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PURE CHEMISTRY

A BRIEF OUTLINE OF ITS HISTORY
AND DEVELOPMENT

By A. BARCLAY

A.R.C.S., A.I.C.

PART I—Historical Review

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LONDON

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PREFACE

THE formation of a Museum of Science was first proposed by the Prince Consort after the Great Exhibition in 1851, and in 1857 collections illustrating foods, animal products, examples of structures and building materials, and educational apparatus were brought together and placed on exhibition in South Kensington. The collections of scientific instruments and apparatus were first formed in 1874, but it was only after 1876 that they became of importance. The Special Loan Collection of Scientific Apparatus which was exhibited in that year in the Museum brought together examples of all kinds from various countries, and a large number of these were acquired for the Museum. Subsequently many additions were made, including in 1884 the collection of machinery formed by the Commissioners of Patents, in 1900 the Maudslay Collection of machine tools and marine engine models, and in 1903 the Bennet Woodcroft Collection of engine models and portraits.

Until 1899 the Art Collections and the Science and Engineering Collections together formed the South Kensington Museum, but in that year the name was changed to the Victoria and Albert Museum, which included both collections until 1909, when it was restricted to the Art Collections; those relating to Science and Technical Industry have since then formed the Science Museum.

The aim of the Science Museum, with its Collections and Science Library, is to aid in the study of scientific and technical development, and to illustrate the applications of physical science to technical industry. This is effected by the informative display of objects, diagrams, and photographs—so arranged as to illustrate in each section the development which has taken place from past to modern practice. The literature in the Science Library is available to the public for consultation in the reading room, or obtainable on loan through the medium of an approved institution or industrial organisation.

Many of the exhibits are so arranged that they can be operated by visitors or demonstrated to them. Others have been sectioned so that the internal structure can be clearly seen. A detailed descriptive label is placed by each object.

The Pure Chemistry Collection contains many objects of great historical interest as well as a large number of carefully selected exhibits arranged to illustrate the development of chemical science up to recent times.

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INTRODUCTORY NOTE

This handbook is intended to serve as an introduction to the study of the history and development of chemistry with special reference to that collection in the Science Museum which has been formed to illustrate chemical science. The subject-matter has been arranged with the aim of providing a general outline of the more important events in development, and an endeavour has been made to present it in such a way as to stimulate interest rather than to record a complete series of achievements. At the same time reference has been made to as many outstanding occurrences as possible, and where omissions occur it is not because they are of no importance, but rather because they would extend the treatment of the subject beyond the intended limitations.

The first six chapters present a continuous account of chemistry from the earliest times, commencing with the records and knowledge of the ancient Egyptians and neighbouring peoples, who constituted the earliest civilisations and from whom have descended so many valuable and interesting objects and records. The history of alchemy, that curious, though human pursuit, is traced and is succeeded by a record of the early struggles to place chemistry on a scientific foundation. During the eighteenth century fundamental discoveries were made which gradually paved the way for a clearer conception of underlying principles. The nineteenth century opens with Dalton's famous atomic theory and as it progresses, proves generally true to history in other branches of science and technology; many important discoveries are made and follow one another in more rapid succession as the century draws to a close.

The subject by this time had grown to such dimensions that it had already become sub-divided into several related branches, which by now have reached very large proportions. The most important of these are described in succeeding chapters on Organic Chemistry and Physical Chemistry, and in a supplementary chapter is given a brief outline of modern ideas on the atom.

The collection itself has been arranged, as far as possible, on the same general lines as the present publication. A catalogue of these exhibits, together with a detailed description of each, will be contained in Part II of this handbook, which is in course of preparation. In addition to many historical exhibits of special interest, the collection contains a large number of carefully selected exhibits arranged in groups with the object of illustrating the more important phases of the development of chemical science.

I. ANCIENT METHODS AND SPECULATIONS

Early Chemical Arts.—Chemistry as an art may be traced back to the most ancient civilizations. The early Egyptians and Sumerians of about 4000–3000 B.C. had for centuries been working and collecting information, which was passed on in the form of trade secrets, and it is probable that the ancient inhabitants of India and China also knew of various processes, though of these nothing very definite is known. Modern knowledge of early chemistry rests upon the discovery of objects and records, pictorial and written, left in the buried cities and tombs of these early civilisations. From the study of such relics it has been learned that the Egyptians carried on chemical processes on a considerable scale long before the beginning of the Christian era. They smelted ores, and with the metals obtained, made tools, weapons, armour, and ornamental objects. They were skilled in the application of dyes and knew how to use mordants in dyeing. They made wine and beer by fermentation, medicines from herbs and from animal and mineral substances, and leather by processes of tanning.

The discovery of articles of glass, such as beads, imitation gems, and ornaments and pottery embellished with enamels, shows that the Egyptians knew not only how to make glass, but also how to colour it variously by the addition of suitable substances. Copper mines appear to have been discovered by them in the Sinai peninsula as early as the middle of the fourth millennium B.C., if not before. Gold, silver and the alloy of the two metals, “electrum,” were also known to them. Large quantities of gold were used, though silver was probably obtained from Phœnician traders, as the natural resources of Egypt did not include silver ores. The remarkable discoveries made in Egypt, and at Ur in Mesopotamia, testify to the skill of these ancient races in fashioning objects of gold, silver and copper, and of covering articles with thin layers of gold and silver.

The chief glass-making centre of Egypt appears to have been at Thebes, a favourite resort of the Phœnician traders, through whom large quantities of glassware found their way into Europe. Although the earliest glass made by the Egyptians was crude and opaque and, indeed, not made entirely of glass in the molten state, with increasing knowledge and skill they were enabled to produce a more translucent ware.

The Egyptians, Jews and Phœnicians also practised the art of dyeing and knew how to produce various colours by the aid of mordants, and Pliny in his writings remarks on the fastness of the colours obtained by using madder dye on mordanted cloth. In this connection it is interesting to note that the colouring principle of madder, now prepared artificially, constitutes one of the most valuable of modern dyes and

is very largely used for producing fast shades on cotton. The highly-prized Tyrian purple of Roman times was obtained from a shell-fish in the Mediterranean. These animals each contained only a very minute amount of colouring matter and considerable quantities had to be collected before they could be of effective use.

