone; but more frequently they occur, like aluminium, combined with oxygen, as oxides. These oxides may occur, as the oxides of iron very largely do, uncombined, or, more generally, formed into silicates or carbonates. If, therefore, we wish to conceive under a general view the nature of the earthelement, we must commence with the earth in its hot,

THE SOLID EARTH

gaseous condition. As far as positive knowledge now takes us, we must conceive some eighty different fundamental stuffs or elements to have been existing then. Between the atoms of these elements there were strong affinities, repulsions, and indifferences. For long, however, they were kept apart by the high temperature; then they began to combine with one another, according to their affinities. Most active oxygen evidently was: forming oxides with metals like iron or aluminium, which were abundant; making oxides also with non-metals like sulphur, silicon, and carbon. These oxides, too, have their acid or basic affinities. Silicates result, as we have shown, from the liquid earth; carbonates, sulphates, sulphides, come when all is cooler and solid crusts begin to form.

The elements of water and the air now remain, to set afoot those new changes in the solid earth which we have endeavoured to adumbrate. The transformations are still actively proceeding without cessation, but without hurry. Now and then overflows of the original earth-rocks in volcanic activity remind us of the conditions of bygone ages; but on the new rocks weathering begins to operate; soils form, and the vast, solid masses are slowly changed and carried off, in suspension or in solution, to be subject to new chemical changes, and transformed anew and again. Earth is really more changeful than water or air, more varied and more complex. We began with "dryness" and "coldness"; we end our chapter with a vision of some eighty elements, organised into many hundreds of compounds by the action of principles far other than "dryness" or "coldness"; and of

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COMPOSITION OF THE EARTH

these compounds obeying, in fusion or solution, those mysterious laws which build crystals of such constant and characteristic shapes. In the earth these compounds are solid, because their molecules are close together, and hamper one another's free movement. We raise the temperature, and the molecules are able to move more freely: "earth" has become "water"! We go on heating, and the molecules have a still greater freedom: "earth" is then "air." There is no difference, essentially, between "earth," "water" and "air"; the elements of the one can enter into the composition of the others, as oxygen does so largely under present conditions. The study of the earthelement shows us well how valuable it has been to leave "principles" and come down to the "things." The things have led us to a knowledge of just and sound principles, such as a mere philosopher could not have conceived, even in his wildest flights of metaphysical imagination.

The table on the opposite page shows in a diagrammatic form the resolution of earth into the chief elements which go towards its formation.

CHAPTER VII

ETHER

I.—Unity of the Elements

WE have seen in our previous pages how the idea of the ancients concerning the constitution of matter has been pulverised by a thorough examination of its various forms. The four elements have been multiplied into some eighty or more; and it would seem that we cannot think of the material universe without all these. The atoms composing these eighty elements represent the foundations of all matter. They are all characterised by that basal property of matter known as inertia, by virtue of which they demand a force of some kind before their state of uniform motion in a straight line can be changed. They differ in the amount of this inertia, but not in the quality itself; in other properties they differ not only in degree, but also in kind. Plainly said, all atoms have weight, but no other necessary quality.

With their four elements only, the Greek philosophers felt the need of further simplification. How much more must we, who have so many more? The Greek mind had, however, nothing but "principles" to reduce; the fifth essence, which vitalised these, and was as hazily fantastic as they, could easily be postulated. But we are dealing with matter, recognised by its property of inertia or reluctance to move, a property measurable under our conditions by its weight. And this matter of ours, as indicated by its inertia, is

UNITY OF THE ELEMENTS

indestructible; so that we seem compelled to postulate matter ab initio; and all that we can ask is by way of a cross-examination of the facts of chemistry concerning the necessity or otherwise of eighty different kinds. To reduce our eighty kinds of atoms into one kind is a thinkable proposition; but to reduce these uniform atoms to something more elementary -to some essence, ether, or other spirit-stuff: that involves the annihilation of the whole sensible universe, the dissipation of all things into an immaterial and insubstantial essence. What has been done in both these respects we are briefly to consider; but we are here in the realm of speculation mainly, with only a few dim gleams of experimental truth to guide our intrepid imaginations.

Hydrogen is the lightest of the known elementsits atom the smallest unit of matter, therefore, whereof we have knowledge. It is a very simple suggestion, made something like a century ago, that all other atoms are but aggregations of the hydrogen-atom, and that hydrogen is the aboriginal world-matter, of which all other is the outcome. Simple and attractive, but impossible. We may waive the difficulty of imagining how sixteen hydrogen-atoms could by any process of mutual arrangement give an oxygen-atom with quite opposite chemical properties; but all the atomic weights would have to be exact whole numbers, else we should have to conceive the atoms as losing or gaining weight by their aggregation. If the weight of an atom of chlorine is 35.45, it is impossible for it to be made of hydrogen atoms of weight I. And the more refined the method of determination is, the more sure are we that our atomic weights cannot be made

to fit in with the supposition that hydrogen is the primordial stuff of the material world; and obviously no other of our eighty elements can be even considered in the case. For a long time the question had to be allowed to rest there, no more probable suggestion or more illuminative evidence being forthcoming.

