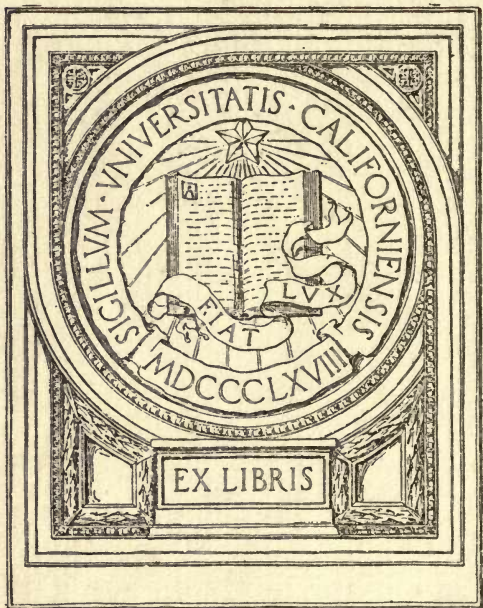


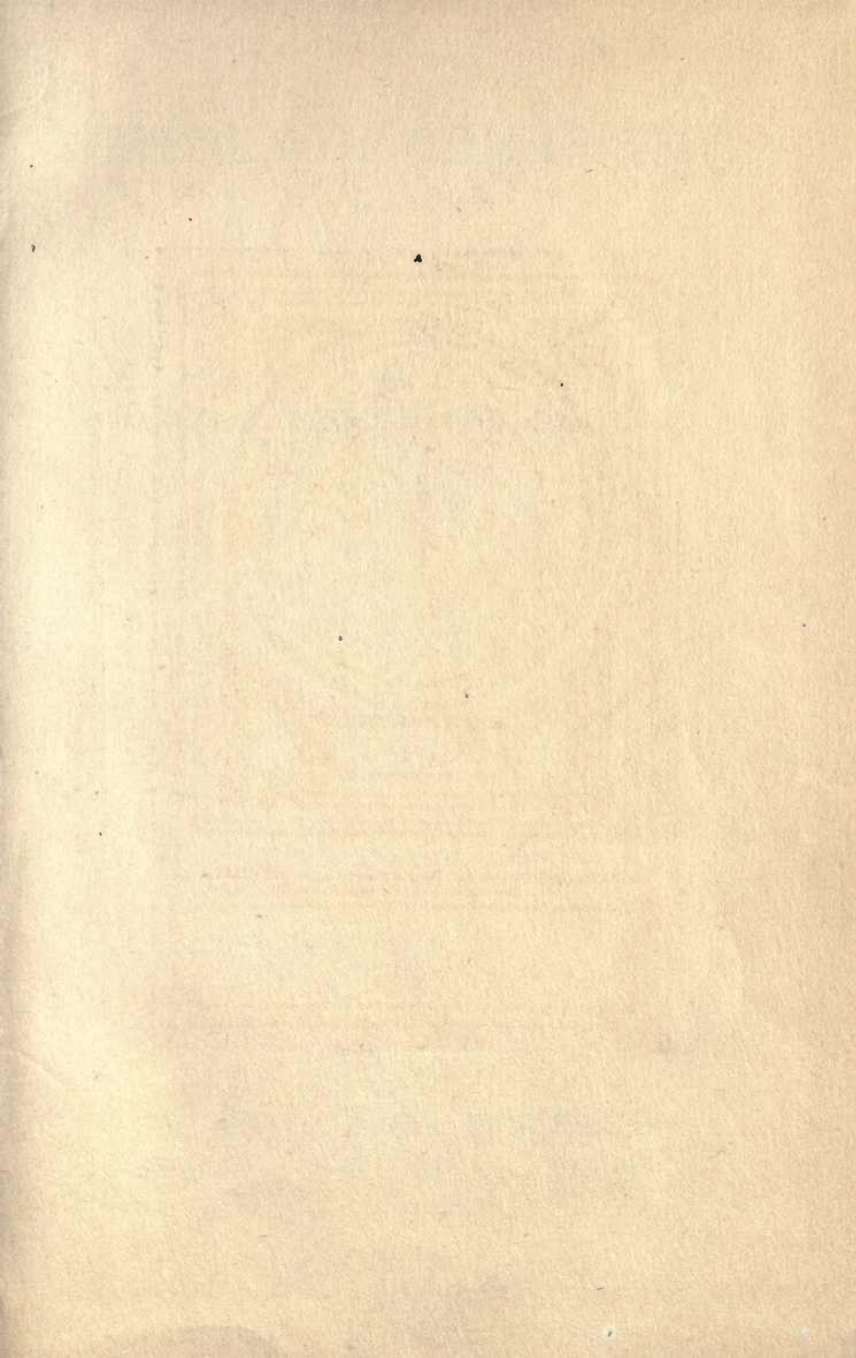
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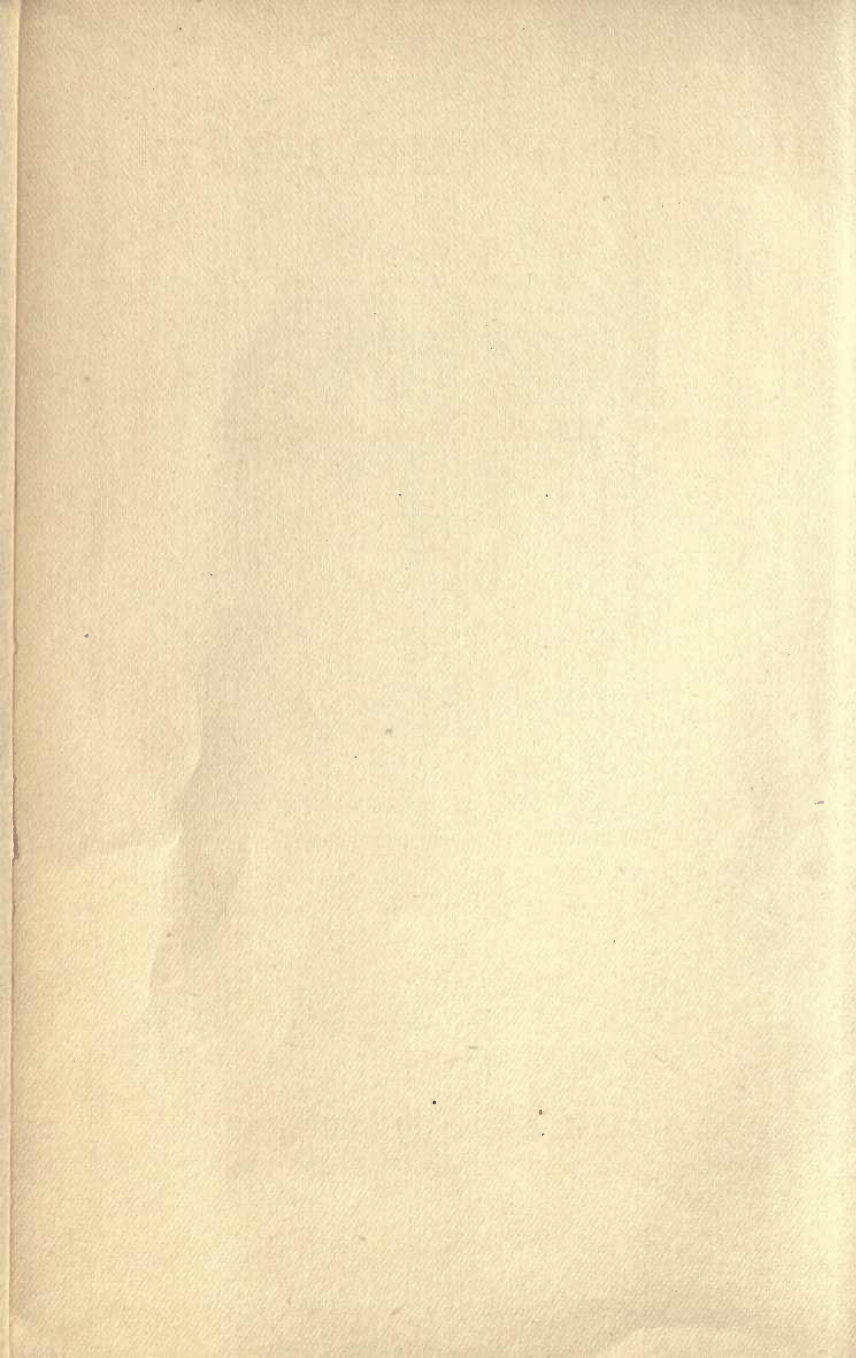


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# HISTORY OF CHEMISTRY

BY

FRANCIS P. VENABLE, PH.D., D.Sc., LL.D.

D. C. HEATH & CO., PUBLISHERS

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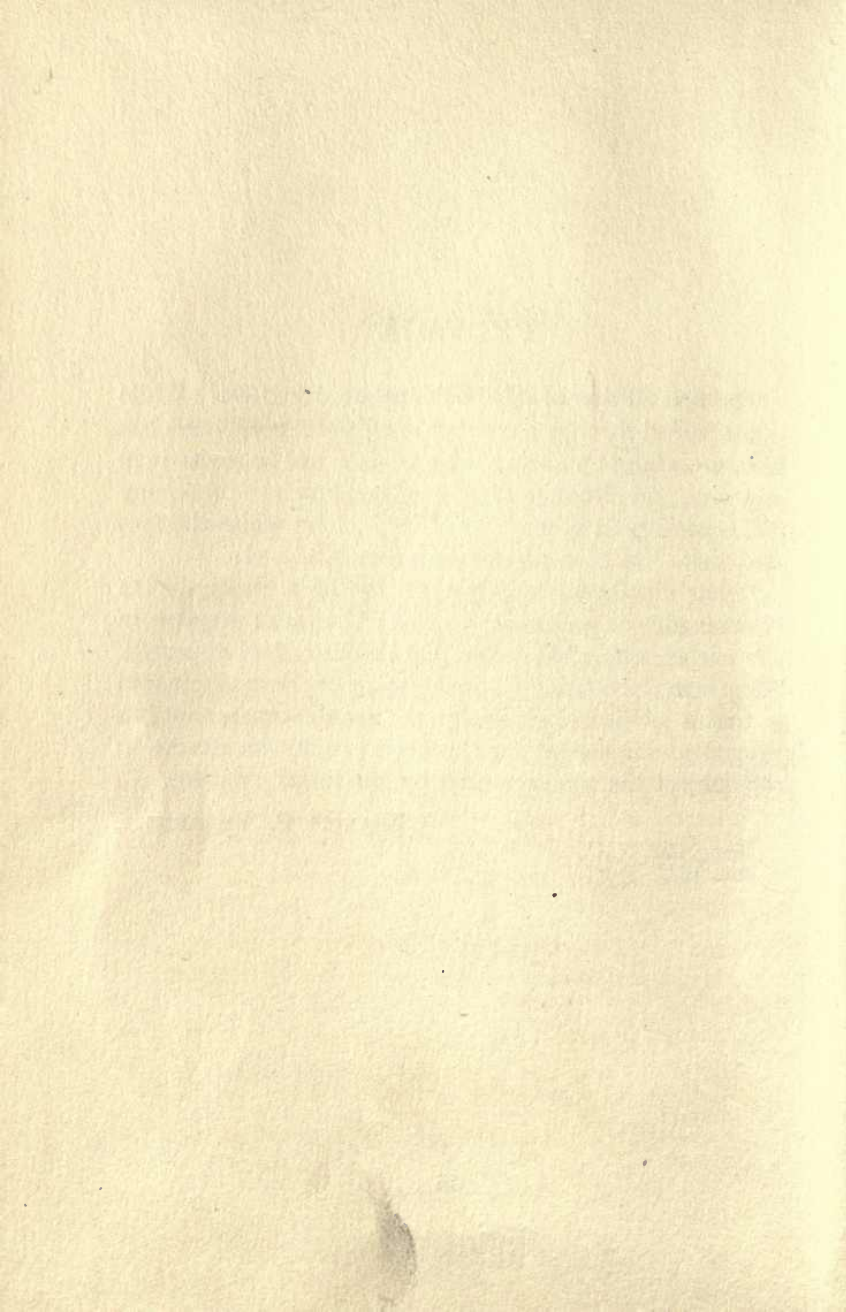
## PREFACE

The first edition of this book appeared in 1894. While it has passed through a number of editions since, there has been no attempt to bring it up to date nor to revise it in any way, and although there has been much to preoccupy me, especially in other lines of work, I recognize the fact that there has been no excuse for such neglect.

It has now been entirely rewritten on a changed plan of arrangement and made to cover the great progress in the science which has taken place since it first appeared. Some material considered unnecessary has been eliminated so that it might be kept within the same compass that has proved so convenient for those who could not devote to the subject the time required by the larger treatises.

FRANCIS P. VENABLE

Chapel Hill, N. C.  
June, 1922





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# HISTORY OF CHEMISTRY

## CHAPTER I

### THE BEGINNINGS

**Evolution of Science.**—In attempting to discover traces of a science in earliest historic times one must first free his mind of the idea that he will find it in anything like the elaborated modern form in which he knows it. These natural sciences are the result of a long and laborious process of evolution. First comes the gathering of facts and observations, and so the beginnings go far back of history to the earliest representatives of the race. The early motive was the struggle to maintain life and increase bodily comforts, and this motive has not lost its force in the modern world. Man is a weapon-using and tool-making animal and so gathered and fashioned the objects which best served his purposes. Comfort demanded clothing and shelter; therefore, he became weaver, tanner, and builder of houses. His higher nature developed the love of beauty and so he sought out paints and dyes; his ailments forced upon him some knowledge of remedies and medicines. With the change from nomad to citizen his necessities became greater and his inventive genius was stimulated. Trades and industries arose and with these came specialization in labor and formulation of knowledge.

Yet there was nothing which could be called science and all is still beyond recorded history. The beginnings

described were found wherever civilization centered — in Mesopotamia, China, India, Egypt, and European Greece. The growth of knowledge through experience, or empiricism, is exceedingly slow. Yet a number of industrial arts sprang up and some were carried on with a high degree of skill. Artificial aids and labor-saving machinery, such as the blast furnace and potter's wheel, were called into use. There were invented tools making use of physical laws, even though these laws were not recognized or understood. Among these were the wedge, the lever, the screw, the wheel. Improvement and wider application of these fundamentals came with growing understanding of principles involved.

**Industrial Arts: Metallurgy.** — An outline of the knowledge attained in some of these arts, many of which date back to the most remote antiquity, may well be considered here. Taking up metallurgy first we find that six metals were well known — gold, silver, tin, iron, copper, and lead. Homer mentions these six and the Bible does also; so they seem to have been in use from very ancient times. Mercury was afterwards added to the list. The derivation of the word metal is from the Greek word *μεταλλω*, to search after, and the noun first meant or referred to mines. The ancients, especially the Egyptians, were very skillful workers in metals. They made gold wire and leaf and fine inlaid work. Gold was apparently the first known of the metals. Its color, lustre, and malleability, as well as its freedom from tarnish and corrosion, attracted the attention of the early peoples. Its rarity and value soon brought it into use as a medium of exchange, and very early coins have been preserved. Its occurrence in the free state

would doubtless account for its being recognized and used among the first of the metals. Early vessels were made from it, as witness those which have been found in ancient Troy. It was also used for coating or plating wood and other materials.

Silver seems to have become known and to have been used at about the same time as gold. It also was found free and was easily made ready for use. Then follow copper, iron, tin, and lead. The Egyptians attributed the discovery of the metals to their sovereigns; the Phoenicians and other peoples to their divinities.

The purification of gold and silver by the cupellation process was known before the Christian era, but there was no means known for the separation of gold from silver. The alloy of the two metals, in which enough silver was present to whiten the whole, was often found and was called *electrum*, being regarded as a distinct metal from the others. Letters made of electrum a foot or more in height, which had been fastened to the walls of the temples, were found in the ruins of Herculaneum. The oldest coins were made of white or pale gold. After a while it was found that this alloy could be made artificially by melting together three parts of gold and one of silver.

Copper was in use before iron and was called *χαλκος* by Homer. From this we get the names for certain copper minerals, as chalcopyrite and others. The Romans obtained it first from the island of Cyprus and called it *aes cyprium*, and from this it became *cuprum*, a name used now in connection with its salts. It was used mainly in alloys, as with gold for coinage and jewelry and with zinc as brass. Zinc itself was unknown to them but the

ore was used along with the copper in making brass. Bronze was an alloy of copper and tin and was known also before the method of extracting tin from its ore had been discovered. This was very strong, much easier to prepare than iron, and more readily worked into shape. It was therefore a more abundant and cheaper material and was used for many purposes where we use iron. Weapons and many utensils were made from it. There is a tradition that the Egyptians knew a way of hardening and tempering copper without alloying it and that this is one of the so-called lost arts.

Iron was known in very early times. As it rusts so easily, very few early implements have come down to us. It had to be extracted from its ore. Probably through some happy accident the method became known. For many centuries down into modern times the art has been practised in India. A little pure ore mixed with charcoal was heated by a blow-pipe and a small lump of iron was produced. These lumps were heated and hammered together and a serviceable cutlery steel obtained. The early Egyptians understood how to harden or temper iron and quite possibly used such iron implements in part of the work of constructing the pyramids. Iron was coined by the Greeks and in the time of Homer they used it for axes and ploughshares. The difficulty of reducing iron from its ores on a large scale would account for its not being used more largely and at an earlier time.

Tin was obtained from India and Spain and afterwards from Britain. It was one of the articles of commerce used in trade by the Phoenicians. Mirrors were made of it and copper vessels were coated over with it.



Lead and tin seem to have been regarded as varieties of the same metal and were called *plumbum nigrum* and *plumbum candidum* respectively. Pliny writes of conveying water in lead pipes and Homer makes much earlier mention of the metal. It came mainly from Spain and Britain. From the former country mercury also was obtained and was used, as now, in extracting gold from its ores. Native mercury was called *argentum vivum* or quicksilver.

**Minerals and Salts.**—The two oxides of copper, as they occur in nature, were used in glass making; verdigris was manufactured and put to several uses; white lead was used as a cosmetic by the Athenian ladies and found further use as a medicine; red lead was used as a paint. The native antimony sulphide was used to paint the eyebrows and is still used for that purpose in the East under the name *kohl*. Black oxide of manganese was used in glass making for clearing up colored or darkened glass and so received the name pyrolusite. The native carbonate of zinc was used in making brass; the two sulphides of arsenic were well-known pigments. According to Davy, the ancient Greeks and Romans used almost the same colors as those employed by Italian artists at the period of the revival of art in Italy.

Soda and potash were used in washing and whitening clothes and in saponifying fats for soaps and unguents. Lime was burned and mortar made from it, though the earliest cementing materials seem to have been pitch and bitumen. Excellent hydraulic cement was made and used by the Romans in their great aqueducts. Salt and saltpeter were used as food preservatives. Alum was used in dyeing. Vinegar was the only acid known.

**Glass Making and Pottery.** — The art of glass making is very old and seems to have originated with the Egyptians. An account of its accidental discovery by the Phoenicians has also been handed down. Certainly the Egyptians reached a high proficiency in making glass, coloring and forming it, and also in the production of imitation precious stones. They were unable, however, to produce clear, colorless, and flawless glass. The seat of the industry was later transferred to Byzantium, the capital of the Eastern Empire, and the art of glass making was brought to Europe by the early crusaders, as also a number of other industries were brought back.

The making of bricks and pottery must have been one of the earliest efforts of man in the line of manufacture. The potter and the potter's wheel were known among all the ancient peoples. Specimens of pottery have been unearthed from the earliest ruins. With the introduction of enamels, glazes, and decorations it became an art, and in this both the Etruscans and Egyptians excelled. The Chinese alone of the early nations knew how to make porcelain.

**Dyeing and Tanning.** — Dyeing was carried to great perfection. Many plant and animal coloring matters were known. Mordants were used and the effects produced were very beautiful. Paints were also prepared and applied with brushes. The following mineral colors were known at the time of Pliny: White lead, red lead, zinc white, cinnabar, smalt, verdigris, ochre, lampblack, realgar, orpiment, stibnite, and the oxides of copper.

Leather was first tanned by means of oils and later with bark, very much after the methods now in use. The hair was removed by means of lime. Some leather,

tanned centuries before the Christian era, has been found in modern times in a state of fair preservation.

**Soaps and Medicaments.** — Soap was made by mixing wood ashes with animal fats, thus saponifying them. It was used chiefly as a kind of pomatum; unguents, oils, etc., were rubbed upon the body in the place of soap as used in modern times. Both hard and soft soap were known. Burnt lime was often added in its manufacture.

Many substances were used as medicaments. Some of these might be called chemical preparations, showing an early union between chemistry and pharmacy. Lead plasters were made from litharge and oil; iron rust was used and also alum, soda, and bluestone. Sulphur was employed as a disinfectant and also for bleaching purposes. Mineral waters were used and likewise various infusions from plants.

Of course all races, and even the lower animals, had in the lapse of time discovered in plants and minerals sundry remedies for their ailing bodies. In the case of man the cures were often brought about then as now by psychic suggestion rather than through the actual curative properties of the substances themselves. Disease was caused by the presence of an evil spirit which had to be exorcised before health could be restored. Thus Homer refers to the use of sulphur to drive away the evil spirits. The first chemists, then, who stored up knowledge of chemical substances might be classed as healers, and the earliest documentary evidences were in the form of lists of remedies and cures. Such papyri have been found in early Egyptian tombs.

## CHAPTER II

### EARLY DEVELOPMENT

**Naming the Science.**—As has been shown, chemistry early became allied with so-called magic and witchcraft, and those who practised it were usually feared and held in bad repute. It is probably this association which gave the name to the science. The Greek word *χημεία* is manifestly a rendering of the Egyptian name *chema* or *chemi*. Plutarch tells us that *chemia* was a name given Egypt on account of its black soil, and that this term further meant the black of the eye, symbolizing that which was obscure or hidden. The Coptic word *khems* or *chems* is closely related to this and also signifies obscure, occult; and with this is connected the Arabic *chema*, to hide. It was, therefore, the occult or hidden science, the black art.

**Arrangement of Facts.**—The second stage in the evolution of the science is the gathering together of facts and observations and their systematic arranging and recording. A beginning of this had been made in so far as they were related to medicine but even there few traces are left. The conception of knowledge having any value apart from its immediate use in the service of man was slow to arise. Further, those who sought such knowledge were largely charlatans and quacks who had nothing to gain by enlightening their dupes and feared prosecution and punishment.

**Mysticism.** — The earliest writings were lost or destroyed. For instance, Diocletian is said to have burned all of the Egyptian manuscripts bearing on alchemy because, as he said, these taught the art of making gold and silver, and by destroying them he took away their power of enriching themselves and rebelling against Rome. Whether Diocletian actually did this or not, it is certain that these books of a feared and prohibited art were subject to many another foray, as is evidenced by the scene recorded in the Acts of the Apostles: "Many of them which used curious arts brought their books together and burned them before all men: and they counted the price of them and found it fifty thousand pieces of silver." Such scenes were often repeated in the early part of the Christian era.

The phrasing used in these writings was purposely so obscure that only the initiated were supposed to be able to understand them, and this persisted throughout the period of the alchemists. It sufficed not merely to cloak knowledge but to conceal ignorance.

Another piece of mysticism is seen in the ascription of a divine origin to their art. Thus Zosimus the Panopolite claimed that the giants, sprung from the union of the angels with the daughters of men, were taught all that was supernatural and magical by their fathers and this wonderful knowledge was recorded in a book called *chema*. The adepts in alchemy were unanimous, however, in ascribing the foundation of their art to Hermes. The name is synonymous with Toth, the god of intellect, the patron of arts and sciences in ancient Egypt. As the god of letters, all books were dedicated to him and he was in one sense the author. Clement of Alexandria

describes the solemn procession in which these books were borne in the great ceremonies. Tin and mercury were set apart as metals sacred to him. During the Middle Ages the science was often known under the name of the Hermetic Art, and alchemists called themselves Hermetic Philosophers. To close anything very securely, as for instance to seal it in a glass tube, is called to this day sealing it hermetically. In old times the symbol of Hermes was affixed and it was thus sealed with "Hermes, his seal." The other metals had their patron deities also. Thus gold was sacred to the sun, silver to the moon, and silver nitrate is still sold as lunar caustic. Copper was sacred to Venus, lead to Saturn, and iron to Mars; and one form of iron oxide can be bought on the market still as *crocus martis*.

It was a custom among the early writers to ascribe their discoveries, books, etc., to fabulous names or ancient heroes and gods. This had two objects, the first being to shield the true author in time of persecution and the second to gain a certain amount of credit and reputation for a discredited art by the use of the names of such celebrities as Moses, Solomon, Alexander, Cleopatra, etc. Thus there is a treatise entitled *Moses the Prophet on Chemical Composition*. It is probable that such treatises were written in the early centuries of the Christian era.

**Manuscripts and Original Sources.** — This brings us to inquire into the existence of any very early records. No original manuscript of the earliest writers on chemistry or alchemy has been discovered. Our knowledge must be gleaned from the pages of those writing upon other subjects or must come from fragments handed down

through several copyists. The earliest manuscripts known are preserved in the museum at Leyden and were found at Thebes enclosed in the wrappings of a mummy. They are written partly in Greek and partly in the Demotic character, though they are known as the Greek papyri. The earliest is somewhat fragmentary, the beginning and the end being lost. It was written apparently about the third century of this era and belonged to the class of books burned by Diocletian. These manuscripts are filled with magical formulas, recipes, and descriptions of chemical processes, together with various forms of apparatus. Other later manuscripts are found in various European libraries.