The value of experiment as an aid to discovery must have been recognised during an early period of Egyptian civilisation ; for there were some processes known to the Egyptians, such as embalming, of which the discovery may reasonably be attributed to design rather than to accident.

(A more detailed account of these early arts, with notes of further substances used by the Egyptians, is to be found in the handbook of the Industrial Chemistry Collection, which also traces the history of applied chemical processes up to modern times.)

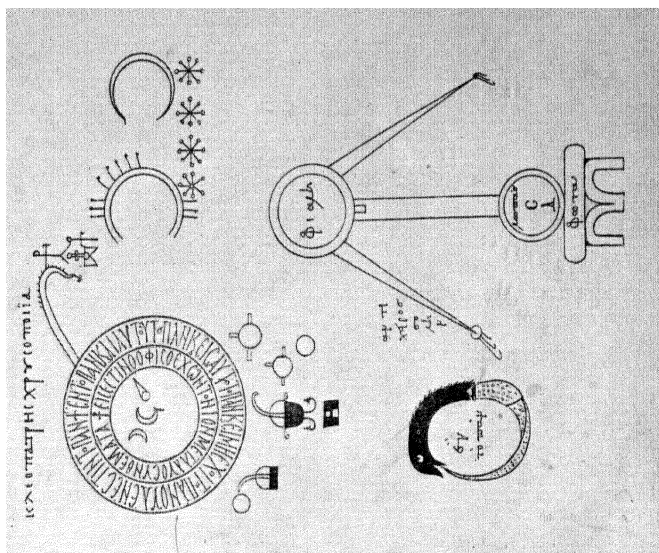
Early Records.—The practice of experimental chemistry in Egyptian times seems to have been a monopoly of the priesthood. Little is known, however, of individual experimenters, for only transcriptions of their original writings, probably long ago destroyed, have been found ; and the transcriptions do not with certainty reveal the true authorship.

One of the earliest of known documents relating to chemical substances, the celebrated papyrus discovered at Thebes by Ebers, is believed to have been written about 1,500 B.C. The original from which it was copied is sometimes ascribed to Hermes, later surnamed Trismegistos (thrice-greatest), who may, or may not, have been an actual personage. The ancient Greeks ascribed the origin of all “hermetic” writings to this Hermes, whom they identified with the Egyptian God, Thoth. The Arabs believed that Hermes was a Chaldean sage who migrated to Egypt and introduced the idea, afterwards fostered for centuries by the alchemists, that gold could be produced artificially from the baser metals. However, the Ebers papyrus, which contains descriptions of natural products and medicines, has no reference to the artificial production of gold, and that either Hermes or his successors had any notion of transmutation, is open to doubt. From Hermes it is not difficult to trace the derivation of such terms as “hermetic,” the “hermetic art” (alchemy), and “hermetically-sealed,” the term applied to a glass vessel sealed by fusion (Plate I).

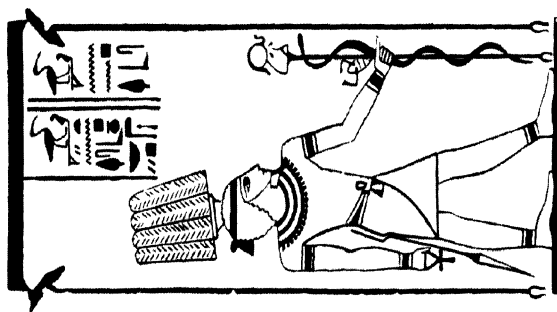
Other papyri written in Greek, are of much later date. In 332 B.C. Alexander the Great conquered Egypt and founded Alexandria. This city soon became the chief seat of learning in the civilised world, and until the fifth century A.D., remained supreme in chemistry. It was during this period that the Greek translations of early Egyptian manuscripts were made.

Some of these records contain clear and precise recipes for carrying out chemical and other operations, such as dyeing, making artificial gems, whitening discoloured pearls, and preparing alloys and amalgams. An extremely interesting Greek transcription, the Papyrus X at Leyden

PLATE I



After Berthelot
 Alchemical Symbolism from MS. of St. Mark, Venice, a 10th century Greek transcription of an earlier MS. "Chrysoporia" (gold-making) of Cleopatra (pp. 14-15).

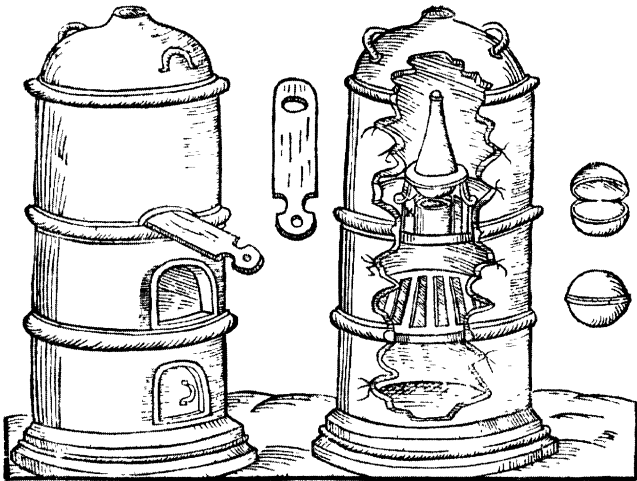


After Wilkinson.
 Thoth of Pnubs. Identified by the ancient Greeks with Hermes Trismegistos, to whom was ascribed the origin of the "hermetic art," alchemy. From a temple at Pselcis, 3rd century B.C. (p. 10).



[Courtesy of British Museum

Alchemical Representation of the "Element" Fire, c. 1600.
(Salamander in Flames)



Alchemical Furnace, "Athanor," c. 1600.

University, contains recipes for the practical working of metals and includes methods for the debasement of gold and silver and for the preparation of base alloys that resemble the precious metals. It appears, however, to contain no reference to the actuality of the alchemists' dream of transmutation. The MS. of St. Mark at Venice, copied in Greek in the tenth century from earlier writings, also contains many allusions to chemical operations and includes illustrations of the crude apparatus then in use.

