THE ORIGINS AND THE GROWTH OF CHEMICAL SCIENCE

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"Nature is very consonant and conformable to herself."

NEWTON.

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PREFACE

IF the request is not too exacting, the reader is respectfully asked not to skip this preface. The preface explains the scope of the work; it allows itself a little criticism, which may be introduced with more propriety here than in the book itself; and, further, some typical examples are given of the methods and characteristics of some of the great discoverers.

In the first place, the attempt is made to show that the science of chemistry has advanced not by fits and starts—by a series of unconnected discoveries, as some have supposed—but rather that the progress has been uniform and gradual, each advance being based on what has gone before, and leading to further advances in a perfectly natural and logical sequence.

When Robert Boyle discovered that mercury calx was converted into metallic mercury by heat alone, he recorded the fact; but the state of chemical knowledge had not advanced far enough at the time to enable him to pursue the matter further. Nature meets no one half way. It was for Boyle one of those paradoxes in which he delighted, that a metal by heating gave a calx and by further heating the calx gave back the metal. When, however, the same fact was re-discovered a hundred years later, the science was ready for it. Joseph Black had already established the fixation of a gas (carbon dioxide) in the carbonates; the genius of Lavoisier enabled him to establish the fixation of another gas (oxygen) in the calces.

There was no science of Chemistry before the seventeenth century, but the art of Chemistry had progressed through long ages, and a great many processes and substances, called chemical, were known; many manufactures also, dependent on chemistry, such as metallurgy, glass, pottery, leather, etc., had been established. At the same time there was no explanation or theory of chemical processes which was appropriate to the facts.

The first theory to be established applied, in the first instance, to a comparatively small class of substances, those which were called salts. The followers of Paracelsus experimented a great deal with acids, alkalis and salts. The opinion eventually came to be held, expressed most definitely by Robert Boyle, that an acid and an alkali produce a salt, and that a salt is composed of acid and alkali. This is the important and fundamental theory on which the whole of chemical science is based. It is the first generalisation with regard to the composition of substances which is appropriate to the facts. This is not a new claim put forward here for the first time. It was suggested about a hundred years ago by Whewell in his *History of the Inductive Sciences*. Shortly after the publication of Whewell's work, Kopp's *Geschichte der Chemie* appeared. Kopp's history must always arouse admiration for its great interest and comprehensiveness. But unfortunately Kopp chose to divide the history of chemistry into epochs, five in number, with appropriate titles for each epoch, these titles being derived from the supposed dominant views or tendencies of the science in each epoch. Epochs themselves, and the main tendencies of the science during a particular epoch, become a matter of somewhat arbitrary choice. There is almost necessarily overlapping, and there may be also differences of opinion as to main tendencies. To take an example, the fourth epoch, 1650–1775, is called the epoch of the phlogiston theory. Now the theory of salt formation (Boyle) and the theory of gas fixation (Black) both fall within this period, and neither has anything to do with the theory of phlogiston. Moreover, Boyle had died some years before the theory of phlogiston was promulgated in 1702. It is therefore inconsistent to include Boyle at all in the epoch of phlogiston, a theory of which he never heard. The theory of phlogiston has disappeared, while the theories of salt formation and of gas fixation have remained an essential part of chemical science. The epoch also of phlogiston is dated to begin ten years before the author of the phlogiston theory was born. Phlogiston, after all, differed little from the sulphur of the alchemists; each was the principle of inflammability. Phlogiston only came into prominence for a few years after 1775, as a weapon to attack Lavoisier. Lavoisier hardly took it seriously. It was not so much phlogiston that he overthrew as the age-old doctrine that fire resolves all substances into their elements.

This division of the history of the science into epochs, each with its appropriate or inappropriate label, seems only to obscure the real progress of the science by insisting on what is comparatively unimportant: it thus becomes difficult to discover when the science began and how and why it progressed at all. In no sense can the phlogiston theory be regarded as the dominant feature of the period in question; the very definition of chemistry given by the author of that theory was out of date at the time it was written: the definition begins "chemistry is the art . . .," and chemistry had already become a science.