**Laws.** — The next stage to be considered in the evolution of the science is the development of laws. Man, with his intellectual gifts, could not rest content with the mere observation of facts and phenomena. Their orderly arrangement so that a certain uniformity or regularity and then a controlling law could be recognized was a slow process. These laws were accepted and utilized as a matter of every-day experience but their definite statement came only with comparatively modern science. A stone tossed in the air returns to the ground and wood burned gives off certain gases along with heat, but it called for a Newton to state the law of gravitation and not even Lavoisier could tell all the story of that burning and the heat. Some of the early Greek philosophers guessed at the indestructibility of matter, but this fundamental conception played little part in their reasoning.

**Mutability in Nature.** — It is easy to see how confusing to the early philosophers were the multiform changes

in nature. Nothing seemed lasting or stable; all was subject to change. The observations of one day might be quite overturned by those of the morrow. The Egyptians and other early peoples held this view of the changing nature of all external objects and the absence of law in these changes. Observation and experimentation, therefore, appeared useless. As for the Greeks, Socrates said that the nature of external objects could be discovered by thought without observation, and the school of the Cynics renounced all attempts at natural science. It is related that one philosopher put out his eyes lest the sight of these changes should impair his thinking. Plato separated logic, as the knowledge of the immutable, from physics, the knowledge of the mutable. That which was subject to indefinite change would not repay observing or recording. Therefore, astronomy and physics could not be conceived of as serious objects for study or contemplation. There was nothing worth while to be learned from fields and trees and stones.

This would seem to be folly to the modern mind, but it must be acknowledged that there is danger from inaccurate observations and undigested facts. The safety of the present day lies in the rigid exaction of experimental proof, a means of finding truth which these philosophers had scarcely learned to apply. There have been and still are deplorable looseness of statement and faulty logic on the part of many, even leaders of science. The Greek philosophers stand preeminent as the greatest, clearest thinkers of all time.

**Theories.** — In spite of this attitude, the early philosophers made a fundamental start in searching for the underlying causes of the changes going on in nature



and the origin of the many objects seen about them. The theories which they advanced in explanation of what they observed form the last and most important step in the evolution which has been traced so far, and with these theories we have truly the beginning of science and the casting off of empiricism. The first question they sought to solve was out of what this world was made. While it was possible that the Greeks got some of their ideas from the Egyptians and they might be traced to the sages of India or the Far East, they have left us the most abiding impression of their theories and these, in part at least, were based on observation and experiment. These philosophers date back to the sixth century before our era or earlier.

Thus Thales of Miletus, who has been called the first of the natural philosophers, affirmed that water was the first element or principle and that out of it all things were made. Thus water, on heating, is changed into air and from air water comes. Solids are left when water is boiled away. This theory had its supporters even during the Middle Ages, some of them carefully proving that plants would grow when fed with water only. The theory was not completely disproved until Lavoisier showed the fallacy by careful experiment. When one recalls its universal presence and what trouble it causes the expert chemist of to-day to avoid entirely its presence in his experiments, it is easy to see how natural the conclusion was that it was the universal, primal element.

Anaximenes regarded air as the primal element; Hera-  
kleitos, fire; Pherekides, earth. According to Anaxi-  
menes, clouds were caused by the condensation of air,  
and rain by the condensation of clouds. Archelaus said

that air, when rarefied, became fire; when condensed, water; and water, when boiled, became air. Of course, the boiled natural water left solids. Empedokles introduced the idea of four distinct primal elements — earth, air, fire, and water — which were not interchangeable but formed all things on being mixed.

**Atomic Theory.** — But a further conception became necessary. In this mixing, what is it that is mixed or, as we would now express it, what is the internal structure of these elements? Are they made up of separate particles? If not, how are they constituted? Long before the time of the Greek philosophers the idea of separate particles seems to have been conceived in India, but for clear and logical thinking we must again turn to the Greeks. Anaxagoras of Klazomene (500 B.C.) was apparently the first to formulate a theory approaching the atomic. This was more clearly expressed by Leukippos and extended by Demokritos, who lived 450–347 B.C. He was the founder of the atomistic school and Aristotle frequently cites his writings. As was customary for men of learning in early times, Demokritos visited Egypt, Chaldea, and various parts of the East in search of learning, and doubtless owed much to the the wise men of those regions.

**Atoms.** — The definition of an atom as given by Demokritos was almost as definite and precise as that found in modern treatises. The word itself means that which can not be cut or divided. There arose two schools of philosophers holding opposite views as to the make-up of the universe. The atomists maintained that it was made up of these indivisible particles separated by empty spaces (*vacua*). On the other hand, the plenists

contended for the view that matter was continuous, nature abhorring a vacuum. The discussion was settled in part by appeal to the old argument, *ex nihilo nihil*. If a particle of matter were divided until further subdivision was impossible, one must arrive at either something or nothing. The latter was impossible, for out of nothing, nothing can be made. Hence there must be an indivisible remnant and this should be called an atom.

During the Middle Ages the word lost its scientific significance and was adopted for small subdivisions of various kinds, as of time or music or anything very small and supposedly indivisible. Thus in general the word denoted a moment, a note, a sand grain, a particle of dust, etc. Where in the Bible we read that man was created out of dust one can quite properly substitute its synonym, atom, and so place it in full accord with the truth as seen through man's study of nature.

**Ether.** — The vacua of the earlier philosophers were filled by Aristotle with his hypothetical ether—the fifth element or *quinta essentia*. This ether is just as essential for the present-day explanations of natural phenomena and its existence is just as evasive of absolute, direct proof. Its invention at that time is perhaps the most marvellous achievement of the most profound intellect which has devoted itself to science and which dominated all branches of science throughout the changes of a millennium and a half.

**Indivisibility of the Atom.** — As to the indivisibility of the atom in the modern theories, it may be added that the compound nature of the so-called elemental atom is well recognized. To the chemist this question of divisibility or indivisibility is a matter of comparative

indifference. It suffices that in all the various reactions of the laboratory the atom retains its individual character and may be regarded as indivisible so far as the usual manipulations are concerned.

**World Building.** — Granted that the world was made of atoms, how was it put together? This problem also was faced and discussed by the Greek philosophers. It must be borne in mind that the modern meaning was not attached to the word element in early times but rather these were thought of as certain principles or essences which were endowed with diverse properties. Thus fire was warm and dry; air was warm and moist; water moist and cold; earth cold and dry. By mixing these elements various combinations and interchanges of properties were thought to be possible.

According to Anaxagoras, there was at first a mixing of these particles of matter, the primal constituents, in infinite disorder or chaos. The act of creation was in the orderly arranging of these by a designing intelligence, *νοῦς*. These particles were like the masses which they produced when brought together and were named *homoeomeries* or like parts, and hence were not the atoms of atomists but corresponded to the molecules of the present day. The act of creation came about through a vortical motion which would separate these molecules and bring together those alike in size and specific gravity, thus building up the various substances known to us. This idea, of course, is drawn from the simple experiment of giving a rotary motion to a vessel containing finely-divided substances of different densities.

The atomists sought to do away with the necessity for a designing intelligence by conceiving the indivisible

atoms or molecules, which were said to possess rapid circular motion, as falling together. These atoms were invisible, indivisible, solid, impenetrable, and unalterable, possessing no other properties except size, shape, and weight. They were influenced by necessity or fate, *ἀνάγκη*. The meaning here seems to be covered by our word law. In falling they had an oblique motion which caused atoms of like shape to collide and gather into masses. Of course, a vacuum or void was an essential for this theory. Aristotle pointed out that there could be no up nor down in mere space, no place to fall from and none to fall to, and hence falling was out of the question. If there were objects falling, they must fall in parallel lines and could never meet. So Epicurus coined a new word to convey a new thought. This word meant inclination. This brought like particles together and in this we have the first suggestion of affinity. This idea was held also by the Hindus, who said, "There is a strong propensity which dances through every atom and attracts the minutest particle to some peculiar object." This "propensity," however, they manifestly confused or identified with gravity. Aristotle regarded the moving ether as the motive principle. Long centuries afterwards Helmholtz proved mathematically that whatever the original motion was it could not have been set up except through the application of some exterior force.

Thus in these very early times the foundations of experience — gathered facts, experimental testing, and workable hypotheses — were laid for the development of a true science with its attendant benefits to civilization. But this decided progress was all but blotted out

in the grave political changes which took place with the fall of the Roman Empire.

**Apparatus.**—It is of interest to inquire by what means experimentation was carried on, and under what conditions, in these early centuries and for a number of those following. Some information as to this may be derived from the Greek papyri. These contain many drawings of alembics and other forms of apparatus which may of course have been later inventions if the great age of these papyri is disproved. The processes used were those requiring fire—dry methods rather than wet. Crucibles, furnaces, etc., abound therefore. There is a treatise by Zosimus on instruments and furnaces in which he claims to describe the various appliances he saw in the ancient temple at Memphis. These were made of gold or bronze or clay. The alembic was a crude form of still and came from the Alexandrian period. The water-bath, or *bain-marie* as it is still called by the French, was said to have been invented at a very early period by Mary the Jewess. The blow-pipe and bellows both figured among these drawings as well as on very early Egyptian and other monuments. The use of glass for apparatus came much later. Jars and bowls of clay and other ware about complete the list. An investigator of the present time limited to such scant equipment would indeed be helpless.

## CHAPTER III

### THE DARK AGES

**The Old Order Overturned.** — With the overturning of the Eastern Empire by the Arabians and the Western Empire by the Goths and Vandals one of the world's greatest civilizations, already decadent, was almost wiped out. In these troubled centuries of the Dark Ages few devoted themselves to literature, art, or science. The creative faculty was blunted and no great artist or philosopher was produced. But happily the light was not altogether extinguished. The useful arts were retained and Greek learning, with its budding science, was transferred to Arabia and Persia. About the middle of the eighth century there was established at Bagdad an academy or university which was visited by thousands of those seeking instruction. Hospitals and laboratories were built and experimental science made some progress. Ancient books were collected and every scrap that could add to the store of knowledge was preserved. This University of Bagdad flourished for several centuries and scholars came to it from distant parts of the world.

This love of learning extended to the western possessions of the Arabians. Universities were founded in northern Africa and Spain. The University of Cordova, for instance, held a high reputation and was attended by many Christian students. Its library was

said to contain 280,000 volumes. But a volume in those days often contained only a single stanza of a poem or a single chapter of a book.

**Progress Made by the Arabians.** — With all their zeal for learning and for hoarding ancient books and the writing of new ones, the Arabs made little progress in science. Centuries passed with but slight additions to what was already known. Nor did they give evidence of the clear thinking, logic, and vision of the Greeks. There was little worthy effort at explaining phenomena or advance in theory. Their chief interest in chemistry lay in finding or preparing new remedies to be applied in the art of healing. This included the search for the philosophers' stone, which at first was a remedial agent or universal medicine. Later it became a supposed means of turning base metals (as lead) into gold. It was to this last object that the time and energy of the alchemists were gradually diverted.

**Transmutation of the Metals.** — When it is recalled that the metals were not in themselves elements to the ancients but a "bundle of properties," it is easy to see how the idea arose that one might take a common and dull or, as they considered it, a diseased metal and purify or change it into one free from corruption, beautiful and valuable like gold. This delusion was a very early one and did much to divert the course of experimental work from its true object, the search after truth, to the vain chase of a will-o'-the-wisp. The tenacious hold of this delusion is shown by the fact that there was an alchemical society in France in the latter part of the nineteenth century, as well as alchemists in America, still trying to transmute lead into gold.



The dream of transmutation was not altogether baseless. There was in a way experimental proof. Much of the lead contains gold and on prolonged treatment the lead disappears and gold remains. When bright iron is dipped into a solution of bluestone it is apparently changed into copper, for the iron disappears and copper takes its place. In a book attributed to an Arabian alchemist of the eight century called Geber we read: "In copper mines we see a certain water which flows out and carries with it thin scales of copper which by a long-continued course it washes and cleanses. But after such water ceases to flow, we find these thin scales with the dry sand in three years to be digested with the heat of the sun; and among these scales the purest gold is found; therefore, we judge those scales were cleansed by the benefit of the water but were equally digested by the heat of the sun, in the dryness of the sand and so brought to equality." Very plausible reasoning from defective premises, as Thomson observes.

**Geber.** — Geber considered all metals to be compounds of mercury and sulphur in varying proportions, an opinion which he said he derived from the ancients and which was handed down with variations through the Middle Ages. His observations on sulphur show the advances made and the limitations of the time. "Sulphur," he writes, "is a substance, homogeneous and of a very strong composition. Although it is a fatty substance, it is not possible to distil its oil from it. It is lost on calcining. It is volatile like a spirit. Every metal calcined with sulphur augments its weight in a palpable manner. All the metals can be combined with this body except gold, which combines with it with difficulty. Mercury

produces with sulphur by way of sublimation cinnabar. Sulphur generally blackens the metals. It does not change mercury into gold nor into silver as has been imagined by some philosophers.”

Glass was by this time included in the materials used for apparatus and the process of distillation was practiced. The product was called a spirit, as spirit of wine, etc. Geber understood the purification of substances by crystallization, solution, and filtration. The latter process was known as distillation through a filter. The majority of the processes in use up to the eighteenth century were known to him.

**New Substances.**—The alkaline substances were known at the time of Geber and caustic soda was prepared. Saltpeter and sal ammoniac or ammonium chloride were also known, as well as the mineral acids, nitric, sulphuric, and aqua regia. These were used as solvents and thus the wet processes of modern chemistry began to substitute the dry processes of the furnaces. Various sulphates, or vitriols as they were called, were spoken of and also borax and purified common salt. Certain compounds of mercury, as corrosive sublimate and the red oxide, were also used. As an illustration of these processes, we may take the method of preparing silver nitrate which Geber discovered: “Dissolve silver calcined in solutive water (nitric acid); which being done, heat it in a phial with a long neck, the orifice of which must be left unstopped, for one day only, until a third part of the water be consumed. This being effected, set it with its vessel in a cold place and then it is converted into small fusible stones like crystal.”

Further addition to knowledge was very limited until

the thirteenth and fourteenth centuries. The decadence of Moorish power in Europe was rapid. The Arabs were driven from Spain, and Bagdad was conquered by the Mongols. Still for some centuries the influence of Arabic thought was great. Their writings were translated into Latin and other languages and formed the chief treasure of medical and scientific workers, and their modes of thought and work were often imitated by their monkish successors. Schools and universities were established at Montpellier, Paris, Naples, Padua, and other places, and the center of learning shifted westward and northward.

## CHAPTER IV

### THE MIDDLE AGES

During the previous centuries of intellectual sterility in Europe the monks had been the only conservators of books and scientific works—a dead treasure in their hands. These orders began to awaken to intellectual life and to labor for the spread of knowledge. The crusaders brought various industries to Europe from the East. The gold-making craze spread and there was much talk of magic. These met with inquisitorial opposition on the part of the church, which indeed held a close control over all progress in knowledge or introduction of new ideas. The only noted scientific workers of the early part of this period came from the monkish orders.

**Albertus Magnus (1193–1280).**— Thus Albertus Magnus was Bishop of Regensburg. His lectures were attended by thousands of students and he wrote a number of books. He introduced the word affinity to designate the cause of the combination of the metals with sulphur.

**Roger Bacon (1214–1294).**— Roger Bacon was the most remarkable man of this time. He was a Franciscan friar in England and was persecuted for his alleged dealing with magic, spending some ten years in prison, though he had written a book to prove that there could be no such thing as magic. He was an astronomer, mathematician, physicist, and alchemist. He was the

first to draw attention to the error in the Julian calendar. It was his success as a mechanic in the production of several automata which brought him the reputation of being in league with the devil. He seems to have known how to make gunpowder and it was first used by the English at the battle of Crecy some fifty years after his death. He is reputed to have been the inventor of the telescope, camera obscura, and burning lenses. He subjected organic substances to dry distillation and noted the inflammable gases given off. Some one during this period by distillation of bones obtained what was called spirit of hartshorn and thus ammonia was discovered. Also wine was distilled and spirit of wine or alcohol obtained. These were about all of the practical gains in the three centuries preceding the sixteenth.

**Changes in the 16th Century.** — In the sixteenth century began a period of restless adventure and discovery, together with a throwing off of the cramping bonds of authority. Just before the dawn of the century America was discovered and men were exploring its wilds. The discoveries of Copernicus as to the stellar system and the Reformation of Luther fall in this age. The art of printing was developed by Gutenberg. Books became more plentiful and about eighty universities in Europe were giving a meagre training to thousands of students. There was a tendency to unite chemistry and medicine. Life processes began to be accounted for on chemical grounds, and medicine was in a measure a branch of applied chemistry and then began to be looked upon as the true aim and end of chemistry. In consequence laboratory work was more carefully carried out and new compounds were discovered. A new object and zest were

given to the study and chemistry became the pursuit of trained scholars.

**Paracelsus (1493–1541).** — One of the noted men of this century was Paracelsus. He taught at the University of Basel, covering the subjects of medicine, chemistry, and pharmacy. His great service lay in breaking away from the ancient authorities, such as Galen, Hippocrates, and Aristotle, insisting that instruction should be given and books written in the language of the people so as to be easily intelligible to them, and stressing the importance of gathering knowledge through experiment and from every first-hand source. As a physician, he was skillful and successful and substituted for the old theory of disease (that it came from excess in either bile, phlegm, or blood) a new one that each disease has its own definite cause and sequences and must be antagonized by specific remedies. This marked the inauguration of the modern method of antagonizing disease.

As a chemist he added much to the previously known analytical methods and the partial discovery of hydrogen is accredited to him, though its distinctive separation and identification were lacking. He laid the foundation for a classification of the metals which lasted for several generations and he was largely instrumental in turning chemistry from wasteful aims into a most useful adjunct to medicine. Pharmacy as a distinct profession and object of study was largely founded by him and he introduced many new and valuable remedies. Mercurial preparations, lead compounds, iron salts, arsenic for skin diseases, milk of sulphur, bluestone, and others might be mentioned. Various plant remedies had been in use as decoctions or simply sweetened with sugar.

He began the search after their active principles and brought them into use as tinctures, essences, and extracts. Tincture of opium, for instance, was first used by him and given its present name laudanum.

**Agricola (1494–1555).** — Contemporaneous with Paracelsus but forming a strong contrast to him was the technical chemist, Agricola. He was born in Germany and studied at Leipsic, and was the first and for a long time the only one to devote his scientific knowledge to the improvement of metallurgy and the industrial arts. His chief work is called *De Re Metallica* and is a connected treatise on metallurgy. This book went through many editions and was for a long time considered an authority on the subject, substituting scientific theories for the persistent ancient beliefs that metals grew in the mines in some such way as vegetables grew in the surface soil, that if a mine were closed and allowed to stand the metal would grow again, and that one metal might be made from another. In his book is given a clear account of the condition of the various industries of his day and the different methods and operations then in use. Agricola was a physician as well as technical chemist but he did not attribute disease and growth to the metals.

**Van Helmont (1577–1644).** — Two more of these physician-chemists deserve mention, both belonging to the seventeenth century. The first was Van Helmont, a Belgian, who studied at the University of Louvain. Most of his life was spent at work in his private laboratory and from this time on we find that in such laboratories most of the real progress was made. He took up the old-world theory that water was the primal element and in support of it advanced many ingenious arguments

from plants and animals. He performed the famous experiment of the willow and it is the most plausible among his experiments adduced as proofs of his theory.

A large earthen vessel was filled with two hundred pounds of dried earth and a willow weighing five pounds was planted in it. This was duly watered with rain and distilled water. After five years the willow was pulled up and found to weigh one hundred and sixty-nine pounds and four ounces. The earth had decreased two ounces in weight. Thus, according to Van Helmont's reasoning, one hundred and sixty-four pounds of root, bark, leaves, etc., were produced from water alone. Fish also, he said, live on water and yet contain all the peculiar animal substances. These are then made from water.

He introduced the term gas to distinguish water vapor and other elastic fluids from air and was the first to study these substances systematically. The vapor coming from fermenting substances, or carbon dioxide, he called *gas sylvestre*. He divided gases into those which were inflammable and those which were not. As he was ignorant of any method of collecting and separating them, his knowledge was very imperfect. He believed in curing diseases by dietetics, by working on the imagination, use of incantations, etc. Still he made use of chemical preparations and greatly advanced them in popular favor. At the same time he was an enthusiastic mystic, believing in the transmutation of metals and in magic. Mice, he thought, could be made by placing a soiled shirt with some flour in a barrel. It may be safely stated that at least this would be one way of collecting them.

**Glauber (1604-1668).** — A more distinguished name is that of Glauber, a German, whose skill was devoted to



increasing the knowledge of chemical substances. He discovered and introduced many new chemical preparations. Purer and stronger hydrochloric and nitric acids were prepared by him. He prepared sodium sulphate, to which he ascribed remarkable curative powers, calling it *sal mirabile*. It has for a long time been known as Glauber's salt. Various other sulphates and chlorides were prepared by him. He used the method of double decomposition in his preparations and thus described it: "Aqua regia which has taken gold into solution kills the salt of tartar (potash) of the liquor of flints (silicate of potash) in such way as to cause it to abandon the silica; and in exchange the salt of tartar paralyzes the action of the aqua regia in such way as to make it let go the gold which it had dissolved. It is thus that the silica and gold are both deprived of their solvents. The precipitate is composed, then, at the same time of the gold and of the silica, the weights of which together represent that of the gold and of the silica originally employed." His appeal to the balance for accuracy and as confirming his theory is noteworthy.

Two mistakes were made by these physicians and iatrochemists, as they were called. They attempted to explain on chemical principles all the changes and processes going on in the body. This was certainly not possible with the deficient knowledge of the day. To Van Helmont, for instance, disease consisted in the excess or preponderance of base or acid in the body juices. Secondly, too narrow a limit was set to chemistry. It was destined to fill a much larger sphere than that of an adjunct to any other science.

**The Rise of Theory.**—The science did not remain

long in this subordinate position. It so grew in extent and importance that it was able to burst the bonds of too close an alliance with medicine and to take for its field the study of the combinations and decompositions of all known substances. The inductive philosophy of Francis Bacon began to have effect and chemistry assumed its place among the sciences. Its study was no longer obscured by gold-hunting nor limited to the preparation of medicines. There came a period of qualitative chemistry, a step toward the higher quantitative work and a great step forward from the haphazard chemistry of the past. There are dangers in relying upon qualitative tests alone and mistakes were made. For a while the guiding principle seems to have been the old saying that similar appearances are due to similar causes, a saying which has much plausibility and yet might lead to error. Minerals were analyzed and new substances discovered. Some synthetic work was done and new compounds formed. There was a growing desire to know something of the underlying causes, to understand better the phenomena observed, and to find explanations for them. Processes in the laboratory became more frequently those of the "wet way" where solutions were concerned. To insure accuracy and assist judgment more frequent use was made of the balance and there was a return to logic and philosophy as in the time of the Greeks. And so the progress made in the seventeenth century far exceeded that of all the previous centuries.

**Robert Boyle (1626-1691).**— First among those to pursue the study of chemistry from a noble desire for a deeper insight into the workings of nature was Robert Boyle. He was born in Ireland, lived at Oxford, and aided

in founding the Royal Society of England. He antagonized the alchemists, except in respect to a belief in the possible transmutation of the metals, and also contended with the views of Van Helmont, though he agreed that one must look to chemistry for the solution of the greatest problems of medicine. He was the first to apply Bacon's inductive method to the science and maintained that experiment alone was the proper basis for theory and that all theories must be tested by experiment. Before attempting any theorizing as to explanations he went to work to correct the faulty experiments and imperfect observations of the past and thus to clear the path for an understanding of the phenomena.

**Experiments upon Air.** — Boyle's experiments were largely upon air and water, choosing two of the commonest and yet most instructive substances in nature. The knowledge of the first, physically and chemically, was greatly advanced by him. He made use of an improved air-pump and examined the behavior of different substances in a vacuum. He enunciated the law of pressure for gases, namely, that the volume of a gas varies inversely as the pressure. This is still known as Boyle's Law. Experiments were carried out also as to the height, weight, and density of the atmosphere. Furthermore, he showed that something in the air was consumed by breathing or by the burning of a substance in it. This was, of course, only a verification of observations made long before. He proved that an increase in weight was caused by calcination and that the calx was specifically lighter than the original metal. The calcination of such a substance as lead, he showed, consumed air. It is strange how near his experiments brought him to impor-

tant truths. But he was not always happy in the interpretation of his results. He could see many faults in the theories of the times but seldom saw his way clear to establishing a theory of his own.

**Constitution of Matter.** — In studying the nature of the various substances known to him Boyle devised a system of qualitative analysis, arranging these substances into classes and groups. Vegetable coloring matters were used by him as indicators for acids and bases. Regular reagents were introduced by him with directions for their use. Many of his tests we make use of at the present day as, for instance, ammonia was driven out of its compounds by lime or caustic potash and tested for by its fuming with hydrochloric acid. His ideas as to the constitution of matter were much like those of the present. He considered all bodies to consist of very small particles and believed that the union of these particles gave compounds. Decomposition was impossible until the attraction between the particles had been overcome. According to this hypothesis, the differences between bodies were due to the inequalities in the form, structure, and movement of the particles. In his opinion one or two primal elements would suffice to explain all the varieties of substances in nature. This comes rather close to the hydrogen-helium hypothesis of the present. And yet when he came to apply his hypothesis his limitations became very apparent. The particles of water, he supposed, might under certain conditions be so grouped and set in motion as to form the substance which we know as air. It is easy to see that all through the ages one of the great puzzles set for thinking men has been the invisible atmosphere surrounding us, forming and buoying up its

cloud masses and pouring down its floods of water, hail, or snow.