Apparently the earlier Alexandrians had no illusions concerning the spurious nature of their products, and it was not until about the first century A.D. that the possibility of converting a base metal into real gold was first seriously considered and attempted.

The extent of chemical knowledge during the first centuries B.C. and A.D. is revealed in the authentic records of Greek and Roman writers of the time. Vitruvius (first century B.C.), a Roman architect, wrote descriptively about the materials used in architecture and civil engineering. Dioscorides, a Greek physician of the first century A.D., compiled a *Materia Medica*, in which he described the natural and artificial substances then in use as medicines; and the Elder Pliny, who perished in the first historic eruption of Vesuvius in A.D. 79, gave in his celebrated *Natural History*, an exhaustive, if not always accurate, account of most of the known facts of nature, including those of chemistry.

Early Ideas.—Theories to account for the origin and constitution of matter, and how it reacts under various circumstances, must have occurred to man from remote times, but it is not until the sixth century B.C. that we find the earliest known attempts at an explanation. The Greek philosophers, Thales, Anaximander and Anaximenes, who flourished at Miletus in Asia Minor at this time, believed that all things were made from one primordial and indestructible substance, differing only in their conception of this material. Thales considered water to be the fundamental substance, Anaximander fabricated a hypothetical "principle" which he called "apeiron," and Anaximenes regarded air as the original material. Not long after, Heraclitus of Ephesus held that fire was the basis of all things.

Empedocles, a Greek philosopher of the fifth century B.C., went further and advanced the theory that matter in all its forms consisted of four ultimate unchangeable elements: earth, water, air and fire. It is to Empedocles, in fact, that the first idea of "the four elements" is frequently assigned, though similar conceptions may have existed before his time. In an interesting theory put forward by Democritus, who also lived in the fifth century, matter was regarded as being composed of indestructible atoms ever moving in an otherwise vacuous space. These atoms were supposed to consist only of one substance and to exist in various types and sizes; and all the phenomena associated with material things were believed to be due to combinations and separations of these atoms.

The idea that vacuous space could actually exist was distasteful to the minds of Plato and his pupil, Aristotle (fourth century B.C.). Accordingly they held that matter must be continuous, indefinitely divisible, and completely filling space ; and rejecting the atomic theory of Democritus on this account, they reverted to the four-element theory of Empedocles. Plato and Aristotle, however, believed that the four elements could be converted one into another, differing from Empedocles in this respect. The development of the theory was due chiefly to Aristotle, who postulated further the existence of a fifth element, the everlasting and unchanging "ether," of which the celestial sphere and the stars were supposed to be composed.

The doctrine of Aristotle was based on the assumption that the only inherent qualities of matter are hotness, coldness, moistness and dryness, and that substances owe their properties solely to the relative extent to which they have these qualities. In order to give concrete form to the abstract qualities the philosophers combined them in all possible ways, and rejecting the combinations that contained opposite qualities they named the remaining four combinations as the terrestrial elements :—

Earth,	embodying	the	qualities	of	dryness	and	coldness.
Water,	"	"	"	"	wetness	and	coldness.
Air,	"	"	"	"	wetness	and	hotness.
Fire,	"	"	"	"	dryness	and	hotness.

These elements were not thought to be identical with the actual substances of the same names. They were conceived rather as principles or quintessences, the name of each suggesting the tangible manifestation of its character. For example, earth conveys the notion of solidity, and solids were supposed to consist mainly of the hypothetical element "earth." The other elements owed their names to similar comparisons.

The hypothesis that the elements could be changed one into another was devised to account for observed phenomena. When heat was added to water the latter became gaseous ; in other words it assumed the chief characteristic of air, or was changed into some substance of which the element air was the chief constituent. Again, when a combustible solid burned it was converted into fire, or so the Greek philosophers thought. Hence : earth (dryness and coldness) plus heat gave fire (dryness and hotness).

The Aristotelian doctrine met with general acceptance and in spite of subsequent attempts to revive the atomic theory, it retained its high position in philosophy until comparatively recent times.

The ancient theories outlined above had little influence or none at all on experimental chemistry until long after their enunciation. The Greek philosophers did not favour experiment, thinking it likely to unfit the mind for the processes of pure reason. On the other hand the earlier experimenters were not theorists and, as far as is known, had no useful contact with the latter. It was not apparently until the Age of Alchemy, which in Egypt began during the early years of the

Christian era, that the theories of Aristotle were consciously used as a guide to experiment, and then they merely proved how misleading erroneous theory may be.

Thus, in summary, it is evident that down to the beginning of the Christian era chemistry was practised as an empirical art. Men discovered new substances, natural or artificial, and where possible they applied such substances to useful purposes, employing them as dyes, pigments, medicines, and so on. Chemical knowledge consisted of a large number of virtually unrelated facts, and so it remained until the alchemists began their directive but misguided labours. It will be seen, too, that the idea of a common material to which the ultimate constitution of the universe could be referred was seriously entertained from early times, and this is not so absurd as it seems when one considers the remarkable and far-reaching theories that have been developed in recent years, notably the electronic theory. The early conceptions persisted, in fact, throughout the subsequent ages of experimental progress and have had no little influence on later thought.

II. THE PERIOD OF ALCHEMY

Gold has always been highly prized by civilised man on account of its rarity, beauty and unchanging nature, and it is probable that from early times the human mind has dwelt upon the attractive idea of the transmutation of metals and particularly of making gold artificially from the commoner metals.

Alchemy, the name afterwards applied to this art, had its germ in the philosophy of the ancient Egyptians, and possibly also of the Chinese, and it was developed and flourished particularly during the Middle Ages. It has already been shown that the Egyptians were skilful in imitating the precious metals, and there can be little doubt that at one time and another much spurious and debased metal circulated in the markets. Serious attempts to transmute the baser metals into gold appear to have been made in Egypt as early as the first century A.D. They probably owed their origin largely to writings which appeared under the name of Democritus, now known as pseudo-Democritus, about the first century A.D. This Democritus re-wrote in obscure language many of the clear recipes of the Egyptian metal workers and added to them, on his own account, a great deal of mystical information concerning transmutation.