II.—RELATIONSHIPS OF THE ELEMENTS

Yet many facts irritate us into our determination somehow to reduce the number of our primitive stuffs. Think of the three elements, lithium, sodium, potassium. Almost every property of the one exists in some degree in the other. They are all soft metals which take fire when thrown into water, liberating hydrogen and giving strongly alkaline liquids. Their compounds with other elements differ only in unessential ways. Their atoms are mutually replaceable in crystals. In solution each gives electropositive ions. Their atomic weights form a regular progression with a constant difference of 16: Li = 7, Na = 23, K = 39. In short, they obviously form a family of elements, wherein it is impossible to avoid seeking some common strain or substratum of matter; and we have the right to do this, because the lithium familycharacters extend also to two rare elements, rubidium and cæsium; and because also the other elements group themselves into well-marked families, some of them almost as strongly inter-related as the members of the lithium family are. Only hydrogen seems at present to stand quite solitary, and out of all relationship with the other elements. We have oxygen linked by many similar properties with sulphur, carbon with silicon, phosphorus with arsenic and anti-

RELATED ELEMENTS

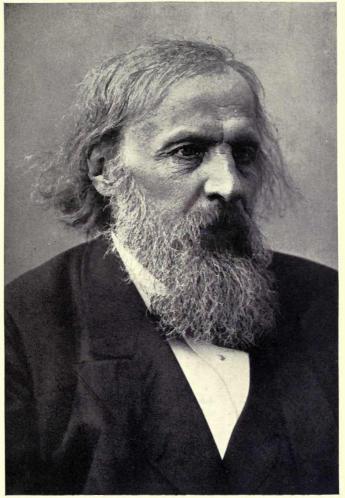
mony, zinc with magnesium: we seek naturally for some cause of these relationships, and find it in the notion that the related elements, if they do not look to a common ancestor, at least have a common material factor running through them.

In 1864 an English chemist, named Newlands, advanced this line of thought by the observation that, when the elements were arranged in the order of their atomic weights, like properties seemed to reappear at intervals of eight. Thus between Li = 7 and Na = 23, there were six elements included; between Na = 23 and K = 39 six also. There seemed to be something in this, but there were too many irregularities, and it was left to the Russian chemist Mendeléeff to establish on a firm basis the Periodic Law which Newlands' "Law of Octaves" had dimly adumbrated. Mendeléeff, boldly leaving gaps and dropping out the elements which refused to adapt themselves to the scheme, produced his periodic table of the elements, which at once groups the elements in their natural families and provides for new elements to be discovered. Additions and alterations of the table have been necessary since the original list was published, as a result, of course, of the additions to the list of elements made since then; but in principle the table shows now, what it showed then, that any particular chemical property seems to ebb and flow as we proceed through the elements in the order of the atomic weights.

Thus, to take one very characteristic chemical property: most of the elements are capable of forming oxides, and these oxides are some of them acid in character, and some basic. Now, as we pass along

THE PERIODIC TABLE

- 1					1			,						-	
	VIII						Fe 56 Ni 58'5 Co 59		Ru 102 Ro 103 Pd 106'5				Os 191 Ir 193 Pt 195		
	VII	7 of 1	Strong Acids to Very Weak Bases:	1	F 19	Cl 35·5	Mn 55	Br 80		I 127	1	1		1	-
	VI	6 or 2	Strong Acids to Weak Bases:		91 0	S 32	Cr 52	Se 79	Мо 96	Te 127.5	-	1	W 184	1	U 238
	Λ	5 or 3	Strong Acids to Weak Bases:		N 14	P 31	V 51	As 75	Nb 94	Sb 120	1	1	Ta 182	Bi 208	1
	ΛI	4	Weak Acids to Basic:		C 12	Si 28	Ti 48	Ge 72	Zr 91	Sn 119	Ce 140	1		Pb 207	Th 232
	ш	3	Basic:	1	Виг	Al 27	Sc 44	Ga 70	68 X	In 115	La 139	1	ï	Tl 204	-
	п	2	Strongly Basic:		Be 9	Mg 24	Ca 40	Zn 65	Sr 87	Cd 112	Ba 137	1	1	Hg 200	7 Ra 226
	I	I	Strongly Basic:	Н 1	Li 7	Na 23	K 39	Cu 63.5	Rb 85	Ag 108	Cs 133	1	1	Au 197	l
	0	0	Unknown	1	He 4	Ne 20	A 40		Kr 83		Xe 131	1	(4) (4)	1	1
	GROUP	Valency.	Oxides .	Series 1	" 2	,, 3	4 "	" 5	9 "	" 7	8 "	6 "	" 10	,, II	" 12



DMITRI IVANOVITCH MENDILÉEFF



THE PERIODIC LAW

the various rows or series from the elements of Group I. to those of Group VII., we find the oxides at first strongly basic and not at all acid; the basic character gradually weakens and the acid character increases, until at last the acidity is the dominant property of the element's most stable oxide. This happens in each series. To emphasise the point still further, let us suppose that we start with Li = 7, whose oxide is a very active base. Adding 5 units, we arrive at C = 12, whose oxide is a weak acid and not in the least basic. But an addition of 16 units brings us to Na = 23, wherein the characteristics of lithium reappear; and a further addition of 5 carries us to Si = 28, where we find a repetition of many of the salient habits of carbon and a weakly acid oxide. A close examination of other properties than these purely chemical ones bears out the broad truth of the table, that the properties of the elements vary periodically with their atomic weight; the addition of about (but not exactly, or regularly) 16 units seems somehow to cause a recurrence of the same properties in the atoms of a new element. It should, however, be clearly observed that these properties do not return in the same degree. There is a very distinct tendency for the heavier elements in each group to be more metallic in themselves, and in their oxides more strongly basic, than their lighter relatives. This process is well marked in Group V. The oxides of nitrogen are strongly acidic, but this feature is far weaker in the oxides of antimony and bismuth. The latter element, indeed, is quite a metal, and its oxide is quite a distinct base in its action towards the stronger acids.

A most important property of the atoms, and one

very difficult to explain, is their valency or combining power. All the elements in Group I. are monovalent, their atoms having the same combining power as the atom of hydrogen; those in Group II. are divalent, and each atom can occupy the place, chemically speaking, of two hydrogen atoms; those of Group III. are trivalent; those of Group IV. tetravalent; and thus we observe a regular increase in the valency of the atoms as we pass across the series. But the elements of the fifth, sixth, and seventh groups show an alternative valency, and the property is by no means so definite as in the earlier groups. Nevertheless, the elements of Group V. are either trivalent or pentavalent; those of Group VI. generally divalent or hexavalent; and those of Group VII. generally monovalent or heptavalent, the change being gradual and continuous in either case. Any explanation of the formation of the elements must take into account these very striking changes.