In defining a chemical compound as one formed by the union of two or more components which lose their properties, the compound having new and different properties, Boyle distinctly placed himself on the plane of the modern chemist. Differences in affinity were also recognized by him in preparing tables giving the relative affinity of various metals towards the acids. Several chemists busied themselves with such lists in later years.

## CHAPTER V

### THE CHEMISTRY OF COMBUSTION

The most important reaction in chemistry is that of oxidation, known in its common, everyday occurrence as combustion. A rational and satisfactory explanation of this process was therefore a fundamental necessity for the progress of the science. Some progress might be attained under a false theory but there would be many misconceptions and errors. The theory of combustion which prevailed through most of the eighteenth century was called the phlogiston theory. This theory was first imperfectly stated by Becher in the latter part of the seventeenth century but was more clearly given by Stahl, who introduced the term phlogiston, or fire substance. Both of these were German chemists. Since the theory was false, it obscured or twisted facts and necessarily retarded progress.

**Phlogiston Theory.** — The theory may be briefly stated as follows. The purpose was to explain the changes which occur when a metal is heated in the air and changed into a powder. The metal was said to be calcined and the resulting powder was called a calx. Of course the burning of wood or coal with the formation of ashes and many similar operations come under the same heading. According to the phlogistics, as they were called, the metals lost something which was the hypothetical phlogiston and the calx remained. The metal, then, was a compound

made up of calx and phlogiston. This phlogiston was present in all combustible substances as coal, inflammable gases, etc., and some substances contained more than others. The supposed proof of the theory lay in the fact that when a metallic calx was heated with a substance rich in phlogiston, such as coal, the metal could be restored. Thus, when iron was heated in the air a red calx was formed, copper gave a black calx, and metallic iron or copper could be recovered by heating these with coal.

The question was asked: What is this phlogiston and why can no one get hold of it to examine it? Wild and absurd conjectures were made as to its nature, some of these placing it beyond experimental evidence. Again the question of weight relations arose, thus appealing to the balance, and it was found that the calx weighed more than the original metal. How could that be possible if the metal had lost something? The explanation offered as to this was that when wood was burned the flame ascended and hence the fire substance, or phlogiston, possessed levity rather than gravity and when combined in substances made them lighter. The trouble was that the discussion became one of logic with neglect or disregard of facts. One of the last of the phlogistics was Priestley, who argued stubbornly in behalf of his views until his death in 1804.

**Composition of Air.** — One of the causes of the failure to recognize the true explanation of combustion was ignorance as to the composition of the air which was essential to all combustions. Of course the necessity for air in burning anything had been recognized in very early times. The phlogistics explained this by maintaining

that phlogiston could not escape unless combined with air. Animals breathing in air were supposed to breathe out phlogiston.

**Hooke's Theory of Combustion.** — During the latter half of the eighteenth century there were three distinguished chemists in England, all of them adherents of the phlogiston theory and its earnest defenders. These were Black, Cavendish, and Priestley. They were either in ignorance of or attached no importance to the theory of Hooke, their fellow countryman, as to combustion. This theory, published in 1665 in his *Micographia*, claimed to be based upon experiment. It is contained in twelve propositions but may be briefly stated as follows: Air supports combustion but this combustion will take place only after the substance has been sufficiently heated. There is no such thing as elemental fire. This combustion is caused by a substance inherent in and mixed with the air which is very much like, if not the very same as that which is fixed in saltpeter. Mayow a little later recognized that the air contains a substance which unites with metals when they are calcined. This substance will also change venous blood to arterial, as shown by the color. It is contained in saltpeter, for substances burn when mixed with saltpeter. He therefore called this component of the air *spiritus nitro-aerius*.

It was the discovery of oxygen that struck the death blow to the phlogiston theory. Strange to say it was discovered and identified in 1774 by Priestley and independently by Scheele, both of them phlogistics, who failed to grasp its bearing upon the phlogiston theory. In the hands of Lavoisier, the great Frenchman, it revealed the secret of combustion. Priestley visited Paris and



showed Lavoisier how to prepare it by first heating mercury in the air until the red precipitate was formed. When this was placed under a bell-jar from which the air had been pumped and was heated, the original mercury was regained with liberation of a gas which would support combustion. By weighing the mercury, then the red precipitate and the gas given off, it was shown by Lavoisier that the increase in weight of the mercury in forming the red precipitate or calx corresponded with the weight of gas which was taken up by it. Lavoisier called this gas oxygen or the acid-producer. Priestley called it dephlogisticated air. The discovery of hydrogen by Cavendish and the fact that on burning it formed water completed the proof of the new theory that combustion is simply combining with oxygen or oxidation. Cavendish called this gas inflammable air but Lavoisier named it hydrogen or the water-former.

## CHAPTER VI

### THE NEW CHEMISTRY

It is manifest from the preceding pages that chemistry was now developing into a science. The gathering of facts was going on apace. The chief lack was a rational system of arrangement based on the distinctive characteristics of the substances involved. A distinction had already been drawn between compounds and elements. An element was a simple body made up of just one kind of matter. For instance, no lighter nor heavier substance could be got from it. A compound was made up of two or more different substances. Since the term element was still in great measure reserved for the four primal principles of the Greeks, what we now call elements were spoken of as simple bodies. The finding of new elements and compounds now depended upon analytical results.

**Analysis.** — Tests for the elements had to be devised depending upon their specific properties. To simplify the work these tests must be systematically arranged. Analysis in the wet way was first outlined by Boyle and chiefly applied to mineral waters, which attracted much interest and investigation. Bergman (1735–1784), a Swedish chemist and professor at the University of Upsala, enlarged the number of reagents and studied their action on such substances as occur most commonly. This branch of the science then began to be exact. In quantitative analysis, also, he took an important step forward

in abandoning the plan of actually isolating the various constituents and introduced the method of transforming each constituent into some compound whose exact composition was known and which could be easily isolated. Sometimes the composition was unknown and the simple body present had never been separated, as silica or alumina, and in such cases the analyst had to content himself with separating the compound which was to him, for all intents and purposes, a simple body. Bergman analyzed a large number of minerals and other substances. For those which he could not dissolve in water or acids he introduced the method of fusion with caustic or carbonated alkalis so as to bring them into solution, a most important addition to analytical methods. Some of his researches were masterly and quite in the spirit of the present time. Such, for example, was his work on the differences between wrought iron, steel, and cast iron; also upon the cause of "cold shortage" in iron. Sweden produced much iron and this made the work of Bergman especially important for his native land. He also analyzed the air and reported: "Common air is a mixture of three elastic fluids; free aerial acid (carbonic acid) but in such small quantities that it does not sensibly alter the color of litmus; an air which can neither serve for combustion nor for the respiration of animals, which, therefore, we call vitiated air until we know its nature perfectly; and lastly an air absolutely necessary for fire and for animal life which forms pretty nearly the fourth part of common air and which I regard as pure air." In this he was the first to give a clear statement as to the quantitative composition of air. This was based on his own and on Scheele's experiments.

**Scheele (1742–1786).** — Probably no one before nor since his day has made so many important discoveries as Scheele, a fellow countryman of Bergman. He was a pharmacist, poor and reserved, and yet out of his poverty and imperfect appliances achieved wonderful success in mastering nature's secrets in his short life of forty-three years. His letters have been published in modern times and they reveal how much he knew and how far he was ahead of his contemporaries. His first work was upon the organic acids, many of which he isolated and examined. Among organic acids he discovered tartaric, oxalic, malic, citric, and gallic; among inorganic, molybdcic, tungstic, and arsenic. Three elements were discovered by him, oxygen, manganese, and chlorine; and one new alkaline earth, baryta. He prepared oxygen by heating manganese dioxide in the same year that Priestley prepared it from mercuric oxide. His chief deficiency lay in the matter of understanding phenomena and formulating theories. It is evident that his acceptance of the phlogiston theory led him astray in this.

**Analysis of Air.** — Scheele examined the atmosphere with a view to determining what part it played in the phenomena of combustion. First, he tried the action of various substances upon the air. These substances were supposed to contain phlogiston and hence, he reasoned, would give it off to the air held in a closed space. Some of the substances experimented upon were moist iron filings, fresh moist iron hydroxide, etc. He observed that the air diminished in amount and that the portion left was incapable of supporting combustion. This diminution of volume he thought was due to an absorption of phlogiston by the air, and hence the air should be specifi-

cally heavier. To his surprise he found the opposite to be true. A part of the air had disappeared and the remainder was specifically lighter. Scheele concluded that the atmosphere consisted of two different kinds of air — one having no power of taking up phlogiston and hence being left behind in combustions, the other taking up phlogiston in an enhanced degree. This was his fire-air, or Lavoisier's oxygen, though as yet unknown to the great French chemist. His experiments as to the relative proportions of these two constituents fall far behind in accuracy those made a little later by Cavendish. He pursued his investigation further and was badly misled by the phlogiston fancy. Thus, in explanation of the experiment just described, he concluded that the union of phlogiston with one part of the air caused a diminution in volume because a tenuous, delicate substance had been formed and this escaped through the pores of the glass vessel. This delicate substance was, in his opinion, fire or heat. Fire then was a compound of fire-air and phlogiston. This fire or heat he believed could be decomposed into its constituents by the use of such substances as would combine with the phlogiston and set the fire-air free. He thought he could do this with nitric acid. He distilled niter and oil of vitriol, or sulphuric acid, and obtained nitric acid and a gas which supported combustion better than the air itself. This supposed decomposition of heat he effected further by heating other substances as manganese dioxide and niter. Thus he isolated oxygen or fire-air, as he called it.

**Boerhaave (1668–1738).** — There was in Holland at this time a very influential chemist named Boerhaave, who was a professor at the University of Leyden and who

did much to clear the way for the new chemistry by exposing the errors of the alchemists and their successors and the falsity of their views. He tested with care and accuracy everything that he taught, and spared neither pains nor time to have his observations correct. For instance, the alchemists maintained that mercury could be fixed in the form of a fireproof metal without the addition of any other substance. Boerhaave kept mercury at a somewhat raised temperature in an open vessel for fifteen years without noting any change. So, too, when heated higher in a closed vessel for six months no change could be detected. It had also been maintained that if mercury were repeatedly distilled, a more volatile essence with peculiar properties could be obtained. Boerhaave carried out this distillation five hundred times without securing the essence. His skill in interpreting facts and the clearness of his theoretical views made him an excellent teacher, and his text-book on chemistry went through repeated editions and translations into other languages and was used for many years after his death. He seemed to take little notice of the phlogiston theory.

**Fixity of proportions.** — It is noteworthy that another foundation stone was being laid without discussion or statement, and that was in the general acceptance of the essential conception that the constituents of each definite compound were always in the same definite proportion. This grew naturally out of the experience of the analytical chemist who tested the quantitative relations with his balance. If these proportions were not fixed his analytical work was futile. No question was raised concerning this until the close of the century.

**Berthollet (1748–1822).** — About the beginning of

the nineteenth century the question was taken up by Berthollet, one of the first and ablest of Lavoisier's supporters. He contended that these proportions were not constant but that the relative masses of the combining substances determined the proportions in which they would unite to form compounds. His views met with immediate opposition on the part of leading chemists and gave a new direction to their investigations. His chief antagonist was his fellow countryman, Proust, and the exact quantitative composition of many compounds was worked out. In the course of these investigations it was found that metals might have several oxides and also that hydroxides existed. The victory finally remained with Proust. This problem has arisen in subsequent years as analytical methods improved greatly in exactness, but the definiteness of proportions seems established.

**Views as to Affinity.** — Several chemists had turned their attention to the attractive force which brought about combination between different substances and held together the different particles in a compound. The name affinity had been given early to this combining force. While there was no measure for this force nor theorizing as to its nature, several chemists endeavored to settle the relative strength of attraction between different substances and constructed what were called affinity tables. The question comes down to this: Which metal, iron or copper or lead, has the greatest affinity for sulphur; or which acid has the greatest affinity for soda? Such tables were helpful in those times but failure to recognize the influence of other factors made them of slight scientific value. Bergman's table was one of the

best of these early efforts, since it shows a knowledge that affinity phenomena depend upon the temperature and physical state.

RELATIVE AFFINITY FOR SULPHURIC ACID

<i>Wet Way</i>	<i>Dry Way</i>
Baryta	Phlogiston
Potash and soda	Baryta
Ammonia	Potash
Alumina	Soda
Zinc oxide	Lime
Iron oxide	Magnesia
Copper oxide	Metallic oxides
Mercury oxide	Ammonia
Silver oxide	Alumina

Berthollet has exerted a lasting influence upon the views concerning affinity and showed in high degree the power of abstract conception and logical development of chemical ideas. He reasoned that affinity was by no means a simple force and easy to determine and measure, but was influenced by temperature, physical state, cohesion, and especially by mass. The latter largely determined the course of chemical reactions. Thus rock made up of the hardest silicates is weathered or gradually decomposed by the action of rain containing one of the weakest of acids, carbonic acid.

**Lavoisier (1743–1794).**—The materials were now gathered and the architect and builder was at hand. Lavoisier has justly been called the Father of Modern Chemistry. Born in Paris, carefully educated, gifted in intellect, accurate in work, and with a clear, far-seeing vision, he was one of that type which is born now and then in time of need to point out the path for succeed-



ing generations. There may be many priests in the temple of science but only at long intervals does a prophet arise. At the early age of twenty-one he was awarded a medal by the government for a memoir upon the best and most economical method of lighting the streets of a city, and at twenty-five he was chosen an adjunct member of the French Academy. Chemistry did not receive the whole of his attention at first but shared it with geology, mineralogy, and mathematics. The remarkable discoveries which were being made in chemistry, especially in connection with gases and the atmosphere, drew him, however, to devote all his energies to chemistry. For more than twenty years he was indefatigable as a worker, repeating the experiments of others and pursuing fresh lines of inquiry. And then his life and activities were cut short by the coming on of the French Revolution. He was executed by Robespierre in 1794 at the age of fifty-one.

**Character of his work.** — Lavoisier's most valuable services were as an interpreter of his own work and that of others. He showed a clear insight into the causes of phenomena, a quick perception of the importance of the many discoveries of his time, and a comprehensive grasp of facts and their inter-relation and connection. These powers enabled him to detect the errors and falsity in the theory and reasoning of the chemists of his age and to lay the basis for the new chemistry of the quantitative era. Exclusive importance had been attached hitherto to visible phenomena, whereas he introduced a deeper study of chemical reactions and the relations of quantity.

**Experiments on Combustion.** — In 1774 he published

his first strictly scientific volume under the title: *Essays Physical and Chemical*. In this he described all that had been done on the subject of gases from the time of Paracelsus down through the work of Priestley. He also gave an account of his own experiments. He showed that when metals were calcined their weights increased and that a portion of air, equal to their increase in weight, had been absorbed from the surrounding atmosphere. He burned phosphorus in the air and observed the decrease in the volume of the air and the increase in the weight of the phosphorus. We are apt to think that the mere proof that the metallic calx weighed more than the metal was sufficient to disprove the phlogiston theory. Both parts of the proof given by Lavoisier were necessary and even then he felt it to be insufficient and merely preliminary to his final work. It had already been shown that the calces were heavier than the metals from which they came and that they were specifically lighter, but the phlogistic chemists had disregarded these weight relations, taking refuge in the hypothesis of a phlogiston unaffected by gravity or actually making substances lighter by its presence.

**Composition of the Atmosphere.** — In Lavoisier's further attack upon the phlogiston theory he examined the atmosphere and its constituents. In the book mentioned above he tells nothing to indicate that he knew the composition of the air or the distinct nature of oxygen. These were discoveries reserved for Scheele and Priestley, but Lavoisier was evidently very near to their discovery and was only anticipated in this. When Priestley visited him shortly afterwards and showed him how to prepare oxygen from the red oxide of mer-

cury, Lavoisier immediately saw what the discovery meant and how it made plain much that was unexplained in his own work. It altered his views and suggested to him the nature of atmospheric air and of the changes taking place in the calcination of the metals. For twelve years he worked over these problems, performing a great number of experiments with an accuracy hitherto unknown. He then boldly proclaimed the non-existence of phlogiston and replaced this old theory by a new one, explaining the phenomena of combustion and reduction as due to the combination with oxygen or its separation. He first won to his views the distinguished French chemists of his day, and before many years all men of standing in the science gave in their adherence to the new explanation offered by him, except a few who could not give up views which had formed the basis of all their scientific work. The year 1786 may be fixed as the date of the overturning of the old theory.

## CHAPTER VII

### THE FOUNDATIONS

**Composition of Water.** — Lavoisier's triumph over the supporters of the phlogiston theory was complete when he made public his researches upon the composition of water. The hydrogen evolved when a metal was acted upon by an acid was considered at first by some to be identical with the hypothetical phlogiston and Cavendish, the discoverer of hydrogen, maintained this view to the end of his life. When Cavendish's further discovery of the formation of water by the burning of hydrogen was told to him Lavoisier saw his way to solution of this puzzle and lost no time in repeating so important an experiment. The explanation he offered to the reaction between the acid and the metal was that the hydrogen came from the water, which took part in the reaction; at the same time the oxygen combined with the metal and thus it was not the metal but the metallic oxide which was dissolved by the acid. In other cases, as in the action of nitric acid upon copper, the metal decomposed the acid and not the water, taking oxygen from it to form an oxide, and this was dissolved by the remainder of the acid. The deoxidized part of the acid, he said, escaped as a gas. A prophet in chemistry is not inspired and can only do his best with such facts as are known to him. Hence one must be lenient as to the instances in which these views fail of the full truth.

**Transmutation of Water.** — One of Lavoisier's early investigations bore upon the nature of water and well illustrates his accuracy, thoroughness, and acute reasoning. It had been noted by many earlier investigators that when pure water was boiled for a long time in a glass vessel a white residue was found in the vessel after evaporation. This was long regarded as a conclusive proof that water could be changed into earth. Appealing to the balance as arbiter, he first weighed his glass vessel and then, after heating pure water in it for one hundred days, found there was no change in the weight of the vessel and its contents; that is, the vessel and the water weighed the same after the heating as before. When the water was removed the vessel weighed less than the original weight of the empty vessel. When he evaporated the water he obtained a residue which he found corresponded in weight to the loss in weight of the empty vessel. He, therefore, concluded that water on being heated is not changed into earth but that a part of the matter of which the glass is composed is dissolved by the water. The analytical work of Scheele afterwards showed that this residue had the same components as the glass, thus confirming the work of Lavoisier. The old notion of transmutation was thus proved to be false and the important generalization was established that matter can neither be destroyed nor created. This principle of the conservation of mass is one of the fundamental laws of science. Of course, Lavoisier's work was only the beginning of the series of experiments on this subject which after many years established the law.

**The Atmosphere.** — Priestley performed various experiments upon the gases known to him with the aid

of the pneumatic trough which he practically invented. He discovered the relation of plants and animals to the atmosphere and the approximate balance maintained by their action upon it. His inaccurate analytical work and his devotion to the phlogiston theory prevented his reaching a true explanation of the facts observed by him. Scheele determined the composition of the atmosphere, and later Cavendish made an exact analysis of it. Lavoisier had shown that it consisted of oxygen and nitrogen and had determined the proportions of each. He was, therefore, in a position to complete and explain the work of Priestley. The processes of breathing and of calcination were chemically analogous. Oxygen was drawn into the lungs by the respiration of animals, and there he thought it combined with carbon and the carbonic acid, or the "fixed air" of Black, was breathed out. This was noxious to other animals and this it was which was removed by plants.

**The Nature of Heat and of Matter.** — Lavoisier disproved the old ideas as to the elemental nature of heat; yet apparently he believed it to have material existence. He wrote of a *matière de chaleur* which he also called *calorique*. He ascribed to it a fluid (gaseous) nature but said it had no weight. His idea and also his views upon the constitution of matter are perhaps best given by a citation from his *Reflexions sur le Phlogistique*. Matter, he says, consists of small particles which do not touch one another, otherwise the diminution in volume on cooling could not be explained; between these particles is the *calorique*. In gases there is most of this *calorique*; in solids least. In his experiments with Laplace upon specific heat he showed that solids differ in their

capacity for taking up this heat. His views are in partial accord with the modern theory of heat when he comes to define that form of energy. He says, "Heat is the result of invisible motion of the particles, the sum of the product of the masses multiplied by the square of the velocities."

**Investigation of Organic Substances.** — Lavoisier also occupied himself with organic chemistry, or the chemistry of life products, and made a beginning towards a scientific study of it in devising a method of analysis by which these substances could be burned and the water and carbon dioxide formed could be measured. Of course such a method was impossible until the composition of these two substances themselves was definitely fixed. That these substances, as well as carbon in imperfect combustions, were formed on burning organic substances had long been known. Their nature, however, and the question as to their pre-existence in the organic substances had been the subject of much discussion. Through his analysis Lavoisier determined that all organic substances were composed of carbon and hydrogen, sometimes oxygen, and less often nitrogen and other elements.

**Theory as to Acids.** — Thus much false theory and confusion in the science had been removed and the foundations for a new system had been laid. Simple bodies or elements were recognized; these formed compounds by the union of their particles drawn together by an attractive force, affinity, and heat had its part to play in these masses. The multiplicity of compounds made necessary a system in their arrangement — such a system as would bring out and explain their interrelations. The funda-

mental reaction was oxidation. Lavoisier recognized the parts played by oxygen in the formation of acids, of oxides, and of salts. For these he gave the simple definitions which form the foundations of the new chemistry.

1. An acid results from the union of a simple body, ordinarily non-metallic, with oxygen.
2. An oxide is a compound of a metal and oxygen.
3. A salt is a compound of a metal and oxygen.

This system was extended further for the sulphides, phosphides, etc., but the true nature of the chlorides was not known and the hydracids were discovered some years later. With their discovery the part played by hydrogen became clearer, but a century had to pass before this could be even approximately explained.

The overthrow of the followers of Stahl and the acceptance of Lavoisier's ideas ushered in a new era in chemistry. A new nomenclature was called for and it was created by Lavoisier and the French Encyclopedists. Of course, as knowledge grew mistakes had to be corrected and changes made, but the essential foundations had been laid.

**Elements.** — It will be helpful here to trace the growth in the ideas regarding the elements, as the proper definition of these was one of the most important and far-reaching changes introduced by the new system. Alchemists and chemists seemingly had not attached much importance to this matter up to this time and the distinctions drawn were rather hazy. Hitherto the name had covered mainly philosophical speculations; henceforward they were to form the basis of systematic chemistry. The four-element theory of Empedokles



and Aristotle was a dream, a philosophical figment without basis or confirmation in real experiments. These elements were regarded as principles with certain material characteristics, entering, all or some of them, into every known substance and not necessarily capable of independent existence themselves. Some chemists, indeed, undertook to prove that certain substances did contain these principles. There was no attempt, however, at a general proof.

The first clarifying definition was given by Boyle (1661), who was far ahead of his times. He defined elements as "certain primitive and simple bodies which, not being made up of any other bodies, or of one another, are the ingredients of which all those called perfectly mixed bodies are immediately compounded, and into which they are ultimately resolved." He did not believe himself warranted by the knowledge then possessed in proclaiming the positive existence of such elements.

During the phlogistic period less and less importance was attached to the old ideas as to elements, and the belief gradually sprang up that a true element must be something which could be prepared and was not subject to change. Macquer, in his *Dictionary of Chemistry*, defined elements as "those bodies which are so simple that they can not by any known method be decomposed or even altered and which also enter as principal or constituent parts into the composition of other bodies which are therefore called compound bodies." But he adds, "The bodies in which this simplicity has been observed are fire, air, water, and the purest earths." Black proved that certain chemical substances were

possessed of a constant and definite composition and fixed properties, unalterable, and hence simple bodies or elements. Lastly, Lavoisier in this *Traité de Chimie* enunciated his definition of an element as follows: "An element is a substance from which no simpler body has as yet been obtained; a body in which no change causes a diminution of weight." Nearer to the modern theory he could not come without knowledge of the atoms and of allotropism. Under such conditions a number of substances were classed as elements which did not belong to the list. Lavoisier first classed the metals as elements.

**Spread of the New Chemistry.**—The teachings of Lavoisier or, as Fourcroy styled it, the "French Chemistry," speedily found acceptance in France, in England, and (through the influence of Klaproth) in Germany, where at first the opposition had been intense. By the close of the century chemists almost universally had given in their adherence to the new doctrines. Chemistry now had the basis of a true theory and, what was of greater value, the knowledge that theories could be deduced only from the weight relations of actually occurring reactions. There were to be no baseless and delusive dreams for the future, although mistakes might be made in the interpretation of facts. We find that though facts rapidly increased in number theories were slowly evolved and gained acceptance only after most careful weighing and testing in every known way. In this respect the experience of the past was invaluable. Great names, so-called authorities, might gain a hearing for a theory but had to show that it was the best logical explanation of facts and laws. Men had cast off forever the burden of authority in science.

**Black (1728–1799).**— There should be mentioned at this time three distinguished chemists, who were of great service in making important discoveries and improving methods and made noteworthy contributions to the progress of chemistry. The first of these, Joseph Black, was of Scotch parentage and, while a student at the University of Glasgow, undertook an investigation into the cause of the causticity of magnesia, lime, and the alkalis. Caustic lime, or quick lime, was made, for instance, by the burning of limestone. Its causticity was supposed to be conferred upon it by the heat of the fire, and this could be transferred by the proper treatment of a mild alkali with quick lime to the caustic alkali. Using magnesia alba in his experiments, he found that there was a loss of weight on heating it and the substance magnesia usta was formed. On treating magnesia alba (magnesium carbonate) with oil of vitriol there was effervescence from an escaping gas, and epsom salt or magnesium sulphate was formed. This was also formed from magnesia usta (magnesium oxide) and oil of vitriol but there was no escaping gas. Mild alkali effervesces on the addition of oil of vitriol but caustic alkali does not. The reasoning then was plain. The presence of the gas set free from magnesia alba and not from magnesia usta makes the difference between the two, and it is also the gas present in mild alkali which enables it to change magnesia usta into magnesia alba, leaving caustic alkali. The burning of magnesia alba or of limestone consists then in the driving off of this gas which Black called "fixed air." This fixed air was afterwards studied by Priestley, who invented the invaluable pneumatic trough to aid him in his researches.