I propose, in conclusion, to give some account of the way in which some of the great discoverers have been influenced to begin and then led on to complete their work. I choose for this purpose three of the greatest names in the science —Joseph Black, Antoine Lavoisier, and August Kekulé. Sometimes a comparatively trivial cause has led to a great discovery. Joseph Black set out to investigate a quack remedy which was supposed to have cured a Prime Minister of gout. Black ended by discovering the fixation of gas. The gout even of a Prime Minister fades in the brilliance of Black's discovery. It is also a matter for congratulation that there was no one to tell the youthful Black that his business was to investigate gout and not to found a new Chemistry. The time was ripe for Black's discovery, for the composition of salts was known and Black at once realized that the gas in question was acid and that it combined with alkalis to form salts.

Black came upon his discovery almost by accident. It was different with Lavoisier, who realised before he began that by his work on the fixation of gases he would entirely change the whole of chemistry. "This subject" (the fixation of gases), he wrote in 1773, "seems to me of such importance as to entail a revolution in physics and in chemistry" ; and he proceeded in a few years to accomplish this revolution.

August Kekulé was a genius of another kind. He was a dreamer. "Let us learn to dream," he said on the occasion of his jubilee, "and then perhaps we may discover the truth." He dreamed the atom-linking theory, as he tells us, on a long night bus ride from Islington to Clapham, and he dreamed the Benzene theory in his rooms at Ghent. But he was a man of action as well ; for he spent the night on each occasion in working out the consequences of his dreams. It is to be noted that by a remarkable coincidence the atom-linking theory was also conceived by A. S. Couper about the same time as it was by Kekulé, but its publication was delayed through no fault of Couper's.

The book begins with some account of the fire theories which, though based on error, led to the amassing of a great store of practical knowledge. This is followed by the history of scientific chemistry, beginning with the theory of salt formation. The influence of this theory is traced in the theory of the fixation of gases, and in quantitative analysis. From this last follow the laws of chemical combination and the Atomic theory with all its modern developments.

Beside many separate memoirs and monographs, I am indebted especially to the following historical works:

A. L. LAVOISIER. History of Gases in his Opuscules Physiques et Chymiques, 1774.
T. THOMSON. History of Chemistry, 1830–31.
K. C. SCHMIEDER. Geschichte der Alchemie, 1832.
W. WHEWELL. History of the Inductive Sciences, 1837–38.
H. KOPP. Geschicte der Chemie, 1843–47.
A. KEKULÉ. History of Organic Chemistry: Introduction to his Lehrbuch der Chemie, 1861.
G. F. RODWELL. Birth of Chemistry, 1874.
T. M. LOWRY. Historical Introduction to Chemistry, 1915.
E. J. HOLMYARD. Chemistry to the time of Dalton, 1925.

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THE ORIGINS AND THE GROWTH OF CHEMICAL SCIENCE

SECTION I

THE FIRE THEORIES

FROM the earliest times, down to the eighteenth century of our era, there has been one main principle underlying all ideas as to the composition of matter. It is based on the destructive action of fire. The principle is, that combustible matter is compound or complex, while burnt matter is simple or elementary. The fire theories are those which are based on this principle. The fire theories are: the Greek theory of the four elements, the alchemical theory of the composition of metals, the iatrochemical theory of the hypostatical principles, and the phlogiston theory. To appreciate these theories it is necessary to bear in mind that they are all based on the supposed destructive action of fire, and that their elements, in so far as they are substances at all, are substances which resist the action of fire. Modern chemistry, led by Lavoisier, rejected these fire theories which had been shaken a century earlier by Robert Boyle, who criticised impartially both the Spagirists and the Stagirists. As far as chemistry is concerned, fire is no longer a sign of disruption but of combination. The fire theories have not survived in modern chemical science; but by drawing attention to the loss and recovery of the power of burning and to the transference of the power of burning from a combustible substance to one already burned, they greatly helped towards the future application of oxidation and reduction processes.