The periodic table is interesting especially because it sets the problem of the relation between the elements in a more definite light. But there are several difficulties about accepting it exactly as it stands. There are the nine elements which form the eighth group and about which no satisfactory explanation can be given. The inert gases of the air, again, have had to have a new "zero" group provided for them; and, still further, there is a group of several known elements related to cerium, rare but quite well defined, for which no suitable place seems to be available. The necessary gaps, too, are numerous. Several of these have, however, been filled since Mendeléef's time: but the awkward lacunæ in the first series remain. Hydrogen

VALUE OF THE PERIODIC TABLE

is still alone, and its companions are only known in hypothesis. With all these limitations, nevertheless, the periodic scheme does suggest some plan of evolution among the elements, and gives us more than a hint for the reduction of the eighty to a few more truly fundamental elements.

III.—Evidences of Decomposition of the Elements

By a careful analysis of the light of the stars it is possible to obtain reliable evidence, both of their physical condition and of their chemical constitution. The industry of a number of astronomers has resulted in the accumulation of a great body of valuable facts of this kind; and from them Sir Norman Lockyer has suggested a classification of the stars, upon which we may found a general idea of inorganic evolution. In the sun a large number of our terrestrial elements have been with certainty identified, so that even at the high temperature there existent those elements retain their individuality unimpaired. Some of the stars, such as Arcturus and Betelgeuse, reveal a similar condition of things; but, though the sun's temperature does not fall short of 15,000° F., it is, as celestial temperatures go, a cold star. Examination of the light of the bluer stars, such as Vega or Sirius, shows unmistakably that they are hotter, probably very much hotter, than the sun; and at the same time the number of the terrestrial elements present is very much reduced. Between stars of the solar type and stars of the Sirius type lie many other examples showing the stages of transition which indicate the development of the one kind from the cooling and condensation of the other; and accompanying this develop-

ment we find a gradual increase in the number of recognisable elements. Thus we may reasonably suppose that, at the very high temperature of Sirius, substances which are elements on the cooler sun are decomposed into simpler substances, just as we are able in laboratory experiments to decompose many compounds into simpler compounds or into elements. As water cannot exist as such above a certain temperature, but must needs resolve itself into its constituent elements, so silicon, which is not decomposed on the sun, cannot resist the terrific temperature of Sirius.

Proceeding still farther back, to the nebulæ, from which, in all probability, stars or suns are to be evolved, we approach more nearly the aboriginal state of matter. The light of these bodies teaches us conclusively that they are gaseous, often of exceeding tenuity; and not necessarily at a high temperature. In those which show no condensation, only three elements are to be recognised-hydrogen and two others which are unknown to terrestrial chemistry; at a later stage helium seems to make its appearance. In this primitive condition of matter, therefore, we have the elements reduced to four only; the process of stellar formation and development is accompanied by the appearance of new elements as condensation, or cooling, or both, goes on. The four simple elements of the nebulæ give rise to a few more, such as calcium, magnesium, iron, and sodium, in the hotter stars, the others being formed as the condensation and cooling of the stars proceed.

What are the four elements of the nebulæ? The universal presence of hydrogen in the nebulæ and the

CHEMISTRY OF THE STARS

stars, in enormous quantities, marks it out as one of earliest forms, even if it be not an absolutely original form, of the primitive world-stuff. Helium we know as a rare gas on the earth and as the head of the indifferent or "zero" group of elements in the periodic table. We can only guess at the other two, and imagine them to be two of the missing elements of the first series and the parents of the elements in the two groups which they head. We do not pursue this point at present, but content ourselves with repeating the statement that the stars do give us the evidence we desire, of a simplification of the elements under the stress of a very high temperature, and at the same time doubtless of greatly modified electrical conditions.

IV.—FORMATION OF ELECTRONS

The intimate association of electricity with matter makes it impossible entirely to separate the two, and certain experiments upon the behaviour of gases under electrical stress have opened up a new line of insight into the nature of matter. When an insulated metal body is electrified in the open air, it is well known that the electrification tends to "leak" slowly away until the body is discharged. This is usually a process of some duration, but it can be considerably hastened by directing towards the electrified body the X-rays, or the radiation of the radio-active substances described below. What the radiation seems to do is to convert some of the atoms of the air into ions, either positive or negative; and these gaseous ions seem to give up their charges to the electrified body, which therefore becomes ultimately neutral, i.e. is discharged.

Now, how do the atoms become ions? We are here asking for the actual nature of the electric charge, positive or negative, which attaches itself to the atom; the question ultimately involves the fundamental structure of electricity itself. Now, let us suppose that electricity is, like matter, atomic in its nature, composed of indivisible particles or units—we will call them electrons, positive or negative. The attachment of these electrons, one or more, to an atom would ionise it, and thus confer upon it electrical properties. But the source of the necessary electrons is still a difficulty, which we may most easily solve by supposing them to be within the atom itself. In this view, the atoms must be considered to contain both positive and negative electrons which will ordinarily counteract one another, leaving the atom electrically neutral. But if by some agency, say the X-rays, a negative electron could be detached from an atom, the atom would clearly be positively ionised, and the said negative electron might attach itself to another atom and ionise that negatively. If this be a correct picture of the process of ionisation, its consequences are far-reaching indeed. The atoms, not of one element only, but of all, would be shown to be themselves of complex constitution. We must therefore indicate the nature of the evidence which shows that the atoms contain the electrons within themselves—contain possibly nothing else but electrons.

When an electric discharge passes through a gas at very low pressures, enFig. 43.—Discharge in a vacuum tube: a, anode: c, cathode:

d. dark space round c; s, flickering strize.