Alchemy appears to have been first practised in Alexandria by a certain section of the Græco-Egyptian population. It is believed that it was commenced there as a secret cult of "magician-chemists" and that practical workers had little, if anything, to do with the movement. This belief is supported by the observation that, whereas earlier documents giving recipes contained straightforward statements and instructions, many of those of later date were couched in vague and figurative language and contained incomprehensible ciphers or symbols and mystic references. It will readily be seen that a cult of this kind, especially if leading to apparently successful transmutations, would be jealously guarded in this way. Religious observances and incantations gradually formed an important part of every operation and there is no doubt that there were many alchemists who firmly believed in the possibility of genuine transmutation. That there was a strong philosophical basis to the art is apparent in the writings of the time and in the logical influence which they wrought upon the minds of later workers. On the other hand, there is ample evidence to show that charlatans and rogues, who wished merely for gain by deceiving wealthy and avaricious patrons, were undoubtedly numerous, especially in later times.

As an example of the symbolic method of expression may be cited one of the earliest representations of the conversion of base metals into precious metals, the "Chrysopœia" (gold-making) of Cleopatra, an author, not to be confused with the famous Queen of that name,

who is believed to have written soon after the beginning of the Christian era. The symbols (Plate I) apparently represent, in the lower right-hand corner, a distillation apparatus, to the left of which is the serpent, "Ouroborus," biting its tail, the symbol of alchemical knowledge. In the left-hand top corner is a circular design representing a belief in the unity of matter, enclosing the symbols for silver, mercury and gold. Underneath this are diagrams of apparatus, and to the right are symbols which appear to express the transmutation of a base into a noble metal.¹

Many other interesting examples can be seen in later mediæval works (Plate II).

Of the Alexandrian alchemists, Zosimos of Panopolis, in Egypt, appears to be the earliest alchemical worker of whom authentic writings exist. Living about the beginning of the fourth century A.D., he is credited with having written many treatises, and in those which survive he refers, among other things, to the art of making gold and silver, which he attributed originally to divine inspiration. Mingled with a diverse assortment of facts, however, is much mystical knowledge derived from the ancient Greek philosophies.

In spite of acts of suppression carried out by the Emperors Diocletian (about A.D. 300), and Theodosius (last quarter of fourth century), alchemy flourished in Alexandria until the fifth century, when the rise of Christianity finally led to the closing of the pagan schools. The dispossessed art found a footing at Byzantium (afterwards Constantinople), where an unimportant school continued to exist for several centuries.

During the period of political turmoil that followed the fall of the Roman Empire, learning of all kinds sank into insignificance. Its revival was brought about by the Arabs, who in the seventh century conquered Syria, Persia and parts of North Africa. Under the name of the Moors they crossed later into Europe and occupied parts of Spain. The conquering race eagerly absorbed the remnants of Greek learning in Alexandria and ensured its continuation and development by founding universities in the conquered countries. In this way important seats of learning were established at Cordova and Granada, and during the following centuries schools modelled on the Moorish universities in Spain sprang up in other countries of Western Europe. Alchemy, one of the studies most industriously pursued in these places, developed steadily up to the tenth century and for 600 years from that time it continued to influence the minds of the experimenters.

Of the Arabian alchemists one of the most interesting and important was Jabir ibn Hayyan, generally known under the name of Geber, who lived about the eighth century A.D. and was long held in the greatest esteem. It seems probable, however, that some of the Latin works attributed to him were compiled by writers of about

¹ The subject of alchemy, as recorded in some of the earliest manuscripts, is dealt with in detail in M. Berthelot's, "Introduction à l'Étude de la Chimie des Anciens et du Moyen Age," 1889.

the thirteenth century, who put forward their own writings as the work of the genuine Geber. The later Muslim chemists, of whom two of the most notable were Rhazes and Avicenna, were primarily physicians, their interest in alchemy having been subordinated to that in medicine and pharmacy. The Persian Rhazes, who studied medicine at Baghdad about the ninth century, was a professed believer in transmutation. Of Avicenna, who lived in the tenth century, it appears that some of the chemical writings attributed to him were compiled by later workers of the thirteenth and following centuries.

The early European alchemists were of the learned class, many of them having been members of one or other of the religious orders of the day. Some were highly intelligent men whose interests extended beyond the restricted scope of pure alchemy. Among well known names of the time are Albertus Magnus, also known as Albert Groot, a Dominican monk (c. 1193–1280); the English alchemist, Roger Bacon (c. 1214–1290), a wide and careful experimentalist and thinker, often wrongly accredited with the invention of gunpowder; Vincent de Beauvais (c. 1190–1264), noted for his general encyclopædia of learning, and also a Dominican monk; and Raymond Lully (1235–1315), the friend of Roger Bacon. All are entitled to remembrance for their contributions to useful chemical knowledge rather than for their efforts to discover the philosopher's stone (*see below*).

Among later European alchemists were many of much lower standing and intellectual attainment, who debased alchemy by deliberate fraud and who played upon the credulity and greed of their patrons to provide funds for their experiments. In spite of this, however, they did some good, for in lowering the prestige of alchemy they unknowingly helped to bring it ultimately into disrepute.

The practice of alchemy began to decline in the sixteenth century. It had, however, a lingering death, for although after the end of the seventeenth century it no longer engaged the attention of serious workers in chemistry, it did not become finally extinct until about the beginning of the nineteenth century. As a branch of learning, alchemy contributed nothing of a positive nature to human understanding; as a practical art, although it failed to attain its prime objective, it yielded a rich harvest of secondary, unsought information, for many important substances, notably the strong mineral acids (nitric, hydrochloric and sulphuric), were discovered by its professors.