Priestley identified this with the gas issuing from fermentations in breweries. Thus carbon dioxide became known. Priestley later discovered carbon monoxide. Black devoted much time to experiments upon heat and made the brilliant discovery of latent heat, or the heat concerned in changes of physical state.

**Priestley (1733–1804).**—The second of these chemists was Priestley who was born near Leeds in England and was largely self trained, as he had the advantage of a high school training only. On account of political and religious persecution he left England, and the later years of his life were spent in America, near Philadelphia. Priestley was a brilliant investigator, performing many most striking experiments. He was not thorough, however, nor very accurate, possessing little analytical skill, and was lacking in the scientific acumen needed for the proper interpretation of his results. It was upon the gases that his most valuable work was done, his pneumatic trough enabling him not only to discover new gases but to investigate the properties of a number of those already partially known.

**Discovery of Oxygen.**—His method of experimentation is well illustrated by his account of his discovery of oxygen. “Having procured a lens I proceeded with great alacrity to examine by the help of it what kind of air a great variety of substances would yield, putting them into vessels filled with quicksilver and kept inverted in a basin of the same. After a variety of other experiments I endeavored to extract air from *mercurius calcinatus per se* (red oxide of mercury) and I presently found that by means of this lens air was expelled from it very readily. Having got about three or four times

as much as the bulk of my materials I admitted water to it and found that it was not imbibed by it. But what surprised me more than I can well express was that a candle burned in this air with a remarkably vigorous flame. I was utterly at a loss to account for it." His experiments showed him that this air "had all the properties of common air, only in much greater perfection," and he called it "dephlogisticated air," regarding it as very pure ordinary air.

**Study of the Atmosphere.** — Priestley seems to have looked upon all gases as easily changeable one into the other, at least in the first part of his work. He made many experiments as to the action of the various gases known to him upon animals and plants. He would place a mouse in a jar of the gas and notice the effect upon its breathing and general life processes. Plants were grown in similar jars and the result upon the growth noted. He showed that air, which had become noxious through breathing or the burning of a candle, could be restored to its original condition by growing a plant in it. This, he said, was due to the impregnation with phlogiston in the first case and to its removal in the second. "It is very probable," he wrote, "that the injury which is continually done to the atmosphere by the respiration of such a number of animals as breathe it and the putrefaction of such vast masses both of vegetable and animal substances exposed to it is, in part at least, repaired by the vegetable creation." He was unable to explain how this was done as he was a poor analyst. This lack of analytical skill is shown in his experiments on the formation of water by exploding mixtures of hydrogen and oxygen (plus air) in a copper globe. He obtained

a blue liquid whose nature he was unable to determine. The analyst whose aid he solicited showed him that it was a solution of copper nitrate in water. The fact that nitric acid was thus formed induced him to deny that water was a compound of oxygen and hydrogen. In the hands of Cavendish, a more thorough and careful investigator, this discovery led to the demonstration of the composition of nitric acid.

**Views as to Combustion.** — He held that all combustible substances contained hydrogen. This was, in his view, phlogiston. The metals contained it and their calces, or oxides, were simply the metals deprived of hydrogen. Thus he showed that when iron oxide was heated in hydrogen gas the hydrogen was absorbed and metallic iron formed. Rich iron slag was, in his opinion, iron with some hydrogen retained. To prove this, it was mixed with the carbonates of the alkaline earths and heated strongly. This gave him an inflammable gas and, according to his belief, all inflammable gases were hydrogen in a more or less impure condition. It was later that he discovered carbon monoxide — also nitrogen dioxide — and he found that water could be impregnated with carbon dioxide and suggested its use in disease.

## CHAPTER VIII

### THE ATOMIC THEORY

**The Proposition of Lavoisier.** — The ground work of the new system of chemistry was laid by Lavoisier in the following propositions:

1. In all chemical reactions, only the form of the materials changes, the quantity remaining the same. The substances used and the products obtained can be brought into an algebraic equation by means of which any one unknown member may be calculated.

2. In all combustions the burning body unites with oxygen, and in general an acid is formed by combustion of a non-metal, and a metallic calx is formed by combustion of a metal. This calx is an oxide.

3. All acids contain oxygen united with a base or a radical which, in the case of inorganic substances, is generally an element; in organic substances it is made up of carbon and hydrogen, and often contains nitrogen and phosphorus as well as other elements.

The next stage in this inquiry into compounds and combination concerned the method or process of combining. What were the combining particles? Here recourse to the Greek philosophers was once more necessary, but sure and enduring foundations had to be laid in support of the old-world vision which had been practically lost sight of. A new Atomic Theory became a necessity. For this we are indebted to John Dalton.

**Richter (1762–1807)** — It is well, however, to refer first to the work of Richter who, through careful analytical work, constructed a table giving the proportions by weight in which substances combine. This was a distinct advance on the affinity tables which have been mentioned. Richter had noted with keen interest that one neutral salt could react with another, and that by interchange two other neutral salts could be formed without change of reaction towards test-papers. The neutrality was preserved, showing an equivalence between the amounts entering into combination. This was a most important observation, having its bearing on the law of definite proportions, and the table of equivalents may be regarded as the forerunner of the atomic weight table.

**Dalton's Atomic Theory.** — John Dalton (1766–1844) was more of a mathematician and physicist than a chemist. Most of his life was spent in Manchester, England, as instructor in mathematics and natural philosophy, which then included some chemistry. He was very poor, beginning to support himself by teaching at twelve years of age, and was largely self taught. He was forced to make most of his own apparatus and lacked skill in carrying out experiments, and in chemical manipulation fell far behind Priestley. But he excelled in logical deductions and in generalizations from his facts, his aim being the establishment of general, underlying laws. Priestley was a brilliant discoverer; Dalton a clear, logical, mathematically trained thinker.

**Constitution of Mixed Gases.** — For years he had been interested in meteorological observations. Those which he made upon dew and aqueous vapor existing in the



air led him to the publication in 1801 of an important paper upon the *Constitution of Mixed Gases*. This was followed by other papers on the properties of gases and these prove that he had formed the idea that gases were made up of small, distinct particles. He wrote of the pressure upon them and the repulsion between these particles and stated that "A vessel full of any elastic fluid (gas) presents to the imagination a picture like one full of small shot." He reported the discovery of some of the fundamental laws of gases. First, there was the law of expansion by heat, according to which all gases independent of their nature expand equally on heating. Another, the law of partial pressures, is still known as Dalton's Law. He found that the composition of the atmosphere is the same at low and high temperatures and that heavy gases diffuse upward into light and light downward into heavy, thus forming always a homogeneous mixture. He noticed that water did not dissolve all gases alike but in amounts varying with their nature. As this matter of solution was a mechanical operation in his opinion, he reached the following conclusion: "I am persuaded that this circumstance depends upon the weight and number of the ultimate particles of the several gases, those whose particles are lightest and single being least absorbable and the others more. An inquiry into the relative weights of the ultimate particles is a subject, as far as I know, entirely new." He presented before the Manchester Literary and Philosophical Society in 1802 a paper which included "a table of the relative weights of the ultimate particles of gaseous and other bodies."

To account for the diffusion of gases and so complete

his vision of the atmosphere, Dalton had to provide a repulsive force. This he solved "without letting in any other repulsive force than the well-known one of heat. . . . There was but one alternative left — namely, to surround every individual particle of water, of oxygen and of azote with heat and to make them respectively centres of repulsion, the same in a mixed state as in a simple state. . . . Atoms of one kind did not repel the atoms of another kind but only those of their own kind."

Of course, the idea of the existence of atoms was neither new nor original with Dalton. The conception of the Greek philosophers was that: "The bodies which we see and handle, which we can set in motion or leave at rest, which we can break in pieces and destroy, are composed of smaller bodies which we cannot see or handle, which are always in motion and which can neither be stopped nor broken in pieces, nor in any way destroyed nor deprived of the least of their properties."

Something of this conception was held and felt all through the earlier days of chemistry. The physicists Newton and Bernouilli held it (the latter believing the pressure exerted by a gas upon the enclosing walls to be due to the constant bombardment of the atoms), although merely the term particle was used by them and by Lavoisier, in whose mind the same idea was present. The credit which belongs to Dalton is that he took this dream and by means of collected facts and laws gave it that confirmation which was necessary in order that it might be ranked as a theory. While its conception was largely on physical reasoning, the grounding which brought general acceptance and established it as a fundamental theory of science came when it served as the only

satisfactory explanation of the fundamental laws of chemistry. This was also the contribution of Dalton.

**Law of Constant Proportions.**—So far the theory as to the existence of atoms had a physical rather than a chemical basis. Its support came when it was recognized as the logical explanation of the basic laws of chemistry. The first of these was the law of constant proportions, namely, that in any compound the relative proportions of the constituents are definitely fixed and will always be found the same. This, one might say, had been tacitly accepted by all analytical workers as the result of their experience and a necessary basis for their work. As the number of compounds known increased and analytical methods improved in accuracy some doubt arose as to the fixity of these proportions. A discussion was carried on for several years between two distinguished French chemists, Berthollet (1748–1822) and Proust (1755–1826), with regard to the existence of any such regularity, and in the course of it much valuable analytical work was done and a number of new compounds discovered. This discussion aroused the interest of the leading chemists of the time. Berthollet maintained that the proportions were variable and noted a number of apparent cases among oxides and other compounds. Proust showed that some of these oxides contained hydrogen, thus discovering the class of hydroxides, and in his analyses of the different oxides very nearly arrived at the law of multiple proportions. One of the good results of the controversy was to bring about a clear distinction between compounds and mixtures. Berthollet lost most of his supporters before the close of the controversy. Another earnest supporter of the law of

definite proportions was Richter, though probably his work was unknown to Dalton. He published (1792-94) the results of his work upon the proportions by weight in various compounds under the title of "A Foundation for the Stoichiometry or Art of Measuring Chemical Elements." This is the first work on systematic quantitative analysis. It was a decade or more before Richter's excellent work received appropriate recognition.

**Law of Multiple Proportions.**—It has already been pointed out how the fact that when two elements combine to form a compound the proportion of each is absolutely fixed and constant became firmly incorporated in the science and a recognized, even if unstated, law. This to the seeing eye meant a combining of atom with atom, though sometimes it might mean a greater number of atoms, provided this number was always the same. There is another law where the call for discrete particles of fixed weight is still clearer. With these two fundamental laws there was an assured basis for Dalton's theory of the existence of unchanging atoms. This second law is known as the law of multiple proportions and was discovered and announced by Dalton himself. The careful analytical work of Proust and Berthollet and others gave him the necessary facts for his generalization. Considering these facts, he found that when two elements combined to form one compound there were certain definite proportions in which they united. If they formed more than one compound, under changed conditions, then the proportion of one progressed by regular increments, an increase of once or twice the first proportion or some simple multiple of it. For this he saw that his hypothesis of atoms gave a plausible explanation

— and the only plausible one — the increase corresponding with a doubling, trebling, etc., of the weight of the original atom. It was this that immediately attracted the attention of the leading chemists. Many set out to test the truth of the law and with its establishment the case was won.

Dalton told his theory to Thomson, a noted chemist who was the author of some of the leading text-books of his day. Thomson published Dalton's views in his *System of Chemistry* in 1807. Sir Humphry Davy opposed the new hypothesis, but was won over to it and so were Wollaston and others, though they saw difficulties in its application which greatly delayed its general acceptance. The essential parts of Dalton's theory can be put in two sentences:

1. Every element is made up of similar atoms of constant weight.
2. Chemical compounds are formed by the union of the atoms of the different elements in simple numerical relations.

All analytical work has been based on these two assumptions and the results have confirmed them. Dalton further speculated on the nature of the atoms, regarding them as spheres surrounded by an atmosphere of heat, not touching one another but in constant motion.

**Determining the Weights of the Atoms.** — If the atomic theory were a true explanation of the facts of chemical combination, then its first and most important application would lie in a determination of the relative weights of the atoms of the various elements. This might be arrived at by a determination of the combining proportions entering into different compounds,

provided the number of atoms in such compounds were known. Now it was in this that the supporters of the theory met their first and greatest difficulty. By what possible means could the number of the constituent atoms in a compound be accurately known?

**Dalton's Rules.**—Following up his conception of the existence of atoms Dalton began to determine their relative weights, taking for his standard or unit hydrogen, the lightest of them. A list of these weights as determined by him was published in 1805. They show very faulty work and were superseded later by the remarkably accurate results obtained by Berzelius. These weights as given by Dalton seem to have come very slightly into use. To overcome the difficulty of telling how many atoms entered into combination to form a particle of any compound, he adopted some very arbitrary rules which were afterwards shown to be without just basis. These rules had the merit of simplicity, however, and were about the best that could be formulated at that time. First, he divided compounds into binary, ternary, quaternary, etc., according as they contained two, three, four, or more atoms. Then he adopted the following rules:

1. When only one combination of two bodies can be obtained it must be presumed to be a binary one unless some cause appear to the contrary.

2. When two combinations are observed they must be presumed to be a binary and a tertiary.

3. When three combinations are obtained we may expect one to be a binary and the other two tertiary.

4. When four combinations are observed we should expect one binary, two ternary, and one quaternary, etc.

How simple the whole matter would be if nature always chose the simplest, plainest paths! But happily for our development, she often has a confusing way of leading into many by-paths. Besides this difficulty as to the number of atoms, Dalton's use of the term atom was often misleading. He made little distinction between the ultimate particles of elements or of compounds or the ideal indivisible atom. This was a most serious flaw. It caused Dalton himself to reject the work of Gay-Lussac; and it caused others, seeing these inconsistencies, to hesitate to accept Dalton's views. Two things were much needed — a clearer definition of atoms and some reliable method of determining the number of atoms in a compound particle.

**Gay-Lussac (1778–1850).** — The latter problem was partially solved by the labors of Gay-Lussac. This distinguished pupil of Berthollet was a well-trained chemist, capable of very accurate analytical work and possessing scientific acumen in a very high degree. He enriched chemical literature by many excellent investigations, working often in company with Thenard, Humbolt, and Liebig. His most noteworthy work was upon iodine, cyanogen (the first compound radical), the alkaline oxides, the isolation of boron, improved methods for organic analysis, and many similar studies.

**Law of Volumes.** — His name is especially associated with his researches upon the combining volumes of gases. He discovered the law of the expansion of gases under the influence of equal temperature increments. He also studied the combining volumes of gases and deduced from his experiments the law of volumes for gases. This law of volumes may be stated thus: The volumes in which

two gases combine bear a simple ratio to one another and to the volume of the resulting gaseous product. Thus one volume of oxygen always reacts with two volumes of hydrogen to form two volumes of steam. Any excess of either oxygen or hydrogen will be left over. So also, one volume of nitrogen unites with exactly three volumes of hydrogen and two volumes of ammonia result. The account of his work and the conclusions he drew from it were given in 1808.

**Objections to the Law.** — Gay-Lussac was well acquainted with Dalton's hypothesis and showed in part how his discoveries accorded with it. A similar molecular condition was essential in order that all gases should behave alike towards pressure and changes of temperature, and, in addition, obey his law of volumes. In other words, equal volumes of gases must contain equal numbers of molecules. Gay-Lussac made no distinction between these molècules and atoms, recognizing but one kind of final particle. Dalton took exception to this reasoning, and in his reply said that he too had once held the same idea as to combining volumes but had seen that it was untenable. He further maintained that the experiments of Gay-Lussac were inaccurate and that the gases did not combine exactly by volumes but often by fractions of volumes. His argument may be illustrated best by taking some substance, as hydrochloric acid, as an example. One atom of hydrogen chloride consists of one atom of chlorine and one atom of hydrogen. On combination of equal volumes of these two gases, therefore, there should result but one volume of hydrogen chloride if the supposition that equal volumes of gases contain equal numbers of final particles is correct. On



the contrary, the yield is two volumes of hydrogen chloride. If these final particles were atoms, then the resulting volumes of hydrogen chloride must each contain only half as many particles as the volumes of the combining gases or the hydrogen chloride is made up of half-atoms of hydrogen and chlorine. This reasoning is manifestly final so far as the theory of the volumes containing the same number of atoms is concerned unless some different definition of atoms is assumed.

**Avogadro's Theory.** — The solution of the difficulty was shown by Avogadro (1776–1856) in 1811. This Italian physicist made a distinction between two kinds of ultimate particles which we know as molecules and atoms. The molecules were compound particles and were made up of the indivisible atoms. In hydrogen gas, therefore, we have as the final particles molecules, each made up of two atoms of hydrogen; and a molecule of oxygen is made up of two atoms of oxygen and chlorine has two atoms to the molecule. With this hypothesis the volume relations, as given by Gay-Lussac, become entirely regular and intelligible. These discoveries of Avogadro have been sometimes credited to the French physicist Ampère, but his statement appeared three years later (1814) and lacks the clarity and fullness of that of Avogadro. He assumed the presence of four atoms instead of two in the molecules of elementary gases and attempted to extend his hypothesis to the constitution of molecules existing in solids. His memoir first appeared in the form of a letter to Berthollet and he showed in it his ignorance of the work of Avogadro.

## CHAPTER IX

### THE ATOMIC WEIGHTS

Taking hydrogen as the unit, Dalton determined a small number of atomic weights but, lacking skill as a chemist, his results were so faulty as to cause much uncertainty with regard to the whole matter. Other chemists took up this task with greater success. Chief among these was Berzelius, who in conjunction with his pupils undertook the determination of the atomic weights of all the known elements. The analytical work, of course, greatly excelled that of Dalton and in the rules laid down for his guidance in deciding the number of atoms in a given compound or molecule his intimate knowledge of the chemical behavior of many substances, his acuteness of observation, his attention to the smallest details, and his painstaking patience render his work truly remarkable. Many of his atomic weights are still quoted and made use of in settling these physical constants over which chemists have been busied for so long a time. His standard was oxygen taken as 100. Still he was at a loss for a reliable method of telling how many atoms there were in the molecules with which he dealt, and his rules for settling this question were in some respects arbitrary and unsatisfactory. As knowledge grew and new aids were discovered for arriving at the number of atoms in a molecule, he availed himself of them and corrected his tables of the atomic weights

which he issued every now and then through a number of years.

**The Standard for the Atomic Weights.**— Since the atomic weights are necessarily relative to that of some one elementary atom taken as the unit or standard, it is essential that the standard shall be the best available and universally recognized as such. The standard has been changed several times since Dalton chose hydrogen, the lightest known atom, and assigned to it the unit value. Hydrogen, however, forms comparatively few compounds with the other elements and that means that in most cases the relative value could be determined only indirectly. A little later Wollaston chose oxygen, giving it the value one. This had the disadvantage of giving fractional values for several of the atomic weights. It was probably to avoid this that Berzelius, when he chose oxygen for his standard, assigned it the value 100. Oxygen was chosen because of the large number of compounds which it formed and hence the possibility of direct determinations. Under this system some of the atomic weights were inconveniently large, running over one thousand. Some years later hydrogen was restored (largely through the influence of Gmelin) to its position as standard with the value 1 and held this position until near the close of the nineteenth century. In the early part of the last decade of that century the prolonged discussion came to an end by the general adoption of oxygen as the standard with the value 16 and the appointment of an international committee which was to have charge over all corrections in the atomic weights and issue annually tables containing all revisions accepted by them.

**Wollaston's Equivalents.** — The uncertainty connected with the atomic weights as determined under Dalton's rules, or indeed under any arbitrary method of procedure, led Wollaston, his fellow countryman, to suggest abandoning the use of the term atom and substituting that of equivalent. This term he adopted from the work of Richter. Wollaston meant by it the relative quantities or proportions in which bodies unite, thus doing away with the idea of atoms. He hoped in this way to escape all question as to the number of atoms in a compound. It is easy to see that his method rather increased than diminished the complications, and the atomic theory, which was based on fundamental laws, was to be done away with because of difficulties in settling their weight. Still the desire to eliminate theory was strong and many chemists, especially the English, continued to use the term equivalent for many decades after the time of Wollaston. The difficulties will be seen if examples are taken. Using Wollaston's standard of oxygen equal to 1, we find there are two compounds with carbon. One gives the ratio of carbon to oxygen as 0.75 to 1; the second gives the ratio of 0.375 to 1. Which ratio shall be taken? If the least equivalent is taken, then what is the other? Manifestly the knowledge of the number of the particles in the compound is just as essential for equivalents as for atoms.

**Law of Specific Heats.** — In the year 1819 Dulong and Petit, while experimenting upon the specific heats of the metals and other substances, came upon the important truth that these were very nearly inversely proportional to their atomic weights. Multiplied by their atomic weights they gave a constant quantity which is .

called the atomic heat. The law as stated by the authors is: The atoms of the different elements have the same capacity for heat. It is possible, therefore, by means of the specific heat to approximate the true atomic weight and arrive at a decision as to which of two or more possible figures represent the correct weight.

There were exceptions to the law which were explained later. Still the law was extended to simple chemical compounds and proved of use after it was more fully understood. Berzelius opposed the acceptance of it at first, partly because it would necessitate a revision of his table of atomic weights and might endanger accepted views as to the atomic relations. He gradually gave up this stand when the law was confirmed by other workers and determinations more accurate than the first ones of Dulong and Petit were made of the specific heats.

**Isomorphism.**— In the same year Mitscherlich announced what was called the law of isomorphism. While engaged in a research upon the salts of phosphoric and arsenic acids, he reached the conclusion that compounds of analogous composition and containing the same number of atoms crystallize in the same form or, in other words, are isomorphous. For this to be really useful in determining atomic weights it was necessary to reverse it and to have it hold true that isomorphous compounds were analogous and contained the same number of atoms. Here many difficulties presented themselves, necessitating narrower and narrower definitions of isomorphism. It is evident that though analogy or similarity of crystal form may have a bearing upon the molecular composition and arrangement, we are as yet unable to determine fully this bearing. Berzelius took up the discovery of

Mitscherlich with enthusiasm and made frequent use of it in testing his atomic weights.

**Electro-chemical Equivalents.**—Mention should be made in this connection of Faraday's law. This was deduced from his experiments in 1834 on the dissociating action of the electric current upon electrolytes. In decomposing different electrolytes such as water, metallic chlorides, etc., he found that there separated at the positive or negative electrodes equivalent amounts of respective constituents, provided the same quantity of electricity were used. The amounts separated were called the electro-chemical equivalents. The intensity of the current needed to bring about the decomposition he regarded as a measure of the force of affinity. Faraday thought that the determination of these equivalents would prove a valuable aid to the correct determination of the atomic weights. The application of this method is to a certain extent limited but it has been used in some recent accurate determinations.

**Work of Dumas on the Atomic Weights.**—In their work upon the atomic weights Dumas and other French chemists made especial use of the law of volumes as given by Gay-Lussac and adopted the distinction made by Avogadro between atoms and molecules. The equivalents suggested by Wollaston were rejected by them as applicable only to a limited range of substances, such as acids and bases, besides being indefinite or not determinable when identified with combining weights, since many substances united in several different proportions to form compounds. Some of Dumas' determinations, as those of phosphorus, tin, and silicon, show that he did not realize the full importance of Avogadro's theory

as an aid in such determinations. Still he believed that this theory gave a surer basis for solving such questions, and drew up a table of atomic weights making use of it and the law of Dulong and Petit. He used the term elementary molecules and said that there was no means of deciding how many smallest particles these molecules contained. In accuracy and correctness his work fell below that of Berzelius.

**Vapor Densities.** — Dumas devised an accurate and excellent method for determining the specific gravities, or densities, of gases which could be used at high temperatures, thus enabling him to experiment upon the vapor densities of iodine, phosphorus, sulphur, mercury, etc. His results, instead of confirming, tended rather to disprove the law of volumes. The trouble lay in the complex nature of the molecules experimented upon, but of course this was unknown to Dumas. He finally declared that even in the case of the simple gases like volumes did not contain equal numbers of chemical atoms. Berzelius also had been practically forced to give up the law of volumes, at least so far as any use in atomic weight determinations was concerned, limiting its application to the uncondensed or so-called permanent gases.

Chemists therefore looked with indifference or disfavor on this law which is the mainstay of modern work upon the atomic weights. The law of Dulong and Petit was also shown to have some notable and unexplained exceptions, and Mitscherlich by his further discovery of dimorphism had thrown much doubt upon his law of isomorphism. So at the close of the thirtieth year of the nineteenth century the atomic theory was regarded by many chemists as relegated to a hypothetical position.

**Gmelin's Views.** — Some took up again the equivalents of Wollaston. Certainly little distinction was made between these and the atoms of Dalton, and the dualistic system of Berzelius lost ground. Gmelin, the author of the most complete handbook or encyclopedia of chemistry up to his time, and the most influential as it went through many editions and formed the basis subsequently of Watts' *Dictionary of Chemistry*, was the leader in this new school of chemistry. In the edition of his handbook published at this time, the fourth decade, he gave up the atomic theory altogether. He recognized no difference between chemical compounds and mixtures. Two substances, according to his ideas, could combine in an unending number of proportions. In the case of a strong affinity between them the tendency was toward a limitation to a few proportions. To each substance then a sort of mixing weight could be assigned and this number could be used in analytical calculations. His table of equivalents halved most of the atomic weights. Thus,  $H = 1$ ,  $O = 8$ ,  $S = 16$ ,  $C = 6$ , etc. Water became  $HO$ . The rule was to make everything conform to the utmost simplicity. Where there was choice between several possible equivalents for any one element he took the the least and simplest. These numbers and formulas were retained by many chemists for some decades afterwards.