It is not, however, suggested that the fire theories were the only guide that chemistry had before Lavoisier. Chemists employed not only fire but also solution; and it was from the study of substances in solution that the "salt" theory arose in the seventeenth century, the theory, namely, that a salt is composed of an acid and a base. This theory has not been rejected. It was amplified by Lavoisier and it has been modified by others; but it has remained and still remains a guiding principle. It is with the salt theory that chemistry begins to be a science rather than an art. The early history of the salt theory is given in the third section. An attempt is made in this book to trace the introduction of new ideas into chemical science from the original discovery that an acid and an alkali react to form a salt. But the fire theories, as being the more ancient, claim attention first.

The earliest discoveries, ideas, theories and industries which can be called chemical are associated with fire. They extend back into prehistoric times. None of the fire theories has remained as a permanent part of the science, but they lasted down to near the end of the eighteenth century. At the root of all what may be called the fire theories is the idea that fire separates compounds into their elements. Although none of the fire theories has survived, certain ideas connected with them have remained and still remain parts of the science. Among them are the ideas of the uniformity of nature, of the indestructibility of matter and its increatability, of elements and compounds, of atoms and of, the most debated of them, transmutation. The discovery of fire was made by prehistoric man and there is no record of it. Nor is there any record of the discovery of the first methods of producing fire artificially. In historic times people in all countries, even the most primitive tribes, have been accustomed to the use of fire. It is, however, unlikely that the use of fire became known all over the world at the same time. Those nations which first began to use fire would have the advantage over other nations in power and in the benefits generally of civilisation. It is probable that use was made of fire long before any method of making fire was known. It is supposed that fire has been used by man for at least 20,000 years. Although in historic times all nations have been familiar with fire and used it, it does not appear that all nations knew how to make it. Tylor says of the aboriginal Tasmanians that, while they had fire and used it they did not know how to make it. And, in any case, until the discovery of phosphorus and the invention of lucifer matches fire was troublesome to make. Consequently, it was the practice to keep fires burning. The Egyptians kept a fire in every temple; the Persians, Greeks and Romans kept a fire burning in every town and village. Fire was also carried considerable distances, in some cases across the sea to islands. In the Greek games in honour of the fire-gods Prometheus, Hephaistos and Athene, there was a kind of torch-relay race which may have had its origin in the rapid carrying of fire from one town to another.

Fire must often have been observed before it came to be used. A conflagration caused by lightning or by a volcanic eruption would at first cause only terror, and fires of this kind would not last long enough or occur often enough for men to become familiar with them and to use them. Yet there are fires on the earth which occur under circumstances not likely to cause any particular terror and which men could soon have become accustomed to and learned to use. Near Baku there are, or were, fires of natural gas which have burned through the whole period of history and probably long before. In Mesopotamia and in other parts of the world similar fires are known. How they became ignited is not known. Probably it was by some natural agency such as a flash of lightning. A. Arnold, who visited Baku in 1875, says, "Twelve versts from Baku we came upon one of the oldest altars in the world erect and flaming with its natural burnt-offering to this day. Surakhani is the ancient seat of probably one of the most ancient forms of worship."

Jonas Hanway, writing in 1751, speaks in his *Travels in the Caucasus* of what the "Guebers or fire-worshippers call the everlasting fire." He says, "The earth round the place for about 2 miles has this surprising property that by taking up 2 or 3 in. of the surface and applying a live coal the part so uncovered immediately takes fire. If a cane or tube be set about 2 in. in the ground, confined and close with earth below, and the top of it touched with a live coal and blown upon, immediately a flame issues without hurting the cane provided the edges be covered with clay; and this method they use for light in their homes. Lime is burnt to great perfection by means of this phenomenon. The stones must be laid on one another and in three days the lime is completed. Near this place brimstone is dug and naphtha springs are found."

Fires of this kind need not have caused any great or lasting terror. Men would soon have learned to use them for light and heat and cooking. No artificial means of making fire would be necessary. Fire would be carried from place to place and its use spread farther and farther away. According to the Greek legend, fire was not given to man by Zeus, the lord of the lightning, but was stolen by Prometheus, and the home, or at any rate the prison, of Prometheus was the Caucasus. If not the cradle, at any rate the schoolroom of the human race, was the place where the use of fire was taught.