Alchemical Philosophy.—It has been suggested that the idea of transmutation owed its origin to the practice carried on by the Egyptians of making base-metal alloys that resembled gold (and silver) in appearance. The statement that an alloy of this kind was actually precious metal made from base metal, would doubtless have acted powerfully upon the mind of some unpractical philosopher, who, reasoning according to the prevailing theories, might readily have convinced himself of the authenticity of the specimen, and of the possibility of transmutation. It is probable, however, that the artificers themselves

were under no delusion that their imitations were other than spurious ; for there is evidence to show that it was already recognised that the precious metals differ more than superficially from the base metals. The primitive methods of assaying depended upon, and made apparent, the property of permanence in the fire, possessed only by gold and silver among the metals known at that time ; and the historic experiment of Archimedes indicates that the high density of gold was regarded, at least by some, as an inherent property. Moreover, the motive that led Archimedes to make the experiment seems to show that the distinction between pure gold and debased gold was clearly appreciated by intelligent men.

On the other hand it may be conjectured that the alchemists had the theory of Aristotle (p. 12) for their first inspiration and for the basis of their experiments. If all material substances were composed of the same four, mutually convertible "elements" associated in varying proportions, it would be reasonable to suppose that one substance, for example a base metal, could be changed into another, gold for preference, provided that means could be found for altering the proportions of the composing elements by addition, subtraction or conversion.

Of early alchemical doctrines very little is known, for only the later records contain reference to coherent theories. Moreover it is not known with certainty when and by whom these theories were formulated.

The metals that were known in ancient and mediæval times, have in varying degree many physical characteristics in common. The recognition of this fact gave rise to the idea that all metals were composed of the same primary material, a perfect metallic substance which, in varying association with one or more of the four "elements," became endowed with the special properties of the individual metals. Gold was considered to be the most nearly perfect metal, and according to the theory it could be produced by purifying a base or contaminated metal. From a slightly different point of view the base metals were regarded as precious metal that had fallen sick ; and it was believed that they could be restored to health by the administration of suitable medicine.

Following such arguments came the conception of the *philosopher's stone*, *magisterium* or *elixir*, the master substance, which it was believed would purify, or cure, the base metals, turning them into gold. The amount of thought and labour devoted to the attempted manufacture of this hypothetical substance in the Middle Ages now seems almost incredible. Though the incentives were strong and, in many cases, the philosophic reasoning of the time appeared sound, the underlying explanations of processes were very often so wild and fantastic as to surpass belief.

The later alchemists found that the four terrestrial elements were inadequate to account for observed phenomena, and accordingly they postulated the existence of three "principles" : sulphur, mercury and salt, as essential and peculiar constituents of metals and minerals.

These principles were conceived, not as identical with the substances named, but, like the four Aristotelian elements, as hypothetical substances, or quintessences. Thus, "sulphur" conferred colour, combustibility, affinity and hardness, and "mercury" gave rise to the "metallic" properties; lustre, volatility, fusibility and malleability. The principle "salt," a conception introduced later, was thought of rather vaguely as an entity that served to unite the sulphur and mercury.

Although, thus barely stated, the notions of the alchemists concerning the nature of metals appear to the modern mind to be absurd and baseless, a little consideration shows that they were probably founded upon observation, and that, according to the philosophy of the time, they were not unreasonable. The minerals galena (lead sulphide) and pyrites (iron sulphide) have some metallic properties and were doubtless considered by the alchemists to be inferior metals. The two minerals were known as sources of the metals they contain and it must have been realised that the production of metal from mineral involved the elimination of sulphur. It was not unreasonable to argue that by the removal of more sulphur from lead and iron the more perfect metals silver and gold could be produced. Many specimens of galena contain silver, and pyrites is sometimes found associated with appreciable quantities of gold. Working upon such materials and endeavouring to remove as much "impurity" as possible, the alchemist would ultimately isolate the precious metal, and not realising that it was an original constituent of the mineral he would delightedly jump to the conclusion that to some extent transmutation had been effected. Thus an incentive to further effort would be provided.

Iatrochemistry.—The only extension of alchemical aims beyond the limits of the narrow range in which they had previously been directed, began during the first half of the sixteenth century. The new development owed its origin not to any change of heart in the old school, but to the formation of a new school, that of the *Iatrochemists*, or physician-chemists, who held as their chief article of faith that the true function of the alchemist was to search for new medicines that would help to cure human ills, and not to seek to turn base metals into gold. The first to point this out was a Swiss physician surnamed von Hohenheim, better known as Paracelsus (1493–1541),* who promulgated the new doctrine with all the vigour of his forceful nature. He argued that the human body was essentially a chemical system and that in order to correct derangements of the system, manifested as sickness, it was necessary to administer chemical medicines. Remedies were, however, largely empirical and there is no doubt that he, and the physician-chemists following him, often prescribed dangerous substances, such as preparations of antimony, arsenic and mercury, with the results that though some remarkable cures may have been effected many patients were probably poisoned.

* References marked with an asterisk refer to exhibits which may be seen in the Collections at the Science Museum.

The chief services rendered by Paracelsus to chemistry lay in extending its scope and in attracting to its study investigators whose aims were not entirely directed by avarice. In medicine they were violently opposed to the older schools, and they did well in challenging, refuting and finally in overthrowing the ancient dogmas. Like many of their predecessors in alchemy they were mystics, believing in the influence of the stars on human affairs and in the interference therein by demons. The old idea of a master substance still engrossed their minds and they sought, not for a gold-making philosopher's stone, but for a wonderful medicine, the "elixir of life," which would confer perfect health and longevity upon its imbibor.

In comparison with the ages that had gone before, the period of iatrochemistry, which lasted for more than two centuries after the death of Paracelsus, was one of great experimental activity and advance in discovery; and many of the workers who devoted their lives to the pursuit of knowledge made their names worthy of record in the history of science. The new spirit of investigation stimulated interest in chemistry and attracted some of the best intellects of the time. As a consequence of this, much was done, especially during the latter part of the period, that helped to free both chemistry and medicine from the mysticism and superstition that had previously been impediments in the way of real progress. Moreover, the philosopher's stone was no longer an obsession and chemists were finally able to rid their minds of the unfounded theories that had formed an essential part of the alchemists' stock in trade. In consequence, clearer, but of course still imperfect, ideas concerning the nature of things were gradually evolved.