**Confusion in the Sixth Decade.** — The middle of the century saw the condition of affairs regarding these physical constants a badly mixed one. Two units or standards were in use. Dalton had used hydrogen as the unit and this was adopted by Gmelin and many others. Wollaston and Berzelius took oxygen as the



standard, Wollaston giving it the value 10 and Berzelius using the value 100, while Thomson gave it the value 1. But, far worse than having two standards, widely differing values were assigned for the atomic weights and all needed revision. In Germany, for instance, the value for carbon was 6 and for oxygen 8. In France these values were respectively 3 and 8.

**Revisions of the Atomic Weights.**—Dumas was especially active in the revision of these numbers. His determination of the atomic weight of carbon and his work, in conjunction with Boussingault, to determine the ratio of hydrogen to oxygen in water are classical. Dumas fixed the number 16 for oxygen. The exact result was 15.96. This ratio has been the subject of more painstaking and careful determinations than any other in chemistry, yet without complete accord. Dumas also determined many other atomic weights. Others taking part in this work of revision were Erdmann, Marchand, Marignac, De Ville, and Scheerer, but easily the greatest of them all in care and accuracy was Stas. His work was monumental in the pains taken to secure absolute accuracy, and yet in a few years errors were found and the so-called Dumas correction, as well as others, had to be applied to the numbers found by him. The atomic weights determined by him with the greatest care were those of silver, potassium, sodium, lithium, lead, chlorine, bromine, iodine, sulphur, and nitrogen.

**Clearing up the Confusion.**—The solving of the problems which confronted those devoting their attention to the atomic weights and the clearing up of the existing confusion were in great measure brought about

through the development of organic chemistry. Much light was thrown upon the distinction between atoms and molecules and the dominant doctrine in this branch of chemistry quietly assumed the truth of Dalton's theory in all its important particulars as the only satisfactory explanation of and adequate basis for the work done. Frankland's researches on the organo-metallic substances practically did away with the old confusion between atoms and molecules. Then, too, the value of Avogadro's law as an aid to the correct determinations of atomic weights became more fully recognized and laboratory methods were more accurate. This was notably the case in vapor density determinations. Much credit for placing atomic weight work upon a more satisfactory basis is due to Cannizzaro. In 1856 he published a small pamphlet in which he took a determined stand upon the necessity for the use of the means already at hand and especially the theory of Avogadro that equal volumes of gases contained equal numbers of particles. In 1860 a meeting was called at Karlsruhe by distinguished chemists of various nationalities to see if some general agreement could not be reached as to standards, atomic weights, and chemical notation. The meeting was presided over by Dumas. No general agreement was reached but Cannizzaro's pamphlet, in which he urged chemists to place reliance in the methods mentioned and so to correct many of the false atomic weights then in use, was distributed towards the close of the meeting. His arguments proved convincing, resulting in the general adoption of the modern methods.

**Constancy of the Atomic Weights.** — The question has repeatedly arisen as to whether the atomic weights

are variable within narrow limits. The approximate agreement of the best determinations would tend to exclude any other than a slight variation. This question Stas proposed for himself before starting upon his classic work on the atomic weights. The conclusion he drew from his experiments was that they were unchangeable. The question was raised again by Schützenberger and Butlerow. These chemists supposed the range of variation to be very slight yet distinctly to be detected by analysis. Vogel also came to the conclusion that the atomic weights vary because those found by the use of certain compounds differ from those derived from other compounds. If this assumption is correct, then the law of conservation of mass and along with it that of constancy of proportions cease to fall under the category of laws.

In 1906 Landolt put the law of conservation of mass to a critical test. A vessel was so arranged that two substances could be accurately weighed and then reaction allowed to take place between them without any possible loss of substance. A large number of experiments were carried out with every refinement as to apparatus. The second weighing revealed a difference of about one part in 10,000,000. Such differences do not exceed the unavoidable experimental error.

A number of years ago Crookes suggested that one might assume the presence of a few of what he called "worn atoms" in the countless numbers of others which must come under consideration in any atomic weight determination. Essentially, this means the presence of atoms of the same element which vary slightly in weight and mass. The presence of a few such atoms would es-

cape detection as falling within the experimental error. Within the past few years the theory of isotopes has grown up and it seems certain that such isotopes exist. In the case of gases they may be separated by the diffusion process. First, an isotopic neon atom was discovered, then hydrogen, chlorine, and others. These isotopes bear a very small ratio to the total number of atoms present in any given volume.

## CHAPTER X

### NATURE OF THE ATOM

It is worthy of note that from the very beginning the modern atomic theory laid little or no stress upon the indivisibility of the elementary atom. For all purposes of the chemist it was sufficient to know that under all manipulations and changes in the laboratory or in nature it seemed to remain intact and, therefore, could be assumed as an ultimate particle so far as experience went. Within a decade after the announcement of the theory there sprang up a hypothesis as to the possible compound nature of the atom and hence its origin or genesis. This was the well-known Prout's hypothesis which was announced in 1815.

**Prout's Hypothesis.** — This hypothesis was based on the assumption that all the atomic weights were whole numbers and, therefore, multiples of the unit hydrogen. From this Prout reasoned that these elements were only different grades of condensation of hydrogen, which was, therefore, the primal element. No additional proofs were suggested in support of this theory. Prout, the author of it, was a physician and did little chemical work of value. Even if the atomic weights had been all whole numbers this was in itself no proof that they were made up of hydrogen. Yet this hypothesis proved to be an attractive one to many chemists. As the years passed the increasingly accurate determinations showed

that some of the atomic weights were not whole numbers and that the fractions persisted, though improved work might vary them slightly.

**Views of Berzelius.** — Berzelius regarded the hypothesis with favor when first brought to his attention. He soon became its first and strongest antagonist. In 1825 he published a table of the atomic weights which contained a number of fractions and he protested strongly against the practice of rounding off these fractions into whole numbers. As Hoffman says, "He could not persuade himself that the numerical relations of these values betokened an inner connection of the elements nor yet a common origin. On the contrary, he was of the opinion that these apparent relations would disappear more and more as these values were more accurately determined. For him, therefore, there existed as many forms of matter as there were elements; in his eyes the molecules of the various elements had nothing in common with one another save their immutability and their eternal existence." Our later knowledge of these matters would tend to show that in this Berzelius had gone too far to the other extreme.

**Testing the Hypothesis.** — In 1832 Turner was specially delegated by the British Association to investigate this question. If barium, chlorine, etc., really had fractional atomic weights then the hypothesis in its original form was untenable. Turner's results were adverse to the hypothesis. So also were Penny's. Margnac suggested that if half the atomic weight of hydrogen were taken then all known atomic weights would be multiples of it. The idea was taken up by Dumas with enthusiasm but he found this factor must be once

more halved, so one-fourth the hydrogen atom was taken. It is not quite clear why this was not a begging and abandonment of the whole question. But the very careful and accurate work of Stas upon the atomic weights made even this position impossible. And so the factor was by some shifted to one-tenth the unit and by Zängerle to the one-thousandth part of the hydrogen atom. With this it passed the limit of experimental evidence and lost all weight and meaning.

**Numerical Relations between the Atomic Weights.** — The first numerical regularities observed between the atomic weights were the triads of Döbereiner. This chemist seems to have observed first that the combining weight of strontium was the arithmetical mean of those of calcium and barium. A like regularity was noted with regard to certain physical properties of these elements and some of their compounds. This led him for a while to question the independent existence of strontium. Several similar triads were discovered among the other elements as lithium, sodium, and potassium; chlorine, bromine, and iodine; sulphur, selenium, and tellurium. He was careful not to let this grouping depend upon the atomic weights alone but insisted that only elements exhibiting decided analogies of properties should be considered together. This idea was taken up by other chemists, notably by Gmelin in his *Handbook*, and many analogies and groups were sought for. In 1857 Lenzen returned to this grouping, endeavoring to force all the elements into some twenty groups. Then Odling sought to build upon them an elaborate system of the elements which he called the Natural System. Such groupings were often forced and failures.

The science was not far enough advanced to enable one to understand the real meaning of these regularities.

**Gladstone's Ascending Series.**—The first to suggest an arrangement of the elements in the order of their atomic weights, beginning with hydrogen, was Gladstone (1853). These numbers were too faulty and there was too much confusion in them to yield any satisfactory results, but the principle was an important one. Manifestly nothing in the way of interrelation or regularity was to be found in tables alphabetically arranged. In 1863 de Chancourtois made use of the revised atomic weights in an ascending series which he called the telluric screw. He drew as a conclusion from his work that the properties of an element are determined by atomic weight. This was a fundamental proposition in the Periodic System which was later announced by Mendeleeff. In the work of Newlands, which followed closely upon that of de Chancourtois (the first publication appearing in 1864), there is a nearer approach to the Periodic System. He also arranged the elements according to their atomic weights and observed that the eighth element was analogous to the first, and so on through the list with an interval of seven. This he called the law of octaves. There were many difficulties and inconsistencies so that little support was attracted to it. Meyer's table, published in the same year, was arbitrary as to the sequence of the elements, arranged in sixes, and was too faulty to receive much attention.

**Periodic System.**—It was Mendeleeff, a Russian chemist, who, independently and with a wealth of chemical facts adduced in its support, gave to the science its central system, bringing order out of much confusion.



Because the elements fell in periods of sevens and threes it was named the Periodic System. The basic law was given in this form: "The properties of the elements are functions of their atomic weights." So nearly is this true that Mendeleeff was able to predict the existence of certain elements, giving a number of their properties.

These were later discovered and the prophecies confirmed. It required an insight into the principles of this system to devise the later table given by Mendeleeff, and the conclusions reached by him give evidence that he had grasped these principles. The most important of these were:

1. The elements, if arranged according to their atomic weights, exhibit an evident periodicity of properties.

2. Elements which are similar as regards their chemical properties have atomic weights which are either nearly of the same value or which increase regularly.

3. The arrangement of the elements in the order of their atomic weights corresponds to their so-called valences as well as to some extent to their distinctive chemical properties.

4. The elements which are most widely diffused have small atomic weights.

5. The magnitude of the atomic weight determines the character of the element just as the magnitude of the molecule determines the character of a compound body.

The table of Mendeleeff was changed but little for thirty years. Its anomalies, as the omission of hydrogen and the rejection of the atomic weight as the deciding factor in such cases as cobalt and nickel, tellurium and iodine, etc., were recognized; but greater knowl-

edge was needed before these could be explained or the underlying law grasped.

**The Zero Group.** — In discussing the Periodic System it had been pointed out by mathematicians that the transition *per saltum*, as from fluorine to sodium or chlorine to potassium (that is, an increase of electro-negative character until the maximum was reached in fluorine and then an abrupt change to the highly electro-positive sodium), could not take place without first passing through either zero or infinity. When Ramsay announced, near the close of the nineteenth century, the discovery of argon, helium, and the other monatomic gases and it was found that these had no combining power, no electro-chemical character, and no valence and were the only known monatomic gases at ordinary temperature, it was seen that the zero group had been found and the table rounded off. The periods were no longer sevens but eights, besides the short periods of three.

**Contributions from Radioactivity.** — The study of radioactive phenomena began in the first decade of the twentieth century. The radioactive elements, with every proof of their elemental character, increased by nearly fifty per cent the number of known elements. How could they find places in the system which was already a bit crowded and in some confusion over the placing of the rare earths? First, it was found that certain gaseous ones belonged to the zero group. Then Soddy announced his theory of isotopes, namely, that there might be several elements which were so much alike chemically that they could not be separated by chemical means and yet differed in their atomic weights. Their

chemical properties were to be taken as decisive and they belonged in one place in the system in spite of their atomic weights. Another contribution from radioactivity was a method of deciding the location of an element by counting the recoil particles. A few years later Moseley, by his remarkable work in photographing X-ray spectra discovered a method by which this location could more easily and surely be settled. In this way were confirmed the exceptions made in the beginning in placing cobalt and nickel, etc. Fortunately in most cases the determining factor coincides with the atomic weight, or influence of mass. Otherwise the discovery of the Periodic System would have been long delayed.

**Composite Nature of the Atom.**—The arguments in behalf of the composite nature of the elements may well be given here. When these arguments were duly weighed they caused more than a wavering in the old faith as to the simplicity of the elemental atom. The revelations of radioactivity have disclosed the internal structure of these particles so that they are known as no longer ultimate. Many chemists in the nineteenth century regarded the atom not as something which could not be divided but as something which had not been divided. A study of the Periodic System brought the conviction that the elements were closely interrelated with constituents common to them all. Remsen wrote: "The so-called elements are shown to be related to one another and it seems impossible in the light of these facts to believe that they are distinct forms of matter. It seems much more probable that they are in turn composed of subtler elements." Gladstone, in an address before the British Association, said, "The remarkable rela-

tions between the atomic weights of the elements and many peculiarities of their grouping force upon us the conviction that they are not separate bodies created without reference to one another but that they have been built up from one another according to some general plan."

**Evidence as to Complexity.** — The first argument for complexity is drawn from the manifest kinship shown by the elements in the Periodic System. A second argument lies in the close analogies to be observed between the compound radical  $\text{NH}_4$  and the alkali elements, the compound radical  $\text{CN}$  and the halogens, etc. These resemble elements in every respect except that they can be dissociated and built up at will. The presumption is strong that the same might be done for the other elements if only the suitable treatment were known. Again, it is known that when the valence of an element is changed the result is comparable to the formation of another element. The analogy to the homologous series of the hydrocarbons was pointed out by Cooke, Dumas, and others. Lastly, the number of lines found in the spectra of the elements can not well be referred to the motion of absolutely simple bodies. The matter has been finally settled by the phenomena of radioactivity, which have shown elements in the process of disintegration and new elements forming and have justified the conclusion that the atoms are made up of discrete units of positive and negative electricity and are, therefore, storehouses of enormous energy. So far, and one may add fortunately, no means of releasing this energy is at our command. Theories as to the structure of the atom and the disposition of this

energy have been advanced by Rutherford, Bohr, Langmuir, and others. It will be seen that the Periodic System thus receives its explanation and the series of elements can be theoretically built up of the two simplest atoms, hydrogen and helium. This, however, is as yet only in a tentative stage. Valence and the electro-chemical characteristics also receive at least a rational explanation, whether final or not, and advanced chemistry has entered the sub-atomic or ultimate stage.

## CHAPTER XI

### AFFINITY, THE ATOMIC ATTRACTIVE FORCE

It was seen from the very earliest times that the hypothesis of the atomic constitution of matter involved also an investigation as to the force which brought about the union of atoms and held them in combination. This was a problem which the earliest philosophers found themselves incapable of solving because of their general ignorance as to the natural forces and the paucity of their experimental or other data.

The oldest idea as to the cause of the union of two substances was that they must contain some common principle. Thus Hippocrates (460-357 B.C.) taught as one of the fundamental doctrines that "like would unite only with like." This doctrine gave rise to the term used at present, affinity, though this ancient belief, cherished for centuries, has long since been lost sight of.

The term *affinitas* seems to have been used first by Albertus Magnus to indicate the cause of the union of silver and other metals with sulphur. The same expression was used by chemists following him and in very nearly the same sense as at present. Glauber, Boyle, Hooke, and others found it useful to designate the unknown combining force. Still it was inferred that some similarity must exist between the combining substances. The greater the affinity, the greater the resemblance. With the eighteenth century there came a change in

this belief. Boerhaave sought to show that affinity was also evinced by dissimilar bodies in their tendency to combine. Solution was looked upon as an act of affinity. Boerhaave maintained that the solution of iron in nitric acid was also an act of affinity and that no relationship existed between the two, but that they were essentially different. His influence as a teacher and the wide distribution of his text-books secured the introduction and general adoption of his views by chemists. Yet physicists opposed the idea of a new force. The term *attraction* used by Newton was too indefinite and general to displace *affinity*, which by that time had become fully incorporated into chemical literature, in spite of the recognition that the latter term was based upon a mistaken idea.

**Strength of Affinity.** — The knowledge of this force grew very slowly. First, it was recognized that the force varied in strength. Glauber maintained that the tendency of one body to unite with another differs in accordance with the nature of the latter and that another substance can bring about the decomposition of such a union when it has a greater affinity for one of the components than they have for one another. And so it came about that two approximate tests were devised for measuring the strength of affinity. First, the readiness of combination and secondly, the displacement of one substance in combination with another. Observations began to accumulate. Glauber and Stahl and others announced certain affinity series. In 1718 Geofroy published sixteen tables, called by him *tables des rapports*, and then followed a number of tables by different chemists, the best and most widely known being the tables of Bergman in 1775. Bergman recognized the fact

that chemical affinity is influenced and varied by temperature, differing also with the physical state of the substances. Berthollet stated that it was affected by mass. He considered it as probably "a phase of the same fundamental property of matter as that to which universal gravitation owes its origin." The differences observable between the two he attributed to the proximity of the reacting substances in the case of affinity and to the influence of special conditions. Berzelius offered as an explanation of affinity the hypothesis that it was dependent upon electrical attraction. This seems to have been first a conception of Davy. According to the thinking of Berzelius, each atom is endowed with a certain quantity of electricity, partly positive and partly negative, which accumulates in particular parts of the atoms and gives to each a positive and a negative pole. The atom as a whole, however, has the character of either a positively or negatively electrified body because of the preponderance of one or the other kind of electricity. When two atoms combine their respective charges are neutralized. Of course this offers an explanation of the greater attraction between unlike atoms. Every molecule then was built up of two parts, one positively and the other negatively charged, and thus formed a dual structure. The theory was known as the dualistic theory. In the imperfect knowledge of the day difficulties presented themselves, especially in the matter of the same element (as hydrogen) sometimes substituting a positive element and again a negative one, and hence the theory lost support. It is astonishing how closely it approaches the modern theory as to the constitution of the atom and attractive binding force.



**Measurement of Affinity.**— Various attempts have been made at measuring the relative strength of affinity, but the many conditions which influence chemical reactions and the lack of definite knowledge as to the nature of the force to be measured render the question a very complex one, and no satisfactory solution has been reached. The formation of a compound is accompanied by changes of energy; also the application of energy can cause the dissociation of a compound. It would seem to be simple to measure the energy liberated or applied, but even then the results would be of little value unless the connection with affinity were accurately known. The part played by heat in reactions was, of course, a matter of early experience. The measurement of the heat evolved in chemical reactions has led to the development of the branch of chemistry known as thermochemistry. The first law discovered was that of Lavoisier and Laplace, namely, that for the dissociation of a compound into its constituents the same amount of heat is absorbed as was evolved in its formation. This is true for endothermic reactions also where heat is absorbed on combination and the same amount given off on dissociation. In 1840 Hess announced the important principle that in a chemical reaction the amount of heat evolved is the same whether the process takes place step by step or in one step. This removed many difficulties which lay in the way of the determination of this evolved heat. Thermochemistry was further built up by the work of Favre and Silbermann, and especially by that of Thomsen. It is possible to arrive at some knowledge of relative affinities by the study of analogous reactions. Thus in the union of hydrogen with chlorine,

bromine, and iodine the heats of formation are respectively 44,000, 16,660, and 12,072 calories. These, however, are not to be taken as proportional to the affinities involved but simply as varying in the same order. As Remsen says, "The difficulties are much increased in more complicated cases and it will, therefore, be seen that it is impossible to measure the affinity by means of the heat evolved in reactions."

Again, it would seem that there is some connection between this combining force and the electrical states of the atoms. Much stress has been laid upon this but little is really understood concerning it.

**Valence.**— Still another important property of the atom remains to be considered. This is called valence and is closely connected with the phenomena of affinity. Where there is no affinity between two atoms no valence can be exhibited. Valence decides the number of atoms which enter into a molecule. As both atoms have a definite valence, necessarily both have to be taken into account. The question of valence did not arise until there had been some development of the theories as to affinity. No necessity was felt for it until the number of known compounds had been greatly multiplied and the need for their classification became pressing. Valence has also been defined as the saturation capacity of the atoms.

**Evolution of the Idea.**— Probably the first conception of valence was in the recognition of the so-called polyatomic compounds. This term was first used by Berzelius in 1827, who applied it to such elements as chlorine or fluorine where he thought several atoms of these elements united with a single atom of another ele-

ment. This use of the term does not seem to have received wide acceptance. It was applied to compounds, however, and for certain of these its use became general. Thus Graham applied it to the acids combining with various proportions of the bases. These were called polybasic acids. Odling and Williamson extended the idea to the compounds which, according to the theory prevailing at that time, were built upon types. Thus both the type theory of Laurent and the substitution theory of Dumas were involved in the evolution of this conception. The substitution of elements for one another would naturally lead up to the idea of the relative value of their atoms. This was called by Liebig the *replacement* value. The comparison between these atoms was inevitable, as they were generally substituted for the same element — either hydrogen or oxygen. The quantities of the various elements thus substituting hydrogen were regarded as the equivalents but when the confusion between equivalents and atoms was cleared up the pressing question became as to how many atoms were involved.

**The Organo-Metallic Compounds.** — The important work of Frankland upon the series of organic substances containing metals, known as the organo-metallic bodies, had much to do with the clearing up of the confusion as to the saturation capacity of the atoms. This work showed that the pairing of the radicals with the elements was to be explained on the ground of some characteristic property of the atoms. Upon these experiments Frankland founded the valence theory, the germ of which one can detect in much that had gone before, especially in the law of multiple proportions;

but the idea had not been clear, nor even expressed in a name except by the vague term *replacement* value introduced by Liebig.

**Polybasic Acids.**—What is known as the doctrine of the polybasic acids contributed to the growth of ideas upon the subject of saturation capacity. Gay-Lussac, Gmelin, and others had held the idea that in the metallic oxides one atom of metal was united with one atom of oxygen, and that these oxides united with one atom (molecule) of acid to form neutral salts. Graham showed by his investigations upon the acids of phosphorus that this view could be held no longer. He proved that in the ortho, pyro, and meta acids for each "atom" of  $P_2O_5$  there were respectively three, two, and one "atom" of "basic water," which could be substituted by equivalent amounts of metallic oxides. The saturation capacity of these acids was then dependent upon the "basic water." Liebig extended this to many other acids and distinguished between mono-, di-, and tri-basic acids. This term *basicity*, along with the ideas inherent in it, clung for some time to the theory of the saturation capacity of the atoms. One sees in the above citation from the work of Graham the confused use of the term atom.

**Polyatomicity.**—The idea of basicity was extended further to the compound organic radicals. Thus Wurtz, in describing the glycerin compounds, wrote of glycerin as a tribasic alcohol. Manifestly there is confusion here since glycerin may combine with three acid radicals and the term should be triacid alcohol. The term *atomicity* was, therefore, sometimes used. Williamson attached the idea of capacity for saturation or atomicity of the radical to the number of hydrogen atoms

capable of substitution. He called these radicals then monatomic, diatomic, etc. Wurtz' study of the amines also bore upon this point and it is easy to see how the notion of atomicity was soon extended to the various compound radicals known. The last step was in the extension of this idea of saturation to the elements themselves. From their combinations and substitutions with these organic radicals their atomicity was deduced.

**Deduction of Valence from Inorganic Compounds.** — When one considers the formulas of the inorganic chemical compounds even a superficial observer is attracted by the general symmetry to be observed in them. For instance, the compounds of nitrogen, phosphorus, antimony, and arsenic show a tendency on the part of these elements to form compounds in which either three or five equivalents of other elements are contained. Without formulating an hypothesis to account for this agreement in the grouping of the atoms, it is clear that such a regularity exists and that the affinity of the atoms of the elements named is always satisfied by the same number of atoms. Frankland did not consider a higher valence than five. Though he mentioned the simple inorganic compounds and used them in illustration, he drew the valence doctrine from his studies of complex organic substances.

**Progress made.** — The ideas advanced by Frankland did not meet with immediate acceptance. There was a somewhat prolonged discussion over the constitution of the polybasic acids and other compound groups, joined in by Odling, Williamson, Gerhardt, Wurtz, and others, which showed the necessity for a valence theory and did much to introduce it into the science. By 1858

the theory had made rapid progress. In this year Kekulé first deduced the valence of carbon from its simplest compounds, declaring it to be quadrivalent or capable of combining with four hydrogen atoms. Hydrogen was taken as the standard or unit with a valence of one. On this basis an unvarying valence of four was assigned to carbon throughout all the compounds of carbon, or organic chemistry. This had already been recognized by Kolbe and Frankland, if not expressly stated by them. But Kekulé rendered further and much greater service by examining into the manner in which two or more of the quadrivalent carbons were united with one another. The doctrine of atomic chains, open and closed, sprang from this and the domination of the structural idea in chemistry became complete.

Following the example set in the compounds of carbon, it was the fashion for some decades afterwards to assign a single valence to each element and so construct the formulas of the compounds as to agree with this. The difficulties met with, and the glaring inconsistencies, caused this effort to be given up and brought about the recognition of the fact that an element might have more than one valence. Further, where the element has more than one valence the change from one to the other can be brought about by the application of energy, such as heat, light, chemical action, etc. It seems now that the explanation of the phenomena of valence is to come through the study of radioactivity. The modern conception of valence is an outgrowth of the knowledge of the electrical constitution of the atom and is based upon the existence of latent or valence electrons and their interchange.