From the use of fire spring the principal chemical arts and manufactures—metallurgy, lime and mortar, bricks and earthenware, and glass. Pliny has related the discovery of glass. Some Phœnicians made a fireplace of blocks of trona, the native sodium carbonate, on a sandy shore. Similarly a fireplace of clay would give brick and a fireplace of limestone lime. Tylor has suggested that earthenware was first made by lining baskets with clay and baking them, the oldest known earthenware having the marks of the wickerwork on it. When fires came to be used far from their source the earth would be searched for combustibles.

Among these are minerals such as the sulphides of copper and lead, the burning of which would give the molten metal. A person feeding a fire with lumps of galena and other combustibles would be likely eventually to find in the ashes an ingot of metallic lead.

The chief modes of obtaining fire artificially, known to the ancients, were (1) by friction of wood, (2) by striking sparks from pyrites, (3) from the sun by concave mirrors. The first method is probably the oldest as it is the most widespread. The second method was generally known, and it was the only method known to the Fuegians and to the Esquimaux, in places where dry wood could hardly be found. The Esquimaux used quartz and pyrites. The Fuegians used flint and pyrites, while the inhabitants of the adjacent South American mainland used fire-sticks. Getting fire by the friction of wood may have originated from stirring the embers of a fire that had died down. Avebury suggests that the sparks struck in working up stone into implements must have been followed sooner or later by the discovery of fire. Plutarch relates that "In Greece where a perpetual holy fire is kept as at Delphi and Athens, and in case by any accident this fire became extinct, it was esteemed an impiety to light it from common sparks or flame or from anything but the pure and unpolluted rays of the sun, which they usually effect by concave mirrors, of a figure formed by the revolution of an isosceles rectangular triangle, all the lines from the circumference of which meeting in a centre, by holding it in the light of the sun, they can collect and concentrate all its rays at this one point of convergence. . . . Any light, dry, combustible matter will kindle as soon as applied under the effect of the rays which here acquired the substance and active force of fire." In Rome, "if the fire of Vesta was extinguished the Vestal Virgins were scourged. Fresh fire was obtained by drilling into a board of auspicious wood" (*Festus Val. Max.*). The method of obtaining fire from the sun seems also to have been practised by the Peruvians, polished concave mirrors of pyrites having been found in their tombs.

The effects of fire form the basis of the earliest ideas as to the composition of substances. Theories that there is an elementary principle of inflammability arose in very early times and continued till the end of the eighteenth century.

Fire Theory.—That a substance when burned is disintegrated into its elements was in the first instance the obvious and natural view to take. Nearly all combustibles are of organic origin. They leave when burned an insignificant amount of ash.

This supposed action of fire was summed up in the old definition of heat, *Homogenea congregare, Heterogenea segregare*, that is, burnt things are elementary, combustible things are compound.

The Four Elements.—The theory of the four elements, earth, air, fire, and water, has had a longer life than any other chemical theory. It lasted from Aristotle to Paracelsus, and to-day the familiar use of the term "elements" generally refers to them in the Aristotelian sense.

That the theory of the four elements, earth, air, fire, and water, is an offshoot of the fire theory, is evident from the familiar explanation given of burning.

This is given here in the words of Themistius, the defender of Aristotle, in Boyle's *Sceptical Chymist.* Themistius regrets that by the conditions of the discussion he is unable to use the best weapons he has. (It had been agreed that in the discussion they should insist rather on experiments than on syllogisms.) "Whereas," he says, "if I were allowed the freedom, in pleading for the four elements, to employ the arguments suggested to me by reason to demonstrate them, I should almost as little doubt of making you a proselyte to those unsevered teachers, Truth and Aristotle, as I do of your candour and your judgment. For it is much more high and philosophical to discover things a priori than a posteriori, and therefore the Peripateticks have not been very solicitous to gather experiments to prove their doctrines, contenting themselves with a few only to satisfy those that are not capable of a nobler conviction; and, indeed, they employ experiments rather to illustrate than to demonstrate their doctrines. For though I shall name but one, yet it is such a one as shall make all others appear as needless as itself will be found satisfactory. For if you but consider a piece of green wood burning in a chimney you will readily discern in the disbanded parts of it the four elements, of which we teach it and all other mixt bodies to be composed. The fire discovers itself in the flame by its own light; the smoak by ascending to the top of the chimney and there readily vanishing into air, like a river losing itself in the sea, sufficiently manifests to what element it belongs and gladly returns. The water in its own form boyling and hissing at the ends of the burning wood betrayes itself to more than one of our senses; and the ashes by their weight, their firiness and their dryness, put it past doubt that they belong to the element of earth."