One of the most important chemists of the time, van Helmont (1577-1644),* born in Brussels, took up the experimental study of gases and introduced the term "gas" to denote bodies of this nature, which appeared to differ in some way from ordinary air, though in what way was not at all clear. He investigated especially the gas, carbon dioxide, which he called "gas sylvestre." He also showed in certain instances that substances still exist in their compounds and can be regenerated therefrom by suitable means, a very important fact that previously had only obscurely been recognised, if at all. The relation between combustion and respiration was indicated by Sylvius de le Boë (1614-1672), who also studied the physiological action of some of the juices of the body. To Sylvius moreover must be given the credit for taking some of the first steps in the liberation of medicine and chemistry from the fetters of mysticism. Some progress in the methods of qualitative analysis was made by Tachenius (c. 1620-1690) as is shown by his knowledge of the composition of compound bodies, and this iatrochemist was among the first to make quantitative experiments. He also used the term "salt" as definitely implying a compound of an acid with an alkali.

Other notable men who lived during the iatrochemical period were Georgius Agricola (1494-1555), the metallurgist, born in Saxony;

Bernard Palissy (1510-1589), the French pioneer in the chemistry of ceramics and the chemistry of agriculture; the German, Johann Glauber (1604-1670), renowned for the salt that bears his name; and Thomas Willis (1621-1675), the English physician and chemist.

With other interesting theories and workers of the alchemical period it is not possible to deal in so brief an account, and for further information the reader is referred to the many excellent works on the history of chemistry.

III. THE BEGINNING OF SCIENTIFIC CHEMISTRY

It is not surprising that the alchemists and iatrochemists failed to convert chemistry into a science. Their researches were directed in the main to definite practical objectives, the philosopher's stone and medicines ; and although new substances were discovered by the way, they were interesting to the philosophers not so much because of their intrinsic value, but because they might form new starting points for the old researches. The accepted theories, founded on imagination, had been formulated in order to explain the more obvious properties of substances in general, and they were sufficiently broad and vague to cover all sorts of phenomena discovered subsequently. Therefore the philosophers were content and scarcely thought of making experiments designed to test the truth of the theories, or of making unbiassed investigation into the nature of substances. In short, the pursuit of knowledge was largely misdirected. It is true that Roger Bacon implicitly pointed out the right road, but his works were ignored and it was not until nearly 400 years after his death that the way was recognised and followed.

Robert Boyle.—The decline of iatrochemistry and the rise of scientific chemistry date from the publication in England, in the year 1661, of a book entitled "The Sceptical Chymist." The author of this volume, which excited great interest and was widely read both in England and on the Continent, was the Hon. Robert Boyle (1627–1691), a son of Richard, Earl of Cork. In the "Sceptical Chymist" Boyle severely criticised the methods of the alchemists and iatrochemists, ridiculed their obscurity and mysticism, and condemned their theories. Following the teaching of Sir Francis Bacon he pointed out that true knowledge can be gained only by the inductive method, whereby general truths are inferred from particular observations, and he made it clear that experiment and observation are the only sure foundations of theory. Boyle argued that the pursuit of chemistry should be of intrinsic interest and value as part of the study of Nature and that it should no longer be regarded and used as a mere adjunct to any trade or profession. He made special endeavours to determine the composition of substances and in so doing, paid considerable attention to methods of chemical analysis, a branch of chemistry which, except for the work of Tachenius (p. 19), scarcely existed before his time. He rejected the Aristotelian and alchemistic conceptions of the elements (the four "elements," Earth, Water, Fire, Air ; and the three "principles," Sulphur, Mercury, Salt), and advanced instead the opinion that only substances that are not composed of "any other bodies," and which form the ultimate ingredients of compound bodies, should be regarded as elements.

The "Sceptical Chymist: or Chymico-Physical Doubts and Paradoxes" is a work of considerable interest. Written in the form of a dialogue, chiefly between two persons named Carneades (Boyle) and Eleutherius, it deals with the theories of the "vulgar spagyrist," as Boyle called the alchemists, in no uncertain, though in reasonable, terms. In explanation of accounts of additional experiments made in support of his case Boyle refers to the alchemists' methods as follows:—"These Things I add, because a person any 'Thing vers'd in the Writings of Chymists cannot but Discern by their obscure, ambiguous and almost Ænigmatical Way of expressing what they pretend to Teach, that they have no Mind to be understood at all, but by the Sons of Art (as they call them) nor to be Understood even by these without Difficulty and Hazardous Tryalls": and this is true of most of the alchemists, whose knowledge, such as they possessed, was purposely obscured in their writings.

Boyle has often been called "The Father of Modern Chemistry," and there is no doubt that the new spirit of enquiry which he inaugurated marked an important turning point in the history of chemistry. His teaching did not at once produce an abrupt change in the practice of the science; enlightenment came gradually and about 100 years elapsed after the publication of the "Sceptical Chymist" before the older methods and ideas were finally displaced.

"Phlogiston," the Seventeenth-Century Principle of Combustibility.—The phenomenon of combustion has attracted man's attention from remote times. Heraclitus regarded fire as the ultimate basis, not only of matter, but also apparently of everything else. Empedocles and Aristotle named fire as one of the four "elements," conceiving it as a more or less substantial entity, and although van Helmont denied this doctrine it remained in vogue until the time of Boyle. Down to that time combustion had been accepted as a manifestation of the "element" fire and none had succeeded in giving a reasonable explanation of it. The first to attempt this was Johann Joachim Becher (1635–1682), a German professor of medicine. Adhering to the ancient ideas, Becher postulated the existence of three modified elements, principles or "earths," namely: the "mercurial," the "vitreous" and the "combustible," as the ultimate constituents of substances, and advanced the explanation that combustion, in its general sense, including the calcination (oxidation) of metals, was due to the escape of the combustible principle from the burning body. It may be conceded that in this Becher made a step forward, but he was still on the wrong path that the alchemists had trodden.