## CHAPTER XII

### GROWTH OF INORGANIC CHEMISTRY

It has been necessary to devote a good deal of time and space to the evolution of the fundamental theories, since growth in accurate knowledge and real progress depended upon these. They form the foundation of the modern science and a correct understanding of them, coming through a study of their development, is most important. It is well now to turn to the multiplication of chemical facts and enlargement of the field until the science of chemistry had to be subdivided into a number of branches. In the earlier half of the nineteenth century there was practically but one field and that was inorganic chemistry in which the metals and most of the elements are to be considered. The discovery of new elements is the first thing to attract the attention.

**Discovery of New Elements.** — Among the early discoverers of new elements was the distinguished German chemist, Klaproth (1743–1817). It was largely through his influence that the German chemists were won over to the views of Lavoisier. He devoted himself mainly to the analysis of minerals and the improvement of analytical methods. He added uranium and titanium to the list of simple bodies and discovered zirconia but was unable to separate the metal zirconium. Proust did accurate and valuable work in connection with the

study of tin, copper, iron, nickel, cobalt, antimony, silver, gold, and mercury, thus contributing to the extension of chemical knowledge. But the two most distinguished discoverers in the first quarter of the nineteenth century were Davy and Berzelius. Their influence upon the science has been very great and more extended mention is, therefore, accorded them.

**Humphry Davy (1778-1829).**— The scientific training of Davy was secured while apprenticed to a surgeon and apothecary at Penzance. At the age of twenty he was put in charge of the laboratory of the Pneumatic Institution at Bristol, founded by Dr. Beddoes for the application of gases to the treatment of diseases. Davy's surroundings here were most propitious for a successful career of scientific investigation. His laboratory was well furnished and was supported by the subscriptions of scientific men. His early experiments related chiefly to nitrogen monoxide. He discovered its anaesthetic action. While in this laboratory he gave some of his time also to experiments upon the decompositions brought about by means of electricity. Becoming professor of chemistry at the Royal Institution in London, he devoted himself to the decomposition of some of the substances then regarded as simple or elementary, among them the alkalis and alkaline earths. In this work he made use of a very powerful voltaic pile.

Nicholson and Carlisle had made the observation in 1800 that water was decomposed into its constituents by the discharge from the voltaic pile. This led to similar experiments upon other substances, among them the remarkable ones of Berzelius and Hisinger upon salt solutions, ammonia, sulphuric acid, etc. Davy was among



the first to busy himself with this interesting and important question, the decomposition of water. From the very first it was noticed that acid and alkaline substances were formed and it was believed by some that water was changed into these through the action of electricity. By most careful experiments Davy showed the error of this view. He carried out this electrolysis in vessels of various materials and showed that the products mentioned, acid and alkali, were due to the glass vessels or to matter dissolved in the water or to the air itself. If the water, distilled in silver, were electrolyzed in gold vessels in an atmosphere of hydrogen the acid and alkali did not appear.

Davy further repeated and confirmed the work of Berzelius upon salt solutions. He, too, observed that the electric current separated hydrogen, metals, metallic oxides, alkalis, and earths at the negative pole and oxygen and the acids at the positive. He concluded that the first-named substances have a positive electrical energy and the latter a negative; and this was the beginning of the electro-chemical theory. Davy sought to explain all chemical combination and decomposition on this principle. According to him, the heat noticed in certain cases of combination was due to and but a manifestation of electricity. Davy was the first to put in a fixed form the conception that electrical and chemical action may be referred to the same force. All the later doctrines that chemical changes are the evidences of electrical attractions take their rise from his work and views.

**Decomposition of the Alkalis.**—In his first experiments upon potash and soda Davy used strong solu-

tions and noticed that only hydrogen and oxygen were evolved. He next passed the current through melted potash. A flame appeared at the negative pole and, on changing the direction of the current, "aeriform globules which inflamed in the air rose through the potash." When the potash was placed upon a piece of platinum, which was made the negative pole of a powerful battery, and the positive pole, in the form of a platinum wire, brought in contact with the upper surface of the potash the latter melted and small globules, lustrous and metallic and much like mercury, were noticed on the negative platinum. Some burst and burned; others tarnished and became coated with a white film.

Great was Davy's delight at his discovery, and one can scarcely exaggerate the impression made upon the chemical world by the decomposition of this supposed elementary body, and the remarkable new metal obtained from it. Its properties were quite the opposite of those which were held to be characteristic of the metals. It was light, oxidized immediately in the air, and contact with water brought about its decomposition. Davy also decomposed soda in a similar way, obtaining a metal with analogous properties. He confirmed his discovery by oxidizing these metals back into the original alkalis. He learned how to prepare larger quantities and to keep them under naphtha. He named these metals potassium and sodium. These discoveries were made in 1807 and were followed next year by the decomposition of the alkaline earths, lime, baryta, and strontia. He was convinced by his experiments that silica, alumina, zirconia, and beryllia could also be decomposed by the electric current but failed to obtain any of the supposed

elements existing in these substances. This he attributed to his current not being powerful enough. Davy's discoveries confirmed the view, which was already widely held, that the alkalis and earths were metallic oxides. It was not yet known that some of these were really the hydroxides.

**Composition of Muriatic Acid.** — Davy's next important services were in connection with the theory of acids. Berthollet, by his work upon hydrogen sulphide, hydrochloric acid, and hydrocyanic acid, had really shown the untenable character of Lavoisier's theory that oxygen was present in all acids and hence deserving of its name, the acid-maker. But Berthollet's experiments were not pressed to their legitimate conclusion and the theory of Lavoisier still held its place, though the existence of hydrochloric acid became a serious stumbling block. Oxygen, according to the theory, should be one of its constituents; yet no one could detect its presence. If this acid contained oxygen, its salts should also. In 1774 Scheele had shown that by its action upon the black oxide of manganese a yellow, pungent-smelling gas was obtained. Berthollet showed that a solution of this gas in water gave off oxygen when exposed to sunlight, and hydrochloric acid was formed at the same time. Therefore, it was called "oxidized muriatic acid." Muriatic acid was regarded as composed of oxygen and an unknown radical. These were not the views of Scheele, who called the gas "dephlogisticated muriatic acid" and regarded it as hydrochloric acid deprived of its phlogiston or hydrogen. In 1809 Gay-Lussac and Thenard showed that one volume of "oxidized muriatic acid" and one volume of hydrogen united

to form muriatic acid. This proved that it contained hydrogen.

Davy next endeavored to find the oxygen which was supposed to be in this acid, but without success. He did show, however, that when "oxidized muriatic acid" acted upon metals salt-like compounds were obtained, and that similar compounds, and at the same time water, were formed by the action of muriatic acid upon metallic oxides. Davy explained these results by regarding "oxidized muriatic acid" as an element and muriatic acid as its compound with hydrogen, but chemists were slow to accept his views. Davy held that this element, to which he gave the name chlorine, resembled oxygen in many respects and in a limited sense was also to be regarded as an acidifier and supporter of combustion. In the ensuing discussion with Gay-Lussac, who endeavored to prove from the work of Berzelius and Davy on ammonium amalgam and from the action of potassium on ammonia that hydrogen was an alkalinizing principle, Davy uttered the following important but often over-looked truth: "The substitution of analogy for fact is the bane of chemical philosophy; the legitimate use of analogy is to connect facts together and to guide to new experiments."

Davy's facts were clear and convincing and in a few years chlorine was generally accepted as an element. In 1812 and 1813 iodine, discovered by Courtois, a French soap maker, and investigated by Gay-Lussac, was added to the list of acidifiers.

**The New Theory of Acids.** — These additional facts necessitated a revision of the theory of acids. It came about that no one element was any longer regarded as

the acid-making principle but the acid properties seemed to be dependent upon the other element or elements combined with hydrogen. An acid might contain oxygen and be an oxy-acid or contain no oxygen. So, too, a salt might contain oxygen or, like the chlorides and iodides, have none in its composition. Thus the old view that a salt was a compound of the oxide of a non-metallic element, or acid, and of the oxide of a metal, or base, was overthrown and salts came to be looked upon as metallic derivatives of acids, a metal replacing the hydrogen. The only element common to all acids was hydrogen.

**The Alkalizing Principle.** — In this connection it is well to take up the discussion which arose as to the constitution of the alkali metals, sodium and potassium. Davy had observed that these metals separated at the negative electrode, while oxygen appeared at the positive when the hydroxide was electrolyzed; also that they had the power of reducing metallic oxides. He likewise showed that by their combustion in oxygen the alkalis seemed to be regenerated. Hence, he concluded, these substances were metallic and elementary. From his investigation of ammonium amalgam a little later he concluded that this was composed of mercury and a hypothetical metal-like substance, ammonium, which broke up into hydrogen and ammonia. The analogy between this substance and the alkalis and the similarities between their amalgams gave rise to the theory that these alkali metals also were combined with hydrogen, a theory which Davy was more inclined to accept because of the combustibility of these metals. Gay-Lussac and Thénard had examined also the action

of potassium upon ammonia gas and noted the liberation of hydrogen and the formation of a green substance, the amount of hydrogen liberated being the same as that set free by potassium from water. From the green substance they regenerated the original amount of ammonia used. Therefore, they said that potassium consisted of potash and hydrogen and that this hydrogen was set free by treatment with water or with ammonia. According to this theory, there was an alkalizing hydrogen.

Davy soon returned to his original ideas as to these alkali metals and gave as his explanation of the experiments of Gay-Lussac and Thenard that the hydrogen came from the decomposition of the ammonia and not from the potassium. In the year 1811 Gay-Lussac and Thénard came over to Davy's views, having observed that the body obtained by burning potassium was not the same as potash but contained less oxygen, and that the melted potash was not water-free, as Davy had imagined. Thus they gave up their theory that hydrogen was an alkalizing principle giving bases when combined with ammonia, soda, or potash and similar substances.

**Berzelius (1779-1848).**— It was peculiarly fortunate for chemistry that two such brilliant and accurate investigators as Davy and Berzelius should have appeared at a time when the framework erected by Lavoisier needed filling out and the foundations of the science had to be broadened and deepened. A succession of mediocre and inaccurate workmen coming just then would have more easily misled and more seriously retarded the science than at a later period. Berzelius ranks as one of the greatest of chemists and the chemists of to-day can scarcely overestimate their indebtedness to him.

Berzelius was born in Sweden one year after the birth of Davy. Poverty greatly hampered both in their younger years and both were forced to follow medicine and pharmacy as a means of livelihood at first. Berzelius became professor of chemistry in Stockholm. Here he lacked the appliances and the leisure afforded Davy by his freedom from class work. Still, his lectures and classes enabled Berzelius to impress himself and his views upon the rising generation of chemists, and some of the noted chemists received training under him. His career was further comparable to that of Davy in that he held an honored post, namely, that of permanent secretary to the scientific society of his native land and was ennobled by his king.

**Contributions of Berzelius.**—It is difficult to give a short and at the same time fair account of the work of this great man, as it covered nearly the entire field of chemistry and hence was of the most varied and extensive character. Only brief reference can be made to some of the more important work. It is interesting to note the difference between the equipment with which this work was done which compares but poorly with the expensive appliances and large means which were at the command of Davy and increases the wonder over what he accomplished. Wöhler, his most distinguished pupil, has left a description of his first visit to the laboratory of Berzelius in which so many famous discoveries had been made.

“No water, no gas, no hoods, no oven were to be seen; a couple of plain tables, a blow-pipe, a few shelves with bottles, a little simple apparatus, and a large water-barrel whereat Anna, the ancient cook of the establish-

ment, washed the laboratory dishes, completed the furnishings of this room, famous throughout Europe for the work which had been done in it. In the kitchen which adjoined and where Anna cooked was a small furnace and a sand-bath for heating purposes."

At the time of Davy and Berzelius the chemist was expected to be something of a mechanic, able to cut and form, fashion and solder, the wood, brass, and iron into the various shapes he needed. He must also have skill as a glass blower, for in most cases he would have to depend upon his own cunning of hand for the success of his experiments.

**Analytical and Experimental Work.** — Berzelius introduced many improvements in the methods of analytical chemistry, devising new means of separating and determining the different elements. His close attention to details led him to the discovery of selenium, ceria, thoria, and many new compounds. He was also the first to prepare the elements silicon, zirconium, and a purer tantalum, and did much towards enlarging the knowledge of the platinum metals. He made a great number of investigations to prove the law of constancy of proportions and also Dalton's law of multiples. He enriched mineralogy by many analyses of minerals and showed that minerals were simply naturally occurring chemical compounds which obeyed the ordinary laws of combination. He introduced a chemical system for the classification of minerals based upon this view of their nature. He extended the law of multiple proportions to organic chemistry and did much to systematize that branch of chemistry.

**Determination of Atomic Weights.** — Berzelius, to-



gether with the pupils in his laboratory, undertook the determination of the atomic weights. The analytical work, of course, greatly excelled in accuracy that of Dalton, and in the rules laid down for guidance in deciding the number of the atoms in a given compound or molecule he showed a far greater knowledge of and insight into chemical reactions. Still his rules were in some respects arbitrary and unsatisfactory. By recalculating the results from his analytical data many of his determinations have been cited and utilized in settling these physical constants in the century which has elapsed since his time. It has already been mentioned that in 1813 this far-seeing man recognized in part the distinction made by Avogadro between atoms and molecules. His first fairly complete table of the atomic weights was published in 1818.

**Introduction of Symbols.**—The rapid development of the science made it necessary to have some shorthand method of recording elements, compounds, and reactions. Of course a few symbols taken from ancient mythology, astrology, etc., had been used by the alchemists and iatro-chemists, and there were later sporadic efforts at shortening the record. Dalton, for instance, had attempted to introduce certain diagrammatic symbols but failed because of their unpractical nature. Thus, oxygen was a circle  $\bigcirc$ ; hydrogen, a circle enclosing a dot,  $\odot$ ; and water became  $\bigcirc\odot$ . Carbon was a solid black circle,  $\bullet$  and carbon dioxide, therefore, was  $\bigcirc\bullet\bigcirc$ . And so the list went on with large circles, barred circles, radiated circles, etc.

Berzelius greatly aided the progress of chemistry by the introduction of a rational, simplified set of symbols,

the meaning of which was caught at a glance. The system was practically the same as that which has been in use ever since. He proposed that the first letter of the Latin name of the element should be used to designate it and that this should represent one atom, or equivalent of it. A compound was represented by placing the proper number of these symbols side by side. Thus H is hydrogen, Cl is chlorine, and HCl is hydrogen chloride. He supposed the existence of certain double atoms where two atoms of an element occur together. These were indicated by a mark across the symbol; thus HO was water, or, as it is written now,  $H_2O$ . For convenience sake an atom of oxygen was often indicated by a dot, an atom of sulphur by a mark at right angles. Thus carbon dioxide  $\ddot{C}$ ; potassium nitrate,  $K\ddot{N}$ .

**The Dualistic Theory.**—In matters of theory Berzelius exercised also a commanding influence. The combining power of the atoms he attributed to their electro-chemical character, his view of the atom being that it carried a distinct charge. The term atom was extended by him to include what he looked upon as compound atoms. These were built up of two parts, each of which might be a simple atom or several atoms in which each of the two parts acted as a single, simple atom. This was the dual structure and formed the dualistic system of Berzelius. This theory has already been referred to and is mentioned again because of the system of writing formulas of compounds which he introduced and which was in vogue for many years. Thus barium sulphate was supposed to be made up of barium oxide and sulphur trioxide, the first positively charged and the latter negatively charged. The formula was

written  $\text{BaO.SO}_3$ . So also  $\text{CaO.CO}_2$ ,  $\text{ZnO.SO}_3$ , etc. To write such formulas correctly required a knowledge of the valences, both of atoms and compound radicals, which was lacking at that time.

† **Additions to the List of Elements.** — During the period covered by Berzelius several new elements were discovered by his pupils and others. In 1817 Stromeyer discovered cadmium and in the same year Arfvedson announced the separation of lithium. In 1828 Wöhler succeeded in obtaining aluminum, beryllium, and yttrium. Some years later Mosander separated several of the metals contained in the rare earths, as lanthanum, erbium, and terbium. Bussy separated magnesium in 1829; vanadium was added by Sefström in 1830. The first of the platinum metals was discovered by Wood in 1741 and the last of these, ruthenium, was separated more than a century later — in 1845 — by Claus. No further discoveries were made until the spectroscope was brought into use. By its aid in 1860 Bunsen added two new elements, rubidium and cesium, and more than a dozen have been found since. This delicate means of testing also revealed the fact that while many of these new elements constituted a very small proportion of the substances making up the crust of the earth they were very widely distributed; and furthermore, that the sun and other celestial bodies were composed of the same sort of matter as was to be found on our planet, and so the universe was one harmonious whole as to composition and governed by the same laws. The fact that each element has its distinctive spectrum furnished a final test as to whether or not the substance under examination was really a new element. Depend-

ence upon chemical methods and tests alone caused many mistakes and something like a hundred false announcements have appeared in chemical literature.

**The Monatomic Gases.** — Great interest was aroused when Ramsay and Rayleigh discovered argon in 1894, and also a few years later when Ramsay announced the existence of its companion gases, helium, neon, krypton, and xenon, all of which are found in the atmosphere. The story of the discovery illustrates well the value of careful and accurate work without neglecting apparently trivial details and the following up of each clue until, so far as possible, everything is known and understood about the subject under investigation. It is sometimes stated that discoveries and important advances are often brought about through accident. Thoroughness does not admit of accident. It would seem more fitting to reserve the term for the one who had his chance and missed it. The opportunity passes and may never return. There have been many such unhappy instances in science.

In his analytical examination of air in 1785 Cavendish subjected an enclosed volume to the action of the electric spark. Oxygen was added from time to time until there was more than enough to combine with all of the nitrogen. The products and the excess of oxygen were removed by solvents. It is a testimony to the accuracy both of his observation and reporting of details that he recorded the presence of a residue or bubble, equal to about  $\frac{1}{120}$  of the original volume. Many others made use of this method and either failed to note or to report the residue, and no attention was paid to the observation of Cavendish.

More than a century later (1894), while determining the density of nitrogen, Lord Rayleigh found that there was a difference between the density of that prepared from the compounds of nitrogen and the nitrogen obtained from air, the latter being half a per cent heavier. This brought to mind the forgotten observation of Cavendish and led to an examination of air to see whether it contained any unknown gas. The investigation was carried on jointly by Rayleigh and Ramsay, who pursued different methods for removing the nitrogen from the air, and their results agreed. The air contained a gas which would not combine with anything else and to this new element the name argon was given. It forms about one per cent by volume of the atmosphere and can therefore be prepared from it in large quantities. It has no combining power and its molecule consists of a single atom. It has its distinctive spectrum and can be detected by this means.

In the following year Ramsay examined a strange gas which had been reported as present in certain uranium minerals, thinking that this also might prove to be argon. He found the spectrum to be quite different and identified it with the spectrum of one of the elements found in the sun some thirty years earlier by Lockyer and named by him helium. In the uranium minerals the helium occurs along with small amounts of nitrogen and argon. It is known now to occur in the atmosphere, in well and spring waters, and in the natural gas which is drawn from the earth in many places. This also is a monatomic gas and forms no compounds. Hydrogen and helium are the lightest gases known and, next to hydrogen, helium has the lowest atomic weight and is

the most difficult of the gases to liquefy. These facts have their bearing on the latest theory of the composition of the atoms.

Many other minerals were examined by Ramsay, but no further new gases were obtained from them. A more exhaustive study was then made of the air, in which Travers assisted Ramsay. The method was to take very large quantities of liquid air and examine the fractions which evaporated at different temperatures. In this way, in 1898, they succeeded in separating three new elements to which the names neon, krypton, and xenon were given. These resembled helium and argon and belonged to the monatomic group. Later Moore made a still more thorough examination, evaporating one hundred tons of liquid air, but found no additional new gases.

**Further Development of Inorganic Chemistry.**—During the century which has elapsed since Berzelius began his most important work a great many able chemists have labored in the field of inorganic chemistry; multitudes of new compounds have been formed and studied and a better understanding reached as to the laws governing their formation and decomposition. It is in this way that science grows—an army of toilers in the ranks, a good and competent captain here and there, and, when the emergency arises, a great strategist who leads the way to masterful accomplishment—a Newton, a Lavoisier, a Dalton, a Berzelius, a Faraday, a Mendeleeff. History cannot tell the story of all, but each faithful private in the ranks deserves his meed of gratitude.

## CHAPTER XIII

### DEVELOPMENT OF ORGANIC CHEMISTRY

In the text-book of Lémery, in use in the latter half of the seventeenth century, all chemical substances were classified and separately treated under the three headings, mineral, vegetable, and animal substances. This division seems to have been made first at this time and was the usual one during the next century. This corresponded with the favorite grouping of the "three natural kingdoms" which was so much used in books on general science a few generations ago. It was the animate and inanimate creation, and between the two lay the barrier of life or vital force which was not to be transcended. So chemists chiefly busied themselves with the mineral world, its compounds and elements and the wonderful laws governing them, and through their study reached down to the unchanging atoms upon which they founded their faith and their working. A building on any other foundation was as futile as a building on the sand.

**The Views of Lavoisier.** — Here also the master mind came to the rescue. Beginning with the foundation of stones, Lavoisier showed that all of these products of life processes were composed mainly of carbon, hydrogen, and oxygen. Some included nitrogen and still fewer contained phosphorus and sulphur. Before this there was great doubt and discussion as to their composition, but Lavoisier

showed how they could be analyzed with fair accuracy. Quite so, one might say and many did say, you can tear down and find of what the building was made but you can never rebuild. Only this strange, evasive, unknowable vital force can do that. Had man halted, blind and impotent, before that man-erected barrier he would have been without most of the comforts of modern life, and it is doubtful whether the huge population now inhabiting the earth could exist. Chemistry is not merely analytical but creative, and so chemists began to regard it.

Lavoisier devised a system of quantitative analysis for these substances so as to decide their composition fully. Acid substances were recognized among them and Lavoisier accounted for their nature by supposing that in these cases the oxygen was combined with a compound radical or organic residue. This idea was later developed by Berzelius and his followers until organic chemistry became the chemistry of the compound radicals. But the first tearing down of barriers came when that erected between the "vegetable and animal kingdoms" was overthrown through the investigation of the fats by Chevreul. These fatty substances are found in both plants and animals and Chevreul proved that many of them were identical. He also showed that the same was true of certain acids and other substances. So the first part of the distinction was no longer tenable, but the line was still very sharply drawn between mineral substances and the products of plant and animal life. These latter, it was believed, could not be artificially formed out of the elements that composed them. They were produced by some mysterious force, life, whose operations could not be imitated. The ordinary laws governing chemical



affinity could not be expected to apply in this field and chemical theories could not explain the phenomena of life.

**Views of Berzelius.**— In 1811 Berzelius attempted to prove that organic substances were nothing more than ordinary chemical compounds, obeying the laws of constant and multiple proportions and offering a fair field for the application of the atomic and other theories. With improved appliances and analytical methods he succeeded in showing the correctness of his views, but only after years of labor. In the third decade of the century he came to look upon organic substances as composed in the same way as the inorganic compounds but having compound radicals in the place of elements. With a satisfactory definition of compound radical this is the basis of organic chemistry, though much work had to be done before it was made clear. Berzelius attempted to apply his dualistic theory to the compound radicals which were recognized by him. He was in a measure led to take up this idea of the compound radical by the research of Gay-Lussac upon cyanogen, in which he showed that this radical behaved like an element. Attempts were multiplied to discover the various organic substances which had complex groupings of atoms and functioned as elements. Thus Gay-Lussac looked upon alcohol as ethylen and water. Döbereiner regarded oxalic acid as carbonic acid and carbon monoxide. Berzelius pointed out that this was in contradiction to the electrochemical theory. There was danger of confusion and error.

**Isomerism.**— The search for the proximate constituents in organic compounds brought about a rapid development of the science. There were many efforts

at settling the chemical constitution of these substances. One of the important discoveries made was that of isomerism. This was at first looked upon as an error, so little were chemists prepared to believe that substances similarly composed could be chemically and physically different. It was in the year 1823 that Liebig announced that his analysis of silver fulminate yielded the same results as Wöhler had obtained in the preceding year for his silver cyanate. He was confident that his figures were correct and believed that Wöhler must have made a mistake. A careful repetition of the analyses showed him that both were correct. Thus it was proved that two substances, totally unlike, could and did have the same composition. Gay-Lussac saw that the only explanation of this lay in the different mode in which the elements were united with one another. Berzelius hesitated to accept the facts or any generalization from them. Then followed in 1825 Faraday's discovery of an isomer of ethylen chloride, and in 1827 Wöhler's transformation of ammonium cyanate into urea. Berzelius himself showed the isomerism existing between tartaric and racemic acids, and chemists became accustomed to the new fact of isomerism for the explanation of which the atomic theory is so necessary. Berzelius suggested the name isomerism. He also adopted as the most plausible explanation of isomerism the different arrangement of the atoms. He seems to have thought it a possibility to determine the mutual relations of the atoms in their compounds, or the manner in which the atoms were united to the compound radicals or proximate constituents.

**The Synthesis of Urea.**—Many of the naturally occurring minerals had been reproduced or synthesized

by the chemist, but it was still a common belief that the synthesis or imitation of organic substances was beyond the reach of experimental methods, as they were the products of life itself and could be formed only in the plant or animal tissue. It is true that new organic preparations had been made by distilling or otherwise treating various products of plant life but the original source or starting point remained the same life products. Chevreul had shown that the natural fats were compounds of certain acids and the glycerin discovered by Scheele, but no one had built up these two components.