The four elements were regarded not so much as actual substances but rather as qualities. The fire and the water of the diamond were qualities resembling fire and water. As Whewell puts it, "The chemical analysis of the Greeks was an analysis into adjectives and not into substances."

The theory of the four elements also formed the basis of Galen's system of medicine. The word "element" frequently occurs in literature in the Aristotelian and Galenical sense.

"*Sir Toby.* Does not our life consist of the four elements?

"*Sir Andrew.* Faith, so they say, but I think it rather consists of eating and drinking.

"*Sir Toby.* Thou art a scholar. Let us eat and drink."

But in Shakespeare's time the word was becoming hackneyed.

"*Clown.* Who you are and what you would are out of my welkin, I might say element, but the word is over-worn" (*Twelfth Night*).

And in the Authorised Version of the Bible the word only occurs twice, and in one passage with the epithets "weak and beggarly." At present the word in this older sense is used colloquially and in the newspapers.

While the Greek theories of matter did not help the advance of chemistry, they probably did not hinder it, since the first beginnings of the science of chemistry had nothing to do with any views on combustion. But many adverse criticisms have been made on the Aristotelian speculations. Whewell (*History of Inductive Science*) says that their experiments were not appropriate to the facts. Bergman (*Origin of Chemistry*, p. 71) says: "The particular theories of the Greeks were seldom founded upon observation and experiment, but were rather the monstrous conceptions of prejudice and frivolous imagination." Lavoisier (Preface to his *Elements of Chemistry*), speaking of the Greeks, says: "The authority of those fathers of human philosophy still carries great weight, and there is reason to fear that it will bear hard upon generations yet to come."

Alchemical Fire Theory of Metals.—The next in date of the fire theories is of uncertain origin. It is found in Geber's works (eighth century A.D.). It was the guiding theory of the alchemists in their efforts at transmutation. It was essentially a theory of the composition of the metals, that the metals are composed of sulphur and mercury. This view is a more natural one than it may appear at first sight. The metals known to the alchemists, with the exception of gold and silver, lose their metallic appearance on calcination. Similarly, many ores, such as pyrites and galena, lose their metallic appearance on calcination and give off the fumes of burning sulphur (sulphurous acid). Thus it was natural to suppose that metals are combustible by virtue of an inflammable substance, sulphur, contained in them, and that they lose their metallic appearance owing to the loss of mercury which was the only volatile metal known; and since the metals are recovered from their calces by heating with charcoal, a vegetable mercury was postulated. These elements were substances and not adjectives, and they are still classed among the elements to-day.

The Theory of the Hypostatical Principles.—This theory is due to Paracelsus, the founder of the Iatrochemical School. Paracelsus was Professor at Bâle, perhaps the first Professor of Chemistry to be appointed anywhere. He signalised his first lecture by burning the works of Galen, thus inaugurating the first chemical lecture experiment.

Paracelsus adopted the sulphur and mercury of the alchemists and added a further element, salt; to these elements some of the iatrochemists added earth and water.

These elements were not derived from the products of burning in an open fire but of the action of heat on substances in closed vessels, that is, products of destructive distillation. They were, further, the products of the action of heat on vegetable and animal substances rather than on minerals, or on metals. Thus they differed from the four elements, since these were derived from the products of actual combustion.

These elements, sulphur, mercury and salt were called hypostatical principles. The theory of the hypostatical principles was also an offshoot of the fire theory. The elements sulphur, salt and mercury, were defined as products of the action of fire. This is evident from Boyle's description of them. "For when they anatomise a compound body by the fire and obtain a substance inflammable, that will not mix with water,