ELECTRONS

vacuum tube, exceptional phenomena present themselves, especially around the cathode or negative pole of the tube (Fig. 43). The appearances can be well accounted for on the supposition that from the cathode there is, during the discharge, a rush of negatively electrified particles, travelling in straight lines at very high velocity. These "cathode rays" can pass through thin sheets of metal, but are stopped by thicker pieces; they cause the walls of the tube to glow with a characteristic phosphorescent light; and they can be bent out of their straight-line course by a powerful magnet, just as we should expect a stream of negatively electrified particles to be. They were at first thought to be merely electrified atoms; but their great penetrative power, and the fact that the nature of the original gas in the tube, or of the metal which made the cathode, caused no essential difference to the rays, led Sir William Crookes to make the pregnant suggestion that they were the particles or corpuscles of a fourth state of matter, an ultra-gaseous, ethereal state which he called radiant matter. The particles of radiant matter are now regarded as electrons, detached from the atoms under the influence of the great electric stress set up in the vacuum tube. Here, then, we appear to have definite evidence of the rupture of the atoms, with these negative electrons as the most readily recognisable products.

An electron is a particle of electricity, and not of matter; but Sir J. J. Thomson has shown that an electric charge in rapid motion would possess the property which we regard as the test-property of matter, viz. inertia. And even more: he has experi-

mentally determined that the mass of an electron (which measures its inertia) is something like $_{1700}$ th of the mass of a hydrogen-atom. He has thus bridged the difficulty of our supposing the material atoms to be ultimately resolvable into electrons, and matter itself to be reducible to electricity in motion. The theory harmonises many otherwise inexplainable facts, and is at present contradicted by none. There are many difficulties in its way, of course; but it does enable us to see, if only in a fitful glimpse, something of the design of the material atoms.

There must be two kinds of electrons, positive and negative; but we have a direct knowledge only of the negative ones. What is known of the positive electrons seems to suggest that they are larger than the negative, and that their mass is comparable with that of the hydrogen-atoms. Either the positive electron is different in its nature from the negative, or it has not been detached from its material basis. Without making any hypothesis on that point, we may follow Sir J. J. Thomson's model atoms, at least with interest.

He has considered the case of a sphere of uniform positive electrification, and studied the possible arrangements of varying numbers of the negative electrons in this sphere. Thus, if there were six negative electrons, they would arrange themselves with one at the centre of the sphere and the other five in a ring whose radius would depend upon their rate of rotation. This is the only stable arrangement of six, and an atom containing only six electrons would necessarily have them arranged so. With larger numbers the problem becomes too difficult unless they are confined to one

ELECTRONS IN THE ATOMS

plane; under this limitation the stable arrangement of, say, 50 electrons would be in five rings containing respectively 1, 5, 11, 15, and 18 electrons. Such an arrangement, though stable, does not preclude the addition of another electron, inasmuch as the five rings, 1, 6, 11, 15, 18, also form a stable arrangement. Two such atoms as these arrangements represent might well belong to elements of the same series, differing only by a unit of valency; but the matter is hardly so simple, inasmuch as in the first place a single electron does not add enough to the atomic weight to make the jump from one element to its neighbour in the periodic series, and in the second place the arrangement is probably not in one plane entirely. But the comparison of an atom with the solar system, in which the sun represents the positive centre of attraction and the planets and their moons correspond to the negative electrons, gives a fair idea of what physicists now conceive the atom to be. This comparison, suggested by Sir Oliver Lodge, is based upon the limits of size and mass that must be assigned to the electrons and the atoms respectively; if, therefore, the electronic theory of the atom be true, by far the greatest part of the space occupied by the atom will be empty, as much so at least as the space from the sun out to Neptune, its most distant attendant: it contains only the unmaterial and all-pervading ether which is the assumed medium whereby light-waves are conveyed.

Atoms thus constituted might differ from one another in very many ways—in the number of the electrons, in their rates of rotation, in their varying arrangements. Thus the eighty different kinds of elementary atoms can be conceptually accounted for;

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and, since there appears to be no frictional resistance between the ether and the electrons, there is no reason why these atoms, if left to themselves, should not be permanent and eternal.

But is it possible that this condition should everlastingly prevail? We know that the atoms are certainly subject to very rapid motion and to continual vibration: the first accounts for their heat, and the latter for the light-waves in the ether by which matter becomes visible.

In the first case, is it not likely that an atom, brought near enough to a neighbouring atom, might so disturb the equilibrium as to detach an electron or a group of electrons, and thus reduce the original atom to a simpler one? Or, two different atoms might be brought so close to each other that they form a system in mutual revolution about one another, and thus give us a molecule of a binary compound, just as we often find two stellar systems "combined" in the heavens into double stars. Or, again, just as a comet or a meteorite may be drawn into or escape from our solar system, so a negative electron might be drawn into or escape from an atom, and thus transform it into a negative or positive ion, as we see happen in the electrolysis of liquids and the ionisation of gases. Or, still again, some atoms, like those of helium or argon, may be conceived to be quite neutral, the total effect of their electric units externally being null, and showing itself in the absence of all chemical affinity from those elements, whereas other atoms might have the influence of the positive electrons predominating, so that they are as a whole electro-positive like those of lithium or sodium; and still others might have the

BREAK-UP OF THE ATOM

negative influence in excess, and thus be electronegative like those of oxygen or chlorine.

The difficult problem of valency seems capable of interpretation in terms of the possibilities of this theory. For, if we suppose an atom, completely neutral and of no valency, to have added to it one small atom with a positive residue, it might become thereby monovalent; and if two such atoms came into its system a divalent element would result; and so on. But while the positive affinity would thus be doubled, it would not necessarily be doubled in its external manifestation, inasmuch as a new balancing of the electric forces would certainly come about; and thus the divalent atom of magnesium is not in the result so strongly electro-positive as the monovalent atom of sodium, from which it is only separated by one unit of atomic weight; and the tetravalent atom of silicon is actually electro-negative. Of course, the negative valency of atoms like those of oxygen or chlorine might also be explained by the similar process of incorporation applied to negative atoms.