It was Wöhler's brilliant synthesis of urea which finally broke down this barrier, proving the forerunner of many syntheses and inciting numbers of chemists to engage in such interesting and valuable work. It was in 1828 that he undertook to prepare ammonium cyanate by evaporating a solution containing ammonium sulphate and potassium cyanate. The evaporation yielded crystals of urea instead. The same change will take place if a solution of ammonium cyanate alone is evaporated. This contains the same elements and the same number of atoms as are present in urea. Heating the solution brings about a rearrangement of the elements. Thus  $\text{NH}_4\text{CNO}$  becomes  $(\text{NH}_2)_2\text{CO}$ . The cyanates were supposed to belong to the inorganic compounds and could be prepared from the elements. Hence the synthesis was complete without the intervention of a hypothetical vital force. Urea is one of the most interesting and best known of animal products, being the compound in which most of the waste nitrogen is eliminated by animals, and no more striking example of the fallacy of the old assumption could have been chosen. While the dying

away of the old belief was not immediate, Wöhler's discovery is commonly pointed to as marking the beginning of organic chemistry as a distinct branch of the science.

**Organic Analysis.**— One obstacle to the rapid development of this branch of chemistry lay in the imperfection of the analytical methods. Lavoisier had laid the foundations for the correct analysis of organic substances and Gay-Lussac, Berzelius, and Döbereiner had successively improved the processes. However, the operations were still slow, difficult, and not very accurate. In 1830 Liebig greatly improved the methods of analysis and his processes have not needed very many nor great modifications to fit them to the needs of the present day. Of course, as the years passed gas and electricity supplanted the charcoal which he used for heating. Improved methods for determining the halogens, nitrogen, vapor densities, etc., were introduced by Carius, Hofmann, Victor Meyer, and others, so that extremely accurate work can now be done.

**Classification of Organic Substances.**— A true and helpful classification of these substances, the known number of which was increasing so rapidly, was lacking. In 1811 Gay-Lussac and Thénard, interpreting the results of their analyses, had divided them into three classes:

1. Those which contain just so much oxygen as is necessary to form water with the hydrogen present. These were carbohydrates.

2. Those containing less than that porportion of oxygen. These were the resins and oils.

3. Those containing more oxygen. These were considered the acids.

Of course, so primitive and faulty a classification as this was of little service. For instance, it quite ignored the many hydrocarbons which contain only carbon and hydrogen. It merely serves to show that in the formative stage of the conceptions held as to these substances no satisfactory classification was possible.

**Extension of the Electro-Chemical Theory.** — In 1819 Berzelius declared that his electro-chemical theory could not be extended to organic chemistry, as here these elements were under the influence of life force. In decay, fermentation, etc., he saw evidences of a striving on the part of these elements to return to their normal condition. He later extended both this theory and that of dualism to this branch of chemistry, seeing in the compound radicals the same dualistic condition which he thought existed in what he called the compound atoms of inorganic substances.

**Extension of the Radical Theory.** — There was continued effort at extending the radical theory to organic chemistry. Thus in 1828 Dumas announced that ethylen was such a radical and gave a table of its compounds, endeavoring to show their analogy to ammonia and its compounds:

Olefiant gas or ethylen,  $2C_2H_2$ ;  $NH_3$ , ammonia.

Hydrochloric acid ether,  $2C_2H_2.HCl$ ;  $NH_3.HCl$ , ammonium chloride.

Ether,  $4C_2H_2.H_2O$ ;  $2NH_3.2H_2O$ , ammonium oxide.

Alcohol,  $4C_2H_2.2H_2O$ .

Acetic ether,  $4C_2H_2.C_3H_6O_3.H_2O$ ;  $2NH_3.C_3H_6O_3.H_2O$ , ammonium acetate.

Oxalic ether,  $4C_2H_2.C_4O_3.H_2O$ ;  $2NH_3.C_4O_3.H_2O$ , ammonium oxalate.

It was a part of this theory that the radicals could be separated and were capable of independent existence. This was called the Aetherin theory and was largely based on the ease with which alcohol could be converted into ether and ethylen. In this the aetherin  $C_4H_4$  was a base, forming hydrates with water and salt-like ethers with acids. This must serve as an illustration of the imperfect attempts at discovering these radicals and the great difficulties attending such researches.

**The Benzoic Acid Radical.**—The radical theory received its greatest support from the classical research of Liebig and Wöhler in 1832 *On the Radical of Benzoic Acid*. This was hailed by Berzelius as heralding the dawn of a new day. It was at least an epoch-making contribution, standing out as a masterpiece amid much that was erroneous and misleading in the work of the day. These two great chemists, then young men, showed that in the oil of bitter almonds (benzaldehyde) and its many derivatives one group of atoms remained unchanged and characterized the whole. This they called benzoyl and assigned to it the formula  $C_{14}H_{10}O_2$ , or the present formula doubled. Benzaldehyde itself was this radical with hydrogen,  $C_{14}H_{10}O_2 + H_2$ ; the radical plus oxygen was benzoic acid; with chlorine it was benzoyl chloride, etc.

**Changes in the Radical Theory.**—This brilliant research aided greatly in the advancement of organic chemistry by the valuable new methods of research which it introduced into the practice of the chemist. Furthermore, a new principle was recognized. Hitherto it had been thought necessary to isolate the radical, and it was the great difficulty or even impossibility of doing this that

rendered much of the work futile. Benzoyl had not been isolated and was not known except in compounds, but one could as little afford to doubt its existence, since its compounds were known, as to question the existence of magnesium or aluminum, whose compounds were well known a long time before the metals themselves were separated. Thus chemists were aroused to search for the common radicals in substances which showed by their chemical behavior or modes of preparation that they should be grouped together.

Berzelius and Liebig entered upon this work with much success. The difficulty in recognizing benzoyl as a radical because of its containing oxygen was done away with by regarding it as the oxide of the real radical. The early idea of a radical was that it was a compound of carbon and hydrogen only and contained no oxygen. Thus ether was the oxide of the radical ethyl, but Berzelius missed the connection with alcohol by regarding that as the oxide of the radical  $C_2H_6$ . This was corrected by Liebig, who, however, doubled the formula of the radical ethyl  $C_2H_5$ . So for him alcohol was the hydrate of ethyl  $C_4H_{10}O.H_2O$ .

Chemists agreed as to the existence of compound radicals in these various compounds. It is not surprising that they should differ as to the nature of the radicals themselves when one considers that this was really only the beginning of organic chemistry and the knowledge of these substances was very imperfect. Berzelius was inclined to the belief that these radicals were unchangeable. Liebig took a wider view of them, looking upon his grouping of the elements merely as a means to a better understanding of the transformations these bodies undergo.

But despite minor differences, the brilliant chemists who have been cited had obtained an insight into the basic principles of classification for organic substances. The hydrocarbons do function here as the elements and do form compounds which correspond to the hydroxides, oxides, halides, sulphides, etc. But since they themselves are capable of combination and change there is a bewildering versatility and great multiplication and complexity of the compounds formed.

**Compound Radicals.** — About 1837 this theory of the compound radicals reached its highest point of credit and influence, and organic chemistry became the chemistry of the compound radicals. Liebig and Dumas united in valuable investigations, and a citation from a joint publication of theirs will serve to show how far they carried the classification:

“Organic chemistry possesses its own elements, playing at one time the rôle of chlorine or oxygen, at another that of a metal. Cyan, benzol, amide, the radicals of ammonia, of the fats, of alcohol, form the true elements of organic nature; whilst the simplest constituents, as carbon, hydrogen, oxygen, and nitrogen become recognizable only when the organic material has been destroyed.”

A year later Liebig clearly defined a compound radical, giving three essential characteristics and using cyanogen as a type:

1. We call cyan a radical because it is an unchanging constituent in a series of substances or compounds.
2. Because it can be substituted in these by other simple bodies.
3. Because in its compounds with a simple body



this last can be separated and substituted by another simple body.

At least two of these conditions must be fulfilled for a group of atoms to be regarded as a radical.

This radical theory aroused great interest and stimulated chemists to much fruitful and even brilliant work. Special mention may be made of the research of Bunsen upon the kakodyl compounds which formed, indeed, one of the strongest supports of the theory.

## CHAPTER XIV

### FURTHER THEORIES AS TO STRUCTURE

**Atomic Theory Confirmed.** — The dualistic theory and that of the compound radicals were necessarily founded upon the atomic theory of Dalton. As they were discussed and struggled over and became entrenched in the science they rendered the atomic theory an indispensable assumption. Even when dualism became discredited and organic chemistry took on a different significance from that of the chemistry of the compound radicals atoms were still necessary, and the only possible changes were in the conceptions of the nature of the ultimate particles.

**Substitution Theory and Overthrow of Dualism.** — Doubts began to arise as to the theory of dualism. Dumas and other chemists felt that Berzelius had pressed his theory too far. It was, however, the discovery of the principle of substitution which really dealt this theory its deathblow and paved the way for the so-called unitary theory. Substitution might have been deduced from the old idea of equivalence. It was also touched upon in the researches of Mitscherlich upon isomorphism, Other facts led up very nearly to it. But, as so often happens, the thought and its suggestion were brought about through an accident.

**Substitution of Chlorine for Hydrogen.** — In 1834 Dumas was called upon to examine into the cause of certain

irritating vapors coming from wax candles used to illuminate the Tuileries. He found that in bleaching the wax chlorine had been used and some of the chlorine remaining in the candles had caused the disagreeable fumes. These consisted of hydrogen chloride, the hydrogen coming from the wax. Dumas felt that this could not be explained on the ground of a mechanical retention of the chlorine as an impurity. He then fully investigated the action of chlorine upon wax and kindred organic substances. He found as a result of his investigations that hydrogen in organic compounds may be exchanged for chlorine, volume for volume. Wöhler and Liebig had shown in 1832 that in preparing benzoyl chloride out of oil of bitter almonds by the action of chlorine two atoms of chlorine took the place of two atoms of hydrogen. This was contrary to the central idea of dualism, since chlorine was electro-negative and should never substitute electro-positive hydrogen. Additional facts accumulated. Liebig had shown that by the action of bleaching powder and chlorine upon alcohol chloroform and chloral were formed. He misunderstood the constitution of these compounds but Dumas determined correctly their constitution and their relation to alcohol, showing here the far-going substitution of chlorine for hydrogen.

**Trichloracetic Acid.**—Dumas by his substitution of chlorine for hydrogen in acetic acid, forming trichloracetic acid, secured the most important support for his theory of substitution. It can be seen from what he wrote regarding this acid what his views were as to substitution, and how the discovery of the acid supported them. In trichloracetic acid there are three of the hydrogen atoms of acetic acid substituted by chlorine.

"It is a chlorinated vinegar," says Dumas, "but it is remarkable, and the more so for those who dislike to find in chlorine a body capable of substituting hydrogen in the exact and full sense of the word, that this chlorinated vinegar is still an acid like ordinary vinegar. Its acid power has not been changed. It neutralizes the same amount of base as before. It possesses the same acidity and its salts, compared with the acetates, show an agreement full of interest."

Thus it was shown that the views of dualistic structure were too rigid and a hindrance to the development of organic chemistry. A negative atom could be substituted for a positive and the compound radical began to be regarded as an atomic structure in which one atom could be substituted for another without regard to its electrochemical nature. Laurent showed that Dumas' statement as to substitution did not hold good for all cases. Often more chlorine was taken up, and sometimes less than corresponded to the volume of hydrogen lost. As the substituted body showed certain analogies to the original, he maintained that the chlorine took the place held by the hydrogen in the molecule and, to a certain extent, played the same rôle.

**Unitary Theory.**—The views as to substitution met with vigorous opposition and had to be modified in some particulars, but soon the molecule came to be regarded as a unitary and not a dualistic structure. Thus there were two opposing theories: The older, dualistic, looked upon the molecules as double natured and composite yet forming one unchangeable whole in which the members lost their individuality and the nature of these molecules was determined by the quality of the atoms; the new,

unitary, theory maintained that the number of the atoms and their arrangement determined in the main the nature of the compound, and that this molecule was not unchangeable but that the atoms comprising it could be substituted by others without a complete change of nature.

**Nucleus Theory.**—Laurent was led to propound further the nucleus theory which was largely adopted. This was in some respects an elaboration of the compound radicals. Many of the ideas in this theory have been incorporated in the science, though the theory itself has been dropped. This theory sprang from the old radical theory but with an important difference, i.e., the radical here is not an unchanging group of atoms but a combination which can be changed through the substitution of equivalents. It is but a step in the evolution of the modern theory, as seen in the benzene nucleus.

**Type Theory.**—The idea of types was introduced by Laurent and Gerhardt and was applied to both inorganic and organic chemistry. It was rapidly taken up and became the dominant structural theory of chemistry in the fifth decade of the nineteenth century. According to this theory, potassium hydroxide was conceived to be not a compound of the oxide and water but rather a derivative of water in which one atom of hydrogen was substituted by potassium. This was called the water type. Gerhardt recognized three types—water, hydrochloric acid, and ammonia—and endeavored to classify all compounds under one or the other of these types. Gradually it was seen that other types were needed and the derivation from types became more and more complicated.

Berzelius, now an old man, contended for his dual-

istic theory and could not be reconciled to the change to the types and to the unitary theory. But the great master was engaged in a vain struggle. In the course of the discussion he formulated a new theory as giving a better explanation of the substitution phenomena and as being more in consonance with his dualistic theory. This was known as the theory of conjugated compounds and associated with it was the theory of copulas. The ideas, however, were not very clear and exerted little influence upon the science.

The discovery of the amines in 1848, the year after the death of Berzelius, did much to strengthen the type theory. This was followed shortly by the important work of Williamson on the ethers, alcohols, esters, and acids, which he showed belonged to the water type. It should be noted that these types were drawn from inorganic compounds, thus building upon that which was already fairly well known. The two great divisions of chemistry have proved mutually helpful in their development and must always be regarded as parts of one harmonious whole. Throughout, the question of chemical constitution has been the important one.

**Homologous Series.** — This was a period of classification — one of striving after a systematic arrangement of the elements in inorganic chemistry and the radicals in organic. Pettenkofer, hoping for an all-embracing system, compared the elements with the compound radicals and suggested that they might be looked at from the same standpoint. The analogies between the radicals themselves had been noted and Schiel suggested that they might be arranged in series which would bring out this homology. The suggestion was adopted by Dumas

with regard to the fatty acids and the idea was further extended by Gerhardt. Dumas transferred the idea to inorganic chemistry and tried to arrange the elements in homologous series, but the analogies were too incomplete for success. As the knowledge of the organic radicals grew and the fullness of their agreement was recognized, homologous series became a necessary fixture in organic chemistry.

**Application of the Valence Theory.** — It was at this time that the valence theory took its rise from the study of the organo-metallic bodies. With its introduction structural organic chemistry had a secure foundation. Its founder was Kekulé, who was born about a year after Wöhler's noted synthesis of urea. In 1858, while professor at Ghent, he showed by a study of the simpler compounds of carbon that its valence was four. Later he became professor at Bonn, dying there in 1896.

Taking his arrangement of the halogen compounds of methane, it will be seen how he applied valence to the type theory of which he was a strong supporter. The series runs:  $\text{CH}_4$ ,  $\text{CH}_3\text{Cl}$ ,  $\text{CH}_2\text{Cl}_2$ ,  $\text{CHCl}_3$ ,  $\text{CCl}_4$ . The quadrivalence of carbon remains, while the valence of the radicals  $\text{CH}_3$ ,  $\text{CH}_2$ , etc., increases by one with each hydrogen lost. But his most original idea was in regard to compound radicals containing more than one carbon atom. His conclusion here was that the carbon atoms were directly connected with each other. Thus the ethyl radical would be  $\text{CH}_3-\text{CH}_2$ ; the propyl  $\text{CH}_3-\text{CH}_2-\text{CH}_2$ , the hydrogens being joined to the carbons and the latter forming an open chain. Kekulé's desire in constructing these formulas was not merely to show how the atoms were united but to give a picture of the way in which re-

actions took place. So these formulas were called rational. He regarded as the most rational the one which at the same time expressed the greatest number of metamorphoses.

The writing of the first graphic formulas was attempted by Couper, also in 1858. He insisted, however, upon halving the atomic weight of oxygen and this necessitated writing two atoms of oxygen where modern formulas would show only one. This was a disadvantage in the matter of making a favorable impression and receiving recognition. In 1861 Kekulé published the first volume of his epoch-making text-book which presented fully to the public his views upon structural organic chemistry, illustrated by a very large number of examples. Kekulé also gave as his explanation of the differences between the two great divisions of organic substances the open chain and closed chain formulas, thus satisfactorily clearing up many difficulties and paving the way for the remarkable development of organic chemistry which followed in the next decades. These two divisions were called, respectively, the fatty (later aliphatic) and the aromatic (cyclic) series. In the former methane and its homologues were the dominant radicals; in the latter, benzene.

**The Benzene Theory.**—The so-called aromatic group or series of substances showed usually a higher ratio of carbon to hydrogen than did the aliphatic. Where the ratio was the same or approximately the same the stability and capacity to form compounds were much greater in the aromatic group. Thus dipropargyl and benzene both have the formula  $C_6H_6$ , but the former is quite unstable while the latter stands the action of the strongest



acids. Manifestly the difference could only be accounted for by assuming a different arrangement of the atoms. But to find an arrangement which would account for such unusual stability was a perplexing problem. It is best to give in Kekulé's own words the account of how he reached a solution, bearing in mind that the case cited above was not the only one; nor was it the special one with which he was concerned.

"I was busy writing on my text-book but could make no progress — my mind was on other things. I turned my chair to the fire and sank into a doze. Again the atoms were before my eyes. Little groups kept modestly in the background. My mind's eye, trained by the observation of similar forms, could now distinguish more complex structures of various kinds. Long chains here and there more firmly joined; all winding and turning with a snake-like motion. Suddenly one of the serpents caught its own tail and the ring thus formed whirled exasperatingly before my eyes. I woke as by lightning and spent the rest of the night working out the logical consequences of the hypothesis. If we learn to dream we shall perhaps discover truth. But let us beware of publishing our dreams until they have been tested by the waking consciousness."

This was the origin of the benzene ring, an assumption which expanded through the labors of many workers into the accepted theory of the present and the basis of many of the most remarkable and important achievements of creative chemistry.

**Stereochemistry.** — One manifest lack in these structural formulas, if they were intended to give a complete picture of the molecule, is that they are written on plane

surfaces and hence confined to space of two dimensions, whereas they must of necessity occupy space of three dimensions. A perspective representation is also necessary. It was Van't Hoff who, in 1874, while still a student, fastened attention upon this and laid down the governing principles a little later in his book *Chemistry of Space*. This branch of chemistry is known as stereochemistry. Necessarily perplexities and difficulties increase if chemists are restricted to a knowledge of chemical reactions as the sole means of determining these space relations. An observation made by Laue in 1913, his subsequent work, and that of the Braggs, father and son, have introduced a new method, at least for crystalline structure, in the X-ray spectra. And already much progress has been made both for organic and inorganic molecules and the outlook is most promising for further revelations. By this method the molecules are actually photographed and can be studied in all the accuracy of detail and perspective. Success turns on the correctness of interpretation of the results.

**Pasteur (1822-1895).**— One of the greatest of scientific men, as well as one of the greatest benefactors of his race, was Louis Pasteur. Born of a peasant family in a small French village he revolutionized the science of medicine when he introduced and proved his germ theory of disease. He also accomplished much for the wine and other industries of his native land.

His most important contributions to chemistry came through his investigation of the tartaric acids and in general the phenomena of physical isomerism. There are four of these acids having the same formula. Their separate existence can not be accounted for by the usual

method of possible changes in the arrangement of the atoms, yet they do exist and exhibit certain physical differences. One of these extra forms had been known for a long time as racemic acid. It is often found in grapes along with tartaric acid and sometimes has substituted to a considerable extent the normal tartaric acid in the juice. Its acid potassium salt is more soluble than that of tartaric acid and hence does not separate out well in the aging of wine and renders the wine of inferior quality. Pasteur noticed that the sodium ammonium salt deposited two kinds of crystals. These crystals showed hemihedral faces so related that one crystal corresponded to the image in the mirror of the other. He found further that the acid from one variety of crystals was dextro-rotary while that from the other was laevo-rotary. This is referable immediately to space arrangement, as was represented in the mirror image. As he published an account of his work in 1848, it marks the beginning from which stereochemistry was later developed. Previous observers, notably Biot, had remarked a connection between optical rotation and hemihedral forms in such crystals as quartz, and it had been shown that the geometrical form determined the direction of the rotation. When one recalls that Pasteur's observations were made with solutions in the tube of the polariscope and also that later it was found that this property was also exhibited in the gases of certain volatile organic substances it becomes possible to trace the phenomenon directly back to the molecule. The construction of the molecule also evidently determined the crystal form. Considering such facts as these, Pasteur reached the conclusion that the molecule itself was unsymmetrical. It is now known

that tartaric acid contains two unsymmetrically arranged carbon atoms. In the undeveloped state of organic chemistry at that time Pasteur was unable to refer the lack of symmetry to any definite atoms.

His study of fermentations and brilliant work in tracing these changes to the life processes of micro-organisms have transformed the outlook of more sciences than one and wrought miracles for human comfort, health, and happiness. His name will be associated always with the conquering and control of contagious diseases.

**Syntheses from Coal Tar.** — The foundations for the important coal tar industries, especially relating to dye stuffs, were laid by Hofmann (1818–1892) and the first artificial or synthetic color was made in 1856 by Perkin, one of his students. Hofmann was at that time a professor in the Royal College of Chemistry in London. At the time of his death he was a professor in the University of Berlin.

Tar is recovered as a by-product in the distillation of coal and until the middle of the nineteenth century little use had been found for it beyond its use as fuel. In 1843 Hofmann found that it contained aniline and this led to his valuable researches upon the amines. In 1845 he found that it also contained benzene and the synthetic production of aniline in large quantities from this source followed. In 1856, in the course of his investigation of the action of oxidizing agents upon crude aniline oil, Perkin discovered the dye known as mauve. This was the first of the coal tar colors. Griess, another assistant of Hofmann, studied the diazo compounds and the manufacture of the azo compounds and dyes was founded upon the results of his researches. In 1868 Graebe and

Liebermann prepared alizarin, the red coloring matter of madder, from anthracene. After some years of costly and toilsome work at a later period Baeyer, who had studied under Bunsen and was then a professor at Munich, worked out the synthesis of indigo from naphthalene. These discoveries mark the triumphant progress of a great industry which soon branched out from the artificial reproduction of natural coloring matters into an almost unlimited field of creation of brilliant colors unknown before. Here the constitution of the molecules was painstakingly worked out and the chromophoric groups of atoms identified.

Further, plant perfumes were synthesized and new ones prepared. So, too, with the remedial agents. New organic preparations were studied as to their physiological properties and action and the field of synthetic medicines opened up. This required coöperation between the chemist and the physiologist and many skilled workers entered this field. New and terrible explosives were discovered and then others sought for among these organic compounds; and in these later years the deadly poison gases were manufactured for use in warfare. For good or ill, chemistry as a creative art came into its own. The modern world has become dependent upon chemical research and the knowledge and skill of the technical chemist.

## CHAPTER XV

### PHYSICAL CHEMISTRY

While in one sense physics and chemistry are distinct branches of science, both are concerned with the same great natural laws. The atom and the electron belong to both and now that matter in its ultimate analysis has been identified with energy there is scarcely a dividing line between them. In the earlier stages of their development one might be both physicist and chemist and often was. The great accumulation of facts and theories has rendered it practically impossible to be master in both. Where the two sciences merge into one another, however, a new branch has grown up and this is called physical chemistry. Its growth has been rapid and its importance, both in pure and applied science, can scarcely be over-estimated.

Physical chemistry may be said to have had its beginning in the teachings of Berthollet in his *Essai de statique chimique* published in 1801. He brought to light the fact that a chemical reaction depended upon the masses, or, as it would be expressed now, the concentration of the reacting substances; and that solubility, volatility, and such physical properties of the products influence materially the course of the reactions. Under certain conditions equilibria were reached. The importance of these observations was not realized at that early date. Chemists were busied with what they regarded as more important

work — the discovery and accumulation of facts and the testing of the more obvious fundamental laws.

Such investigators as Gay-Lussac with his gas laws, Avogadro and Ampère with their basis of the kinetic theory, Dulong and Regnault with their researches upon specific heat and the laws controlling its action, were most prominent among the early builders in this middle ground between the sciences. A still greater influence was exerted by Bunsen some fifty years later. In coöperation with Kirchoff he constructed the spectroscope which has contributed so much to the knowledge of nature and its changes both on the earth and in the extra-terrestrial bodies. By means of this instrument Kirchoff showed that radiations are absorbed by the vapors of the substances which emit them, and so revealed the meaning of the dark lines which had been found in the solar spectra. Other absorption spectra are given by solutions the exact physical explanation of which is still an unsolved problem. Bunsen's photochemical investigations taught that the degree of change brought about by light was proportional to the intensity of the light and the time of exposure, and that the light absorbed in a reacting medium was proportional to the change produced. His "photochemical induction" is yet without satisfactory explanation. Still it was of first importance to learn that photochemical absorption followed the usual laws. The invention of the polariscope and the study of polarization phenomena, the progress of hydrolysis, etc., aided greatly in the development of physical chemistry.