In view of what happened subsequently it is of interest to consider contemporary opinions regarding the nature of combustion. Aware of the fact that metals gain in weight on calcination, Boyle thought that a substance of the nature of fire, having an appreciable weight, was added to a material during combustion. Robert Hooke, in 1665, and more especially John Mayow, in 1669, expressed the view that some constituent of the atmosphere, common also to the substance nitre,

called by Mayow "spiritus nitro-aëreus," was an essential factor in combustion and calcination and in the conversion in the lungs of venous into arterial blood. Hooke went little further than the bare statement of his opinion, and Mayow died at the age of thirty-four. In these unfortunate circumstances the correct ideas of these two men were passed over and a hundred years elapsed before the truth was again brought to light (p. 28).

Evidently the majority of investigators were still hampered by belief in the old conceptions of "elements" or "principles," for it was Becher's theory, founded upon the same conceptions, that obtained general support in spite of certain important objections well known at the time. The chief of these objections arose from the undisputed facts, first that metals gain in weight when calcined, whereas there should be a loss in weight commensurate with the amount of escaping "principle"; and secondly that combustion cannot continue in a closed space to which air is not admitted. Nevertheless, the theory was otherwise sufficiently plausible to secure acceptance, the objections to it probably having been regarded merely as incidental difficulties that would doubtless receive adequate explanation in due course. Explanations were indeed given later, but they were of a fanciful nature entirely lacking experimental support.

The development of Becher's theory of combustion into a general system of chemistry was due almost entirely to George Ernest Stahl (1660-1734), a German physician, to whose ardour and energy the doctrine also owed its propagation. To Becher's "combustible principle" Stahl applied, though he did not invent, the name "phlogiston," from the Greek, *phlogistos*, meaning "burnt"; and he endeavoured to explain all known chemical phenomena, and also other phenomena, by reference to this hypothetical entity.

Although, apart from a superficial plausibility, there was nothing to support the theory, it reigned supreme until the beginning of the last quarter of the eighteenth century, when accumulated experimental knowledge clearly revealed its absurdities and ultimately led to its total abandonment. It is often asserted that it had a retarding effect on chemical discovery and there is no doubt that it greatly delayed the general acceptance of Boyle's scientific principles. Nevertheless, great advances were made during this period and it is probable that the phlogiston theory, though erroneous and misleading, did not actually affect practical results so much as may be believed, for, like all theories, it gave stimulus to research and exercised a directive influence. Moreover Stahl, its chief exponent, had ideas similar to those of Boyle concerning the nature of the elements, and the propagation of this doctrine in the train of phlogiston was of very great benefit to chemical science.

As the major doctrines of Boyle were slowly assimilated, practical workers began to show increasing interest in the analytical examination of bodies. Many substances long accepted as simple were re-examined from a new point of view and were found to be composite, and

substances hitherto confused with one another on account of general similarity were for the first time clearly distinguished. Marggraf (1709-1782), a German analytical chemist, established the separate identities of lime, magnesia and alumina. Scheele (1742-1786), one of the most distinguished discoverers of the time, prepared a large number of substances previously unknown and made other highly important contributions to chemical knowledge (p. 27).

IV. THE BEGINNING OF QUANTITATIVE CHEMISTRY

Joseph Black, 1728–1799.*—Between the years 1752 and 1755 occurred an event of considerable importance which had a direct and profound influence on the course of chemistry. Joseph Black, Professor of Chemistry, first at Glasgow and then at Edinburgh University, carried out a memorable series of researches on certain alkaline substances, one result of which was the establishment of the identity of the gas, carbon dioxide.

In 1752, Black showed that this gas, which he named “fixed air,” was an individual substance distinct from ordinary air, a fact which had already been indicated in a general way by van Helmont, who called it “gas sylvestre” (p. 19). The name “fixed air” was given to carbon dioxide on account of the fact that certain substances of an alkaline nature combine with it, thereby “fixing” it in a solid form. In 1755, Black proved that limestone (calcium carbonate), magnesia alba (magnesium carbonate) and the mild alkalies (sodium and potassium carbonates), consist of lime, magnesia and the caustic alkalies (soda and potash), respectively, compounded with “fixed air.”

If this demonstration had been merely qualitative it would nevertheless have been highly important, for it not only indicated the relationship between certain compound bodies and their constituents, but showed also that the carbonates were not, as had previously been supposed, simple substances. Black’s achievement was, however, of even greater importance, for he used the balance, and thus gave quantitative precision to his discoveries. Although this was not the first occasion on which quantitative experiments had been made, previous investigations of weight relationships had lacked the definite aim that characterised Black’s work and on this account they had failed to set the fashion. As a result it can fairly be said that to Black belongs the chief credit for first emphasising proportions by weight in chemical investigation and thereby of inaugurating quantitative chemistry.

Although before 1752 several gases had already been isolated, including hydrogen, carbon dioxide, carbon monoxide, sulphur dioxide, nitric oxide and marsh gas, they had not been recognised as distinct substances. The erroneous impression had been prevalent that all gases consist of modified kinds of ordinary air. The disproof of this in Black’s distinction of carbon dioxide stimulated interest in the nature of air and other gases and marked the opening of the period of “pneumatic chemistry,” or the chemistry of gases. The experimental activity thus arising resulted twenty-two years later in one of the most important discoveries ever made, that of oxygen. Black’s work

is described in his paper, "Experiments upon Magnesia Alba, Quicklime and other Alcaline Substances," published in 1755.

As the various terms applied to gases at this time are of frequent recurrence in the following accounts it will be convenient to summarise them here in order to avoid confusion :—

Dephlogisticated Air	Oxygen.
Phlogisticated Air	Nitrogen.
Inflammable Air	Hydrogen.
Nitrous Gas	Nitric Oxide.
Fixed Air	Carbon Dioxide.

(Phlogiston : "The Principle of Combustion.")

*Joseph Priestley, 1733–1804.**—A notable contemporary of Black was Joseph Priestley, a nonconformist minister who practised chemical research as a hobby. His name is known chiefly for his discoveries in "pneumatic chemistry," referred to above, in which the well-known pneumatic trough for the collection of gases played an important part. In this respect, Priestley made an important advance, for on some occasions he filled his troughs with mercury instead of water and was thus enabled to collect gases which are soluble in the latter (Plate VII).