V.—RADIO-ACTIVITY

The development of this new atomic theory, in which we only postulate the positive and negative electrons, has been very largely stimulated by the discovery of the strange element, radium, and its still stranger properties. Following up the clue afforded by the cathode-rays, Röntgen was led to his discovery of the X-rays; his revelation of these mysterious and highly penetrating rays led to further search for similar rays, and soon Becquerel announced his discovery of the ray-giving property in the salts of the

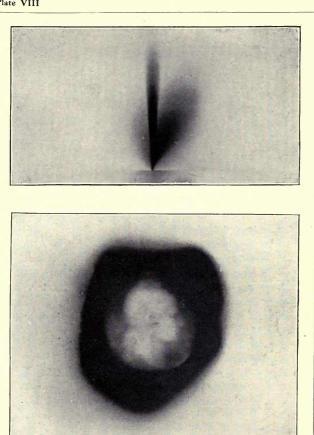
element uranium. These rays, even through a thin sheet of metal, affected a photographic plate, and slowly discharged an electrified body by ionising the air. Minute though this action was, it was nevertheless sufficient to show certain irregularities, which led Madame Curie to investigate the uranium minerals closely; and, as the result of a very patient and laborious series of separations, she succeeded in isolating the compounds of a new element, radium, in which the properties of the uranium rays were enhanced a million times.

The radium occurs in company with the uranium in a number of rare minerals; but in so small a quantity that some 200 tons of the richest of them (pitchblende) were required to yield 300 grains of radium bromide, and the value of this is something like £300 per grain. It is therefore clear that experiments with radium can be made with only very small quantities of the substance. In spite of this, Madame Curie has examined several of its compounds, recognised it as a divalent element of the second group, found its atomic weight, and recently isolated the metal itself. In addition, its radiations have been thoroughly examined, and applied to therapeutic uses; we have a theory of its atomic structure, and its behaviour has modified our vista of geologic time. A slight and unsuspicious phenomenon has thus fired a train of theoretical and practical consequences, great enough to undermine the very foundations of the science of matter.

Radio-activity, as this phenomenon is called, means the discharge by the active substance of rays, either in the form of projected particles or in the form of waves in the ether. The X-rays are of the

1

2



By kind permission of Prof. Fean Becquerel

RADIO PHOTOGRAPHS

- 1. Deviable and Non-Deviable Rays of Radium [cf. Fig. 44].
- 2. Radiograph of Aluminium Medal produced by Rays of Uranium.

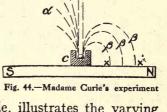


THE RAYS FROM RADIUM

latter type, the cathode rays of the former. The rays from radium, however, belong to both kinds, and afford us some very strong circumstantial proof of the spontaneous transformation of its atoms.

Three kinds of rays have been recognised and thoroughly examined by Rutherford and others; they are differentiated experimentally by their penetrative powers, and by their different attitudes towards magnetic forces. The a-rays are stopped by a very thin sheet of aluminium, and behave like positively electrified particles, of a mass something like that of the hydrogen atom, and moving with a speed which is about one-twelfth that of light. The β -rays are able to penetrate 100 times the thickness of aluminium; they behave towards a magnet exactly like the cathode rays, i.e. as negative electrons moving with a velocity of the same order as that of light. Finally, the y-rays are still more penetrating, are not affected by a magnet, and behave generally like X-rays. The lower photograph in Plate 8 shows the nature of the photo-graphic effect produced. The whole radiation keeps the radium salt itself phosphorescent, and produces

phosphorescence in many other substances besides: each kind of ray ionises the air, and affects the compounds on a photographic plate, just as light does. The accompanying figure S (Fig. 44), based upon an Fig. 44.-Madame Curie's experiment experiment by Madame Curie, illustrates the varying



extent of the magnetic action on the different rays. The projection of these particles with such high

velocities is eloquent of a great liberation of energy during the process of radio-activity; and careful measurement has shown that radium salts produce also enough heat by their activity to melt more than their own weight of ice in one hour. This makes the atomic disruptions which are the beginning of the activity far more violent than the molecular collapse which accompanies the explosion of nitro-glycerine, and bewilders us when we attempt to contemplate the enormous stores of energy that are locked up in the atoms of matter. The heat given out by a quantity of radium in one hour would be sufficient, if converted into mechanical work, to lift it more than twenty miles against the action of gravitation.

As if the evidence of degradation afforded by the α - and β -rays were not sufficient, it has also been proved that radium compounds give rise to a small quantity of a true gas. Very small quantities of this radium emanation, as it is called, have been obtained; but modern methods have made it possible to work in certain directions upon very small quantities of gases, and radium emanation has been subjected to a rigorous chemical examination, which shows it to be a completely inert substance, as loath to enter into any chemical combination as helium or argon. It is in all probability, therefore, a gas of the same family as these. But the interesting fact about this emanation is its radio-activity and its rapid change. No change of temperature that has yet been applied seems to modify in any degree the rate of radio-activity, either in radium or its emanation; the whole process is plainly an inherent act of the atoms. But the emanation is found to have lost half its activity in 3.7 days, and to have

RADIO-ACTIVITY

given rise during that time to an easily recognisable quantity of helium. Meanwhile the walls of the tube containing the emanation have themselves become highly radio-active, and this induced activity itself decays irregularly to half its value in about half an hour, after having produced a-, β -, and γ -rays. Further experiments by various scientists have revealed the identity of the α -particles with atoms of helium containing enough positive electricity to neutralise two electrons. We thus obtain:—

Radium produces Radium $\{ + \text{Helium} \}$ $\{ + \text{Electrons} \}$ Radium $\{ + \text{Helium} \}$ $\{ + \text{Helium} \}$ $\{ + \text{Helium} \}$ Radium $\{ + \text{Helium} \}$ Radium $\{ + \text{Helium} \}$ $\{ + \text{Helium} \}$ Radium $\{ + \text{Helium} \}$ $\{ + \text{Heli$

The substance here called Radium A has been shown to decay and form new radio-active substances down to Radium F, this latter being apparently identical with an element polonium, likewise discovered by Madame Curie. Thus the original radium, by the elimination of atoms of helium, has produced a series of new elements. Some of these have had only a few minutes of existence; others last for years, but ultimately decay, leaving at the end a totally inactive product.