**Law of Mass Action.** — As has been pointed out, the basis for this was laid by Berthollet, but its bearing was not realized and the observations were practically

forgotten. After half a century had elapsed the details were gradually worked out. Thus Wilhelmy, in his investigations upon the inversion of sugars by acids, studied the hydrolysis of sugars by means of acids under conditions in which temperature, acids, etc., were varied. From these observations he deduced a mathematical expression for the velocity of the reaction. A little later Berthelot examined the hydrolysis of the esters. Guldberg and Waage, after more extended investigation, summarized the results and proposed as a law which would cover the known facts that when an equilibrium has been reached the velocity of a reaction is determined by the product of the active amounts of the interacting substances. To account for the relationships obtaining in heterogeneous equilibria the phase rule has been adopted. The essential principles involved in this were worked out by Willard Gibbs, whose work was published in 1876. This rule is now a matter of everyday application in work which would otherwise prove very baffling.

**Electrolytic Dissociation.** — With the announcement by Arrhenius in 1887 of his theory of electrolytic dissociation the importance of physical chemistry and its intimate bearing upon the ordinary reactions and phenomena of the laboratory began to be recognized and the attention of chemists generally was attracted to it. Much work had been done previously on electrolytic association but at various times and in a disconnected way. Arrhenius gathered these facts in addition to his own observations, showing the connection between them and the important conclusions to which they led. Faraday had found that in the decomposition of an electrolyte by an electric current definite amounts of the products are obtained at



the electrodes on the expenditure of a given quantity of electricity and these amounts are in equivalent weight proportions. The intensity of the current necessary for the dissociation was determined, in his opinion, by the strength of the attraction holding the molecules together. He concluded that the atoms or radicals composing the electrolyte acted as the carriers of the current and called them ions, naming the positive electrode anode and the negative cathode, and the ions anions and cations, respectively. At first the assumption was that the anion and the cation migrated with equal velocities. Hittorf showed that this was not the case. Williamson introduced the idea that a molecule was not a rigid structure always made up of the same identical atoms but was capable of exchanging with corresponding atoms of neighboring molecules. Thus an ion did not pass directly from one electrode to the other but migrated from one molecule to the next, effecting the necessary interchange. Clausius adopted this idea of exchange and brought additional facts to its support. Later Kohlrausch carried out many experiments upon the conductivity of solutions and confirmed the work of Hittorf. His conclusion was that each ion, regardless of the electrolyte of which it was a component, had a definite migration velocity which might be measured by its relation to some standard.

**Physical Properties of Solutions.**—The problem of what takes place in solutions was next attacked from a different point of view. It had been known for a long time that the freezing point of a liquid is lowered by dissolving various substances in it; also the vapor pressure is lowered or, as ordinarily expressed, the boiling point is raised when the liquid contains substances in solution. No regularity

had been observed, however, nor law deduced. The only observation bearing on this is that of Blayden, who worked in the laboratory of Cavendish. He studied the influence of various dissolved substances upon the lowering of the freezing point and found that when he compared solutions of the same compound the degree of lowering was proportional to the amount of substance dissolved.

In 1881 Raoult took up the investigation of this lowering of the freezing point and showed by his experiments that when different substances were used with the same solvent the lowering of the freezing point in each solution was inversely proportional to the molecular weight of the substance dissolved. Hence if the quantities taken were proportional to the molecular weights the degree of lowering would be the same. Turning then to the influence of such dissolved substances upon the boiling point he found an analogous influence upon the raising of the boiling point. In the hands of other investigators it was soon found that the matter was not so easily solved. There were many irregularities and exceptions which demanded explanation. The statement that behavior in solutions was independent of the nature of the solvent and of the dissolved substances could not be generally applied and was not true in that form. The difficulties were removed and the explanation made clear by experiments carried out along an apparently different line.

**Osmotic Pressure.** — More than one hundred years earlier Nollet had observed that when water and alcohol are separated by a membrane the water passes through the membrane into the vessel containing the alcohol and at the same time exerts a considerable pressure upon it. In 1877 Pfeffer measured this pressure, which is ex-

hibited also between water and an aqueous solution or between different solutions, and de Vries showed that solutions could be prepared which exhibited no pressure when thus separated.

**Experiments of Van't Hoff.** — The connection between osmotic pressure and the facts discovered as to boiling and freezing points and vapor pressure was worked out in the latter part of the nineteenth century by Van't Hoff, who also made a thorough investigation of the phenomena of osmotic pressure. He found in the course of the latter investigation that when a substance is dissolved in a liquid the molecules exert the same sort of pressure on its surface as they would if they existed in the form of a gas and occupied the same volume. The bearing of the molecular weight relations then is evident. When substances are taken in the proportion of their molecular weights they contain the same number of molecules and will obey the gas laws as to pressure, etc., provided there is a freedom of movement similar to that in a gas and no change in the molecule.

**Ionization Theory.** — Further light on the subject came through the work of Arrhenius on electrolysis. He reached the conclusion that in a solution through which a current is passing only a portion of the particles take part in the conduction. The proportion of such conducting particles he called the "activity coefficient." This activity coefficient was found to be proportional to the "affinity coefficient" of Ostwald. From a comparison of these facts of electrolysis with the facts above mentioned the modern theory of ionization was reached. The various compounds are divided into two classes: those which conduct electricity, or electrolytes, and those which

do not, or non-electrolytes. The electrolytes vary in their conducting power. When electrolytes are dissolved in water they separate or ionize into two ions, one positively and the other negatively charged. In the case of complete ionization there would, therefore, be twice as many particles present as there were molecules originally. This is approximately the case when strong acids or bases are the electrolytes. Twice the pressure would, therefore, be exerted, as this is due to the number of the particles and is independent of their nature. Those which do not electrolyze show no change in the number of particles and hence behave normally. The strong support of the ionization theory by Ostwald did much to bring about its general introduction. It has served to explain many reactions which were before difficult to understand, though there are still instances which present difficulties in the way of its application.

**Colloidal Chemistry.** — The conceptions introduced by physical chemistry now play an important part in all branches of chemistry and are essential to the understanding of much that goes on both in experimental and technical work. Among other things it has been made clear that besides the well-known molecular compounds with definite constitution and structure there are other molecular aggregations, often containing hundreds of atoms, which do not follow the fundamental laws of chemistry, as, for instance, the law of definite proportions, and which play a most important part in everyday life and in the industries. These are grouped as colloids and form a distinct division of the science under the name of colloidal chemistry. The first work upon these substances began with Graham's diffusion experi-

ments in 1850 in which he found that by means of dialysis substances could be separated into crystalloids, which form real solutions and diffuse more or less readily through an animal membrane, and colloids, which do not diffuse at all or only very slowly. Some colloids are apparently soluble in water, but it has been proved that they are really present in a state of very fine subdivision and are only suspended in the liquid. A very large number of substances have this property of existing as colloids, whether elements or compounds, and a new field of very interesting and complex phenomena has been opened up. Colloids form what are called adsorption compounds which are more or less stable to the action of water. In these the components may be present in indefinite proportions.

## CHAPTER XVI

### BIOCHEMISTRY

As has been related, the old man-erected barrier of a hypothetical vital force was overthrown and organic chemistry developed into that branch of the science which embraced the largest number of known compounds, running up into the hundreds of thousands, and attracted most of the investigators. It was realized that life processes, as they are still called, are identified with physical and chemical changes which obey the ordinary laws of those sciences and can be relied upon to bring about the usual results. These changes are definitely subject to the influence of the various forms of energy and take place normally at a normal temperature and under a normal pressure. Under changed temperature or pressure they take an abnormal direction or velocity. Many of the reactions belong to the reversible class. They also obey the mass law and are affected by changes of concentration. Until these facts were duly recognized the art of medicine was chiefly on an empirical basis and could not be called a science.

The complexity of the molecules involved, many being colloidal in nature, and the diversity of the possible changes render this the most difficult of the sciences to master, requiring as it does an expert knowledge of physics, chemistry, and physical chemistry, besides other sciences. Just what constitutes life remains unknown.

There is no spontaneous generation or autogenesis, and life processes which have once come to a definite end cannot be started again, though some of the minor reactions have been caused to repeat themselves under artificial conditions. So there is in a way a life barrier after all, but not one which forbids the reproduction of substances formed in plants and animals and which nullifies the laws and conceptions of the sciences. The field is open for intelligent study and in biochemistry the chemist finds the culmination of his science.

The study of the constituents of plants and animals and especially of the chemical changes taking place among them, forms the branch known as biochemistry. This is a far cry from the ancillary position occupied by the science in its earlier periods. The term physiological chemistry covers in part the same field but has a more limited significance in so far as chemistry is concerned. Of course the examination of the constituents of organic nature did not escape the attention of those early chemists who laid the foundations of modern chemistry. Fourcroy, Vauquelin, Chevreul, Berzelius, and others contributed investigations along these lines. After learning the composition of organs, secretions, etc., to which knowledge many chemists contributed, the next step was to find out the conditions under which these substances were formed, their relation to one another, and the changes they underwent — in other words, the reactions going on in the body. This has proved a far more difficult task. A vast amount of work remains to be done along these lines. Still chemical investigation has rendered great service in clearing up much that was obscure and in disproving mistaken conceptions and

misleading hypotheses. The number of these investigations is far too great to be detailed here, or in most cases even mentioned. There was the early work of Mulder and Liebig and others on the proteins, followed many years afterwards by the epoch-making researches of Emil Fischer in which he studied their hydrolysis and showed certain of them to be made up of amino-acids, synthesized them, and revealed the products of their hydrolysis. The proteins play a leading part in the life processes and a knowledge of them is of the utmost importance. They still form probably the chief point of attack on the part of chemists. The almost endless variety of these substances tells us that we are yet far from fully understanding their composition and functions.

Through the investigations of Chevreul and those who followed him the composition of the fats and their hydrolytic products are known. Emil Fischer has given a deep insight into the constitution of the sugars. Starch and other carbohydrates and the results of their hydrolysis have been studied. The Schmidts, Hoppe-Seyler, Nencki, and Ludwig have revealed much as to the blood, its composition and coagulation, and the gases carried. The differences between venous and arterial blood have been much discussed and, in fact, satisfactorily solved. The researches upon inhaled and exhaled air and the processes taking place in the lungs are far too numerous to recount; and so also with regard to the metabolism of foods. The distinction drawn by Buchner in 1896 between fermentation changes caused by micro-organisms and those caused by enzymes — hydrolytic changes brought about by the cell itself or by a substance secreted by the cell but acting apart from it — was of import,



though intracellular action must be taken into consideration and the mechanism of the changes is not yet definitely understood.

Of the many other contributors to the development of biochemistry mention may be made of Abderhalden, Atwater, Lusk, Chittenden, Hammarsten, and Van Slyke. The field is too large to do more.

## CHAPTER XVII

### RADIOACTIVITY

**The Discovery.**—The story of radioactivity, this latest and crowning marvel in scientific discovery, really begins with the phenomena in the tubes which were constructed by Crookes in 1879 and which have been named after him. The phenomena observed in these high-vacuum tubes when a current of high potential was passed through them led Crookes to suggest that one might be dealing with a fourth state of matter, which was not a bad guess when one considers the revelations which have followed. There were observed streams of minute particles which could be deflected by a magnet and so had some of the properties of matter. These proceeded in straight streams through perforations in the anti-cathode. There were also contrary streams of negative electrons, and later Röntgen found that by use of the anti-cathode very penetrating rays were obtained. These were after the order of light and easily passed through the glass walls of the tubes. They affected sensitive plates and photographs could be taken with them. He called these X-rays.

As these phenomena were accompanied by phosphorescence, Becquerel conceived the idea that similar photographs might be taken by means of naturally occurring phosphorescent substances, a number of which were known. His efforts failed with all phosphorescent sub-

stances known to him until he tried the salts of uranium with which he had previously done some experimental work and some of which he had noticed were phosphorescent. One class of these salts is phosphorescent, while the other is not, but he found that both classes gave off rays that acted upon the sensitive plates. These new unknown rays for a time, therefore, were known as Becquerel rays. Further investigation showed that all minerals containing uranium showed this effect. Examination proved that the intensity of the activity of an uranium compound was determined solely by the amount of uranium and was independent of the other elements present with which it might be combined. It was accordingly a property of the uranium atom and to be classed as a new atomic property. Others were attracted to this search and it was found that only one other element possessed this property in any marked degree and that was thorium. Rubidium and potassium showed very slight and partial activity.

**Radium.**— During an examination of other uranium minerals in which the intensity of the radiations was measured Madame Curie discovered that certain of them showed a much greater activity than could be ascribed to the amount of uranium present. From this she concluded that they must contain some unknown element or elements which were more radioactive. Working with very large quantities of material and in a most painstaking and laborious manner, she found that by using ordinary laboratory methods, such as precipitation and crystallization, she obtained a minute residue which was intensely radioactive. One such residue was obtained when bismuth salts were used as the reagent.

This gave spectroscopic indications of the presence of a new element which she named polonium but which she was unable to isolate completely. When barium salts were used as the precipitating reagent she obtained another residue, also exceedingly active. From this the active element was separated, its spectrum mapped, and its atomic weight, valence, and other properties determined. To this she gave the name radium. Two other elements have been detected by analogous processes — actinium by Debierne and ionium by Boltwood — but their separation in a pure state has not been accomplished.

**The Radiations.** — When the emanations coming from these radioactive substances were examined by the ionization method they were found to be electrically charged. By means of the electroscope some were found to carry a positive and some a negative charge. Their power of penetration, as tested by thin sheets of metal, etc., differed greatly, and their velocity ranged from one-fifteenth that of light to one many times greater. Also, by examination in a magnetic field it was found that some were not deflected, some slightly, and some very greatly. It was evident that the radiations were composite and made up of different kinds of rays. Comparing the results noted above, three classes of rays were distinguished and identified. One that was called the alpha ray was positively charged, was slightly deflected, and had a low penetration but the greatest power of ionization. It had the least velocity, about one-fifteenth that of light, and produced scintillations upon a zinc sulphide screen. This was identified with the canal rays which had been observed in the Crookes tubes. A second,

the beta ray, was negatively charged and greatly deflected. It had an ionizing power of only one per cent of that of the alpha ray, a greater penetrating power, and a velocity after the order of light. This was identified with the negative electron. The third variety of ray was identified with the X-ray. It was not charged electrically nor deflected by the magnet, had only the hundredth of a per cent of the ionizing power of the alpha ray and by far the greatest penetrating power. Its velocity was found to be after the same order as that of light. In other words, here were chemical substances — elements — which gave rise to the same phenomena that had been observed in the Crookes tube.

**Radioactive Substances.** — It was soon discovered that radioactivity could be induced in a wire or sheet of metal suspended over a radioactive substance; also that the radioactive substance could be separated from a solution of a thorium or uranium compound by the ordinary chemical operation or precipitation. In this it showed its nature or behavior to be similar to that of the ordinary chemical element or compound. But this additional fact was noted. When in the solution of the uranium salt, for instance, the radioactive substance had been separated by precipitation the uranium salt became inactive and the activity was transferred to the precipitate. In the lapse of time, however, the uranium regained its activity and the precipitate which had been removed lost it. The operation could be repeated as often as desired. Some process was going on in which the uranium or thorium atoms played the part of a chemical factory producing continuously hitherto unknown substances. But the process was either one of producing

something out of nothing or generating these products out of their own substance.

A number of new substances were obtained in this way, were separated, examined, and found to be themselves sending off radiations and undergoing changes. Some lasted only a very short while, others days or years, and there were yet others whose life period could only be calculated in terms of centuries after measuring the rate of decay. These new substances were distinguished from one another chiefly by their duration value and by the character of their emanations. At least three of these are gases and these gases are monatomic and belong to the argon group in the Periodic System. For some the spectra were mapped and chemical properties, valence, and other distinguishing characteristics determined. They were distinct elements with the usual elemental physical and chemical characteristics. Altogether more than thirty of these strange new elements have been discovered and three distinct equilibrium series determined.

**Disintegration Theory.** — Rutherford proposed as an explanation of these transformations a theory of disintegration which has been generally accepted. While there have been many workers in the field who have rendered valuable service, it is to this distinguished man, who combined the attainments of mathematician, physicist, and chemist along with rare insight and vision, that science is chiefly indebted for the elucidation of the phenomena of radioactivity and the resulting clearing up of many of the unsolved problems of the past.

According to this theory, one out of a vast number of uranium atoms becomes unstable in every minute

fraction of time and bursts with great violence for so tiny an object, expelling one or two alpha particles and forming a new atom. This is much more unstable and breaks up after a shorter interval, losing an electron; and so there is a series of transformations in which alpha particles and electrons are expelled and the great energy transformed, it may be, into the gamma or X-rays. In this series we come to radium, more stable, it is true, but also disintegrating. Finally an end-product seems to be reached and in this the change is at least exceedingly slow, though it is still radioactive. This end-element is so similar or closely akin to lead that it can not be separated from it and is called radioactive lead. Its atomic weight has been most carefully determined by Richards, Hönigschmid, and others and the atomic weight found to be over one-half a per cent less than that of ordinary lead. In the same way the thorium atom breaks up and there is formed a different series in which the rate of disintegration is different. The end-product again is a radioactive lead, and this time the atomic weight is greater than that of lead. It has been noted that in uranium and thorium minerals there are fairly accordant ratios between the amount of the uranium or thorium and these end-products, indicating that a sort of equilibrium has been reached.

This disintegration is entirely beyond outside control. No means of starting or stopping it is known. There would seem to be an inherent instability in these the two largest of the atoms. Neither the highest nor the lowest temperatures obtainable have any effect in increasing or retarding the velocity of change. Furthermore, the energy freed is beyond all comparison greater than that

from any other known source. This has been shown by calorimetric determinations.

The rays emanating from a substance like radium are known to exert a profound effect upon various organic and inorganic substances, the molecules of compounds and elements undergoing dissociation, and proof has been brought forward that at least one atom — that of nitrogen — has been decomposed when subjected to the action of the alpha particles. That the atom of one element can be built up by these rays has been clearly shown by a remarkable experiment of Rutherford. In this experiment alpha particles coming from radium emanations passed through thin glass walls of a tube into a surrounding tube with thicker walls through which they could not pass. This outer tube had been carefully evacuated, so far as possible, of all gas before the beginning of the experiment. A sufficient amount of the alpha particles had entered it in the course of two days to yield a distinct spectrum which coincided fully with the spectrum of helium. The helium atom, therefore, is built up of alpha particles and electrons obtained from the glass or during the sparking necessary to get the arc spectrum.

**Constitution of the Atom.** — Basing his conception on this experiment and on the disintegration phenomena, Rutherford announced his theory as to the constitution of the atom. In this the atom is conceived to have a nucleus of positive electricity surrounded by one of negative electricity or, to express it a little differently, to be made up of a positive nucleus of protons and electrons with outer envelopes of electrons moving in orbits. This theory received confirmation from the facts



discovered in connection with the "recoil atoms" and the "stopping power" exhibited by various metals and gases. Rutherford's atom was supposed to be spherical. Cubical atomic models have also been suggested. Bohr's model and that of Langmuir differ from that of Rutherford in details but all agree as to the atom being composed of negative and positive electricity. It is interesting to note that after the lapse of a century there is a return to the suggestion of Davy and the more elaborated conception of Berzelius. Changed in form and detail and amplified through greatly increased knowledge, the conception comes back with a firm basis of experimental evidence.

**The New Atom and its Properties.** — It would seem that at last there was at hand an explanation of such unsolved problems as the combining power and the valence of the atom and the underlying principle of the Periodic System. Soddy and others have done much to bring the new facts to bear upon such problems as these. Entire agreement has not been reached but some results can be given without going into details.

In the first place, it was found that the loss of an alpha particle reduced the atomic weight of one of these new elements by four, which is the atomic weight of helium. At the same time the atom in its chemical relations changed two groups from the negative to the positive side in the Periodic Table. The loss of a beta particle, or electron, caused a change of one place in the opposite direction, involving a change in valence and combining power or affinity. The loss of two electrons neutralized the loss of one alpha particle. Noting that three alpha particles are lost from uranium to radium, the atomic weight of radium should be  $238 - 12 = 226$ , which

agrees with the actual determinations. So, too, the atomic weight of the radioactive lead has been calculated with strong confirmatory experimental evidence from actual determinations.

In ionization there is an exchange of electrons between the separating ions. When a current is passed through a solution of an electrolyte these ions, on reaching the electrodes, regain or give up the electron, respectively, and ordinary atoms result. Again, the properties of the atoms are not dependent upon nor determined by the atomic weights, which had practically been recognized by Mendeleeff in constructing his table, though he laid down as a fundamental principle that the properties were functions of the atomic weights. The mass or weight is just one of the properties and is itself determined by the positive nucleus. The properties are determined by the electrical relations and valence is changed by the loss of an electron. For instance, when the valence of iron or copper is changed the atom is definitely transferred to another group, a process which can readily be reversed.

So a new conception arises, namely, that in the building up of these elements there is a definite order and that in the series each has an assigned place corresponding to a number which is now called the atomic number. This number can be determined by the "stopping power" of the element in question, that is, its relative penetrability. The atomic number is now determined more conveniently and accurately by the method of Moseley in which the shifting of certain lines in the X-ray spectra of the elements is mapped and their order definitely settled.

**Factors in Element Formation.** — It is manifest that

given certain factors of balanced electrical relations it would not be difficult to construct a series such as that which is found in the known elements presenting numerical regularities as to their atomic weights. It was this that Cooke and Dumas attempted to do in the middle of the nineteenth century, though they were of course in ignorance as to the bearing that electricity might have in the matter. A number of chemists and physicists of the day have been engaged in this task since the Rutherford atom was recognized. The work is necessarily in the tentative stage as yet. The factors usually taken are helium and hydrogen, as suggested by Harkins, though others have been suggested. As Rutherford has pointed out, helium is a secondary structure and itself made up of four hydrogens.

**Isotopes.** — In attempting to place the radioactive elements in their proper positions in the Periodic Table Soddy found that when they were classified according to their properties and the losses of alpha particles and electrons sustained, several closely analogous elements would fall in the same space, though their atomic weights might be widely different. Thus there are nine isotopes of lead with the atomic number 82. This name isotope was suggested by Soddy to designate an element which is so closely analogous to one of the known elements that it is chemically inseparable. The difference lies in certain physical properties, notably the atomic weight. It has been suggested that certain of the rare earths which have presented great difficulties in the way of their proper placing in the Table are also isotopes.

Another recent development in this matter of isotopes is that some of the well-known elements, such as neon,

chlorine, hydrogen, etc., can by physical methods, mainly diffusion experiments, be separated into portions which exhibit all of the chemical properties of the element but have distinctly differing atomic weights. It is probably true then that in determining the atomic weight of an element the final result is an average of the weights of the atoms present.

Recent methods devised by J. J. Thomson and Aston have made it possible to determine the number of isotopes of an element, their relative proportion with an accuracy of 10–20 per cent, and their masses or atomic weights with great accuracy. These methods can be applied to the determination of the atomic weights of the known elements and exceed in accuracy the best chemical determinations. By this means it has been shown that atomic weights are whole numbers when referred to the standard oxygen as sixteen. This is true up to and including chlorine and probably will be found true of the others. In the case of hydrogen the atomic weight 1.008 obtained by chemical methods is confirmed.

The nucleus, therefore, is made up of alpha particles called protons and of electrons. According to Aston, it is electrically neutral. This is called the electrical content and decides the atomic weight of the element and its position in the Periodic System. The surrounding electrons in their orbits decide the valence and the chemical characteristics. The term isobars has been adopted for such elements as have the same atomic weight but differ in chemical characteristics, while an isotope is one which has the same chemical characteristics but different atomic weight.

It is suggested that the term atomic weight be used

for the average weight of the element as accompanied by its isotopic companions and that atomic mass be used for the weights of the individual element and its isotopes.

**Matter and the Universe.** — The impression left after all of this is one of instability and change constantly going on, not merely in the visible objects around us and in their components but in the very atoms themselves. If these, which were once called simple bodies and then atoms are proved to be unstable, the question of stability has merely been pushed one step farther and we reach the electrically charged units or the individual electric charges and adopt the more recent term electron. Mutability drove some of the early Greek philosophers to despair and an abandonment of the search. But man has grown in many ways into a higher being and the very difficulties that would thwart him are but an incentive to all that is finest and highest in him.

To show how far it is possible to peer into the invisible and the minuteness of detail to which the search has been pushed, it is well to close this account by citing certain figures given by Rutherford and confirmed by independent investigators as J. J. Thomson and others:

Charge carried by the hydrogen atom,  $4.65 \times 10^{-10}$  electrostatic units.

Charge carried by the alpha particle,  $9.3 \times 10^{-10}$  e.s.

Number of atoms in 1 gram hydrogen,  $6.2 \times 10^{23}$ .

Mass of an atom of hydrogen,  $1.6 \times 10^{-24}$  gram.

Number of molecules per cc. any gas,  $2.78 \times 10^{19}$ .



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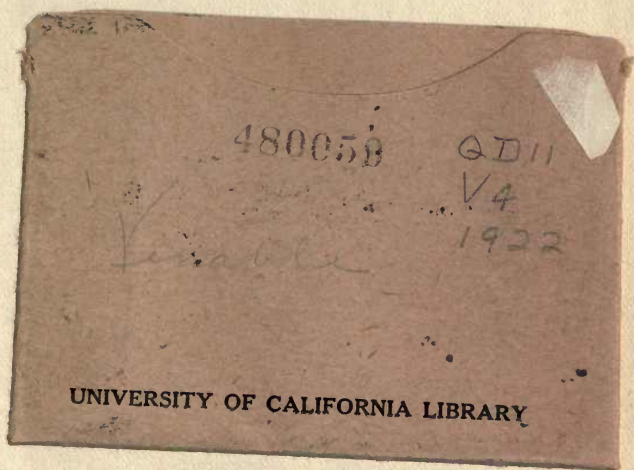
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