Radium itself differs from its products chiefly in its life-duration, which goes into some thousands of years. It loses half its activity in 1760 years. But there is very strong reason for regarding it as itself a product at three removes of the disintegration of uranium, and so its presence in uranium-minerals is explained. This element, whose atom is the heaviest known, is radio-active in a slight degree; it produces an element. Uranium X, which decays with fair rapidity into a

new element, ionium, that has been separated in independent quantities, and is supposed to be the immediate parent of radium itself. We have thus the following series of radio-active elements formed successively from uranium by the loss of α -rays, which consist of atoms of helium of atomic weight 4, and of β - and γ -rays, whose weight we may ignore.

THE URANIUM SERIES

Name of Element	Rays Given Off (a-rays = He)	Atomic Weight [He = 4]	Half-life Period*
Uranium Uranium X Ionium Radium Radium Emanation (Niton) Radium A to Radium F (= Polonium) (in five stages) Polonium Final Inactive Element (=Lead?)	α, β, γ, α α, β, γ α α	238·5 [230·5] [230·5] 226·5 [222·5] [218·5]	About 10° years About 20 days About 1,500 years About 1,760 years About 4 days About 17 years (in unequal stages) About 140 days

^{*} This means the time taken for the radio-activity of the substance to diminish to half its value. It is independent of the amount taken, and must not be read to mean half the life of the element.

The final product of the radio-active changes in uranium is an inactive element, supposed, for two reasons, to be lead. Small quantities of lead are found in all uranium minerals, although lead ores do not occur in the same strata; and the atomic weight obtained by subtracting eight atoms of helium from the atom of uranium is very close to that of lead (206.9).

If this be the case, we have Nature slowly trans-

TRANSMUTATION OF URANIUM

forming the atoms of uranium, by a process lasting millions of years, into atoms of lead—a spontaneous, self-originated process unconditioned and unmodified by external circumstances. Evidently the uranium atom is over-bulky and unstable. Of the other elements on the periodic table, thorium (232·5) appears to go through a similar series of radio-active changes; that, too, is an element of high atomic weight, and so unstable. But in a small degree the property belongs to several other elements: notably potassium (39) emits β -rays with considerable freedom. Further, there is good presumptive evidence that certain compounds of copper give rise to lithium when subjected to the action of radium emanation.

It is possible to measure the rate at which a given radio-active substance produces helium by a direct measurement. Now helium is not, of course, radioactive; hence, if a natural mineral is active, the helium it produces will gradually accumulate in it. Knowing the rate at which a mineral is producing helium now, and knowing also how much helium it contains, we can arrive at a reasonable estimate of its age. In this way Strutt has examined the mineral thorianite, and finds from the helium enclosed in it that its age cannot be less than 250 million years. Lord Kelvin, from considerations derived from the earth's loss of heat, would only grant it 100 million years of past history. It is easy to see how radium has vitiated his calculations, which could not be assailed by any physical facts then at his disposal. For the radium also produces heat in such quantity that, if we had about 120 lb. of it distributed evenly through a solid crust fifty miles thick all round the

earth, it would be sufficient to compensate the earth for its loss of heat by the processes of cooling. Thus the unexpected discovery of this strange substance has compelled us to lengthen the earth's past life to an unknown but certainly very great extent.

All the transformations that we have mentioned. supposing them to be verified by further research, are in the nature of devolution from the larger atoms to smaller and simpler ones. Nothing suggestive of the opposite process has yet been observed; but this is hardly remarkable when we reflect upon the immense concentration of energy in the atoms. The architecture of an atom like that of radium is not merely a matter of bringing a few simpler atoms together; it involves also the communication to them of a high velocity comparable with that of light. Still, it is a pleasing symptom of the rapid progress of true science that we are able to picture in any way the atoms of the elements, still more that our conceptions are prolific of new lines of thought and research, as well as illuminative of present facts.

VI.—Evolution of the Atoms

The simplification of the larger atoms may now be regarded as an established fact. Beyond this, the scientific imagination has liberty to probe tentatively, using our known laws as our weapons. How many fundamental kinds of matter are there? Arguing from the periodic table, we might be inclined to say eight; but the hottest stars suggest four at most; and the bold theory that the electrons are the ultimate units of the atoms seems to require two. In the latter case we are dealing, not with matter as we

EVOLUTION OF THE ATOMS

understand the term, but with electricity; and we have still the electrons to inquire about.

What are these? The attempt is made by Lodge and others to reduce these to strains or twists in the ether—the something which permeates all matter and fills the relatively large spaces within the atoms themselves. This ether has properties most difficult to conceive: great elasticity, high density, perfect fluidity, offering no friction to the movement of atoms in it, yet able to be distorted—caught up into twists, or vortices which are the electrons, or the beginnings thereof. Thus, on this bold theory, matter is reduced to electricity, and electricity to ether. This ether is thus the progenitor of all material things; and, though not easy to comprehend, it is still far from the evanescent quintessence of the Greeks; its existence is as sure as any intellectual conception can be, and scientists have been driven to define its properties from phenomena of light and electricity which are incontrovertible.

Leaving this alluring speculation as something for the future to elucidate further, it is possible and fair to conceive the existence of three entities at a very early period in the history of the universe—viz. the ether, and the positive and negative electrons possibly formed out of it. We will denote these E and E. By condensation of these together in varying numbers, we arrive at the systems of electrons which we call atoms. Among the earliest of the known atoms to appear were doubtless those of hydrogen and helium, with possibly other atoms now no longer known in the free condition, except perhaps in the hotter stars. The simpler atoms, with more of E and E, produced

the more complex by still further condensation. These atoms, by virtue of their valency, can unite to form the compounds which make up the many aspects of matter that we have met in our previous chapters. All these changes and rearrangements involve also the transformation of energy, often in vast quantities.

The source of this energy, like the source of the ether itself, is of course beyond the ken of science entirely. It is unprofitable for science to venture upon this ground; but in attempting to picture the processes by which the universe has become what it is—in seeking to read the past in the light of the present—we are not only using our intellects and knowledge wisely, but forging helpful weapons for the advancement of the powers of both. As soon, however, as our speculations are found to be inharmonious with a single well-attested fact, they must, and will, be abandoned.

VII.—REAL WEIGHT OF THE ATOMS

Twenty years ago it was open to a chemist to deny the real existence of his atoms, and to regard them merely as convenient mental conceptions for the units involved in chemical actions. The atom of hydrogen was the smallest quantity of hydrogen known to enter into any chemical combination; it need not be the smallest conceivable piece of hydrogen. Such a chemist might, indeed, have denied the necessity of assuming the existence of such an atom. But it is difficult to take that attitude now. Radioactivity has made the atom again a reality to us. Several lines of thought also converge towards a fairly consistent value for the actual weight and size

WEIGHT OF THE ATOMS

of the atoms. Some of the arguments depend upon electrical or other physical questions which we cannot discuss here; but, results obtained from electrical considerations, from the thickness of soap films and from the optical theory of the blue sky, are of the same order of magnitude as the following result given by Professor Rutherford.

We have said that there is very good ground for the belief that the a-particles given off by radioactive elements are atoms of helium, positively ionised. Now it is possible to count the rate at which these a-particles are being given off by a weighed piece of radium salt. Sir William Crookes has found that a screen covered with sulphide of zinc becomes phosphorescent when the a-rays strike it; each a-particle produces a distinct momentary scintillation. By means of a microscope a very small area of such a screen may be examined and the number of bombardments in a given time counted. Assuming that the rays are discharged evenly in all directions, we may thence calculate how many are emitted per second. The counting may also be directly done by permitting the a-rays to enter through a very small hole in a sheet of lead into an electrometer which will indicate a very delicate electrical charge. A helium ion, falling upon the needle of such an instrument, indicates its presence by a deflection of the needle; and the number of such deflections in a given time reveals the number of charged atoms that have entered the hole.

From these two methods of counting it is estimated that one gram of radium discharges about 14 × 10¹⁰ or 140 thousand million atoms of helium in one second. But other experiments show that one

gram of radium produces 5 × 10-9, or one two-hundredth-millionth part of a cubic centimetre of helium in one second. Hence one cubic centimetre (about 16th of a cubic inch) of helium contains (14 × 1010) ÷ $(5 \times 10^{-9}) = 2.8 \times 10^{19}$ atoms, i.e. about 30 million million millions! But this quantity of helium weighs 1.8 × 10⁻⁴ grams. Hence 2.8 × 10¹⁹ atoms of helium weigh 1.8 × 10-4 grams, and each atom weighs 1.8 × 104 $\frac{1.0 \times 10^{-7}}{2.8 \times 10^{-9}}$ = about 7 × 10⁻²⁴ grams; or, reduced to English weights, each atom weighs something like 1 × 10-24 OZ.

Of course, a number so small is quite meaningless to our senses; but it serves to convey, however vaguely, to our minds some notion of the real atomic weight of helium; and it is extremely interesting because a number of a similar order of smallness is derived from other and quite different methods of working.

In these experiments, it will be observed, we have really been counting ions of helium, not the true atoms; where it is merely a matter of number, however, this does not affect the result. It is the fact that the helium atom is ionised that enables us to detect it. An ion differs from the atom in the presence of an electric charge of some kind; and this charge confers upon it new properties. Thus an ionised atom or molecule causes the condensation of a droplet of water from an air that is saturated with water vapour. Each α - or β -particle that moves through such an air ionises one molecule, and this is rendered visible by the drop of condensed water. The number of drops gives us the number of ions. A few ions can therefore

IONS AND ATOMS

be rendered visible; but the smallest quantity of unelectrified gas that can be examined would contain at least a million million atoms. This can easily be worked out by finding the number of atoms in the smallest workable quantity of gas; neon can be recognised in the air by suitable means when there is only one half-millionth of a cubic centimetre of it. It is the ionisation of the atoms, then, that enables us to get so near seeing them individually.

Recalling the comparison of an atom to a solar system, we may liken an α - or β -particle to a comet which bursts into the system. If it is retained, clearly the atom would be ionised. But in most cases it would not be retained; in that case it might go through the system, i.e. the atom, without injuring it, as most comets do with us; or, alternatively, it might draw one of the external members of the system out of the range of the central attraction, and this, by disturbing the electrical equilibrium, would again ionise the atom. It is an interesting thought that the atoms of matter can be thus penetrated, and that even the densest solids are mainly composed of holes. The number of electrons in an atom is approximately known from electrical experiments of Sir J. J. Thomson, which show that the β -particles (electrons) have a mass about Trooth that of a hydrogen atom.

Inconceivably small as the atoms are, the excessive delicacy of radio-active methods enables chemists to detect the presence of even a few in minerals which contain radio-active substances. The presence of a hundred atoms of radium in a gram of pitchblende could be detected. No other method of detecting substances can vie with this in its wonderful delicacy.

VIII .- ETHER, ELECTRONS, AND ATOMS

On the most recent hypotheses we have reduced our atoms or material units down to electrons or units of electricity moving in an infinite ocean of ether. This ether is a pure creation of the scientific imagination, made necessary by the facts of light and electricity; and, incidentally, we may remark that it is an essentially English conception, a long list of distinguished Englishmen, from Newton to J. J. Thomson and Lodge, having been chiefly occupied with its properties.

Now, concerning this ether, it is necessary to postulate many remarkable properties. It is similar to an incompressible perfect fluid, able to rotate and to vibrate, but not to move. It permeates all matter. and allows matter to move through it without friction or drag of any kind. It carries electric waves, and can thus become the vehicle of energy. Sir Oliver Lodge calculated that it has a density 1012, or a million million times that of water; this high density is due possibly to the enormous pressures it has to sustain; and perhaps it would only have the density of an excessively rarefied gas, which Mendeléeff supposes it to be, under such pressures as ordinarily prevail with us. Its strength must be enormous in order to sustain the gravitation of suns and planets. For instance, the force between the earth and the sun is something like 4 × 1018, or 4 trillion tons weight. How can the ether be a fluid, and yet sustain such a stress as this? Its rigidity must be incomparably greater than that of steel. This can only be conceived by supposing that the minute parts of the ether are in rotation; only

ETHER

thus can a fluid simulate the characters of a solid. If this is so, the ether must have a boundless store of e. gy locked up in it; and Sir Oliver Lodge has expressed this in a striking comparison in the statement that one cubic millimetre of free ether contains enough energy to run "a million horse-power station, working continuously, for forty million years."

Portions of the ether can be caught up and individualised somehow as centres of electric force: these are the electrons, made of ether, yet different from it and able to move freely through it. No figure can yet be given to represent the manufacture of an electron, or to suggest its nature. Nor are there any phenomena which suggest the destruction of an electron; and possibly the electrons are discrete and different entities from the ether. How they may form the more complex atoms of matter we have already seen. As compared with the whole volume of ether enclosed, even by a dense solid substance like platinum, the space filled by electrons is extremely small, something akin to that occupied by gossamer floating in the air. This must be the case, because even a piece of platinum is enormously less dense as a whole than the ether of which its component electrons and atoms are supposed to be made.

These alluring and beautiful speculations, the reader will no doubt have noticed, have in one sense inverted the method and the results of our first chapter. There we started with five elements which were purely theoretical and metaphysical; and we proceeded to urge upon the student of chemistry the necessity of fixing his mind upon the actual, material elements; from metaphysics we drew him on to

R

reality. And, we hope, the story of four of the elements of speculation has shown him the value of this method of study. But here we draw him back to the mists: matter vanishes, and we have only a most extraordinary ether, animated by an equally mysterious energy, wherewith to construct the universe. There is, nevertheless, a difference. In contemplating the vast reaches of the Unknown, we do not leave entirely that territory which is surely our own. The verge is clear, on which we stand; the Science which is content with that is assuredly perishing; but the Science which leaves that is no longer Science. The method of inquiry, of patient questioning of Nature as she is-the inductive process by which theories are the servants of the observed facts-has made Chemistry what it is: a weapon with which man has harvested a notable crop of invaluable practical achievements, and a star which throws a ray into the philosophic deeps wherein lies intricately hidden the ultimate rationale of Nature.

APPENDIX

LIST OF ELEMENTS, SYMBOLS, AND ATOMIC WEIGHTS

Element	Symbol	Atomic Weight	Valency
Non-metals			
Argon	ABBTCCIFHEHHIKNOPPSGISTE	39'9 11 79'96 12'00 35'45 19 4 1'008 126'85 81'8 20 14 16 31'0 79'2 28'4 32'06 127'6 128	Tri Mono Tetra Mono Mono Mono Mono Totra Mono Mono Tri and penta Di Tri and penta Di Tri and hexa Tetra Di and hexa Di and hexa
METALLOIDS (imperfect metals) Antimony Arsenic	Sb As	120 .75	Tri and penta Tri and penta
METALS			
Aluminium Barium Bismuth Cadmium Caesium Calcium Cerium Chromium Cobalt Columbium (Niobium) Copper Erbium Gallium	Al Ba Bi Cd Cs Ca Ce Cr Co Cb Cu Er	27·1 137·4 208·5 112·4 132·9 40·1 140·25 52·1 59·0 94·0 63·6 166 70	Tri Di Di Tri and penta Di Mono Di Tri and tetra Tri Di and tri Penta Mono and di Di and tri Tri

APPENDIX

Blement			Symbol	Atomic Weight	Valency
METALS					
Germanium			Ge	72.5	Tetra
Glucinum (Beryllium)			GI	9·I	Di
Gold			Au	197.2	Mono and tri
Indium			In	114	Tri
Iridium			Ir	193	Di and tri
Iron	·		Fe	56	Di and tri
Lanthanum .			La	138.9	Tri
Lead	Ĭ		Ph	206.0	Di and tetra
Lithium			Li	7.03	Mono
Magnesium			Mg	24.36	Di
Manganese	•		Mn	55	Di and tri
Mercury	•		Hg	200	Mono and di
Molybdenum .			Mo	96.0	Tri and penta
Neodymium .	•		Nd	144.3	Penta
Nickel	•	-	Ni	58.7	Di
Osmium	•	٠	Os	20.7	Di and tri
Palladium	•	•	Pd	106.2	Di and tetra
Platinum	•	•	Pt	194.8	Di and tetra
Potassium	• *	•	K		Mono
	•	•	Pr	39.12	Penta
Praseodymium .	•	•	Rd	140.5	Di
Radium	•	•	Rh	225	Di and tri
Rhodium	•	٠	Rb	103	Mono
Rubidium	•	•	Ru	85.4	Di and tri
Ruthenium	•	*	Sm	101.7	
Samarium	•			150	Tri Tri
Scandium	•	•	Sc	44·I	
Silver	•	•	Ag	107.93	Mono
Sodium	•	•	Na	23.05	Mono
Strontium	•	•	Sr	87.6	Di
Tantalum	•		Ta	183	Penta
Terbium	•	•	Tb	160	Tri
Thallium	•	٠	Tl	204.1	Mono and tri
Thorium	•	•	Th	232.5	Tetra
Tin			Sn	110.0	Di and tetra
Titanium			Ti	48.1	Tri and tetra
Tungsten			W	184	Tetra and hexa
Uranium			U	238.5	Tetra and hexa
Vanadium			V	51.2	Tri and penta
Ytterbium			Yb	173	Tri
Yttrium			Yt	89	Tri
Zinc			Zn	65.4	Di
Zirconium			Zr	90.6	Tetra

Other elements less definitely known and occurring in small quantities only are: Europium (Eu=152), Gadolinium (Gd=157), Dysprosium (D=162'5), Thulium (Tu=168'5), Luteclum (Lu=174), and the elements of the Uranium series (See p. 248).

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