The confusion existing at this period as to the nature and individuality of gases led to the common appellation of "air" to most gases, and though Priestley realised that there was a distinction, he continued to use the term "air" in preference to that of "gas." His experiments are described under the title of "Experiments and Observations on Different Kinds of Air." This work, originally published in six volumes between 1774 and 1781 gives a full and interesting account of his discoveries. Priestley states that he was very fond of making what he called "random experiments" and consequently many of his discoveries, among them some of the most important, were the result of chance.

Among other things, Priestley showed that air unfit for respiration, or for supporting combustion, has its natural property restored to some extent by shaking with water, or by the action of living vegetation. In the belief that the spoiling of air was due to its impregnation with "phlogiston" he devised means for measuring what he termed the "goodness" of air, using a long graduated glass measuring tube for the purpose. In this way he initiated the practice of "eudiometry" (eudiometer=measure of goodness), employed in the analysis of gases and later elaborated with much skill by Bunsen. The method was based on John Mayow's discovery of "nitrous gas" (nitric oxide) about a century earlier. Mayow had observed that when this gas was mixed with air confined over water, a diminution in volume occurred (owing to the combination of nitric oxide with oxygen and the absorption by the water of the resultant nitrogen peroxide), a fact which Priestley rediscovered. He had only to determine the change in volume taking place when given volumes of air and nitrous gas were mixed in order to obtain a measure of the original "goodness" of the air.

Early determinations made by this method in the hands of some experimenters apparently indicated that the atmosphere varied considerably in quality according to time and place. They must, however, have been subject to large experimental errors, for not only did Priestley find little difference in the composition of the atmosphere, but Cavendish later proved that it is remarkably uniform.

Discovery of Oxygen.^{1*}—During the summer of 1774, Priestley was engaged in trying the effect of heat on various substances out of contact with air. For this purpose the substance under investigation was introduced into a glass phial that had previously been filled with mercury and inverted with its mouth in a basin of the same metal. The substance passed to the uppermost end of the phial, and remained there between the mercury and the glass, in which position it could readily be heated by means of a large burning glass. On August 1st, 1774, Priestley heated in this way some calx of mercury (mercuric oxide) and obtained from it a colourless gas (later known as “oxygen”), which on further investigation was found to support combustion more strongly than ordinary air. At this time he had no idea that the newly discovered gas was respirable. During the spring of the following year, however, he measured the “goodness” of the gas by means of the eudiometer and found to his surprise that it was much better than common air. It then occurred to him that the gas might be respirable, and on putting his supposition to the test, first on a mouse and then on himself, he found that in this respect also the gas was very much superior to common air. On account of these properties, which, according to the prevailing theory, indicated that it contained less “phlogiston” than common air, he called the gas “dephlogisticated air” (*i.e.* it supported combustion).

In the collections may be seen a reconstruction of the oxygen apparatus (Plate VI), partly made from Priestley's own accounts of his experiment. The large burning glass of 12 in. diameter is of considerable interest as showing the source of heat employed, a method particularly favoured by Priestley and also employed later by Cavendish.*

Priestley was a staunch supporter of the Phlogiston Theory, as is seen in the name he gave to oxygen (“dephlogisticated air”), and although many of his discoveries actually provided the disproof of the doctrine, he remained firm in his belief to the end of his life.

Carl Wilhelm Scheele, 1742–1786.—The gas discovered by Priestley in 1774 was discovered independently, probably a year earlier, by Scheele, a Swedish apothecary, who called the gas “empyrean air,” or “fire air.” The results of Scheele's work were not, however, published until 1777 and consequently the major credit for the discovery has usually been assigned to Priestley. It may be observed in passing that Scheele came to the definite conclusion that atmospheric

¹ See also under Scheele, below.

air is a mixture of two elastic fluids, a view that is approximately correct if one excepts the small total volume of the remaining gases present.

Scheele ranks as one of the most distinguished experimenters of his day. Though he died at an early age he made many important discoveries, among which chlorine gas and hydrofluoric acid, the latter used for etching on glass, are two of the best known.

Antoine Laurent Lavoisier, 1743-1794.—It is to this noted French chemist that we owe the first useful interpretation of combustion and calcination (oxidation). By arguments based on known facts, and by experiment, he proved beyond reasonable doubt that these changes are due to the combination of the affected substance with oxygen, thus completely disproving the phlogiston theory. (That combustion does not always imply union with oxygen, *i.e.* oxidation, we now know, but Lavoisier's theory was essentially correct in the majority of cases.)

The steps leading up to this result are of great interest. Between 1772 and 1774 Lavoisier, as a result of experiments, found that combustibles and calcinable substances increase in weight on undergoing this change, that the air in contact with them diminishes in volume and that the residual air differs in properties from that originally present. Although these discoveries were not new, Lavoisier's interpretation of them was new. Ignoring phlogiston, he came to the conclusion that the phenomena observed were due to the absorption by the affected substance of some constituent of the atmosphere. Becoming acquainted later with Priestley's discovery of "dephlogisticated air" (oxygen) and with the nature of its properties, he realised that this might well be the constituent of the atmosphere in question, and in 1775, after repeating the experiment, he put forward the view that the conversion of a metal into its calx (oxide) was due to the combination of the metal with Priestley's gas, which he termed variously "l'air éminentment respirable," "l'air pur" or "l'air vital." Lavoisier observed also that although the gas combined with metals to produce "calces," which in general have basic properties, it combined with non-metallic substance, such as carbon, sulphur and phosphorus, to produce bodies of an acid nature, and accordingly he gave to Priestley's "dephlogisticated air," and Scheele's "empyrean air," the name "oxygen," from the Greek *oxus*, sour, or acid, *gennaō*, I produce, because he was under the impression that it was a constituent of all acids. In this latter belief, however, he was wrong, although he endeavoured to maintain it as a general theory.

Lavoisier's opinions did not at once gain acceptance. The phlogiston theory was firmly rooted and chemists were reluctant to abandon an apparently adequate theory in favour of one that had no additional advantages. It needed the brilliant researches of Cavendish, which led to the discovery of the composition of water, to complete the evidence. They will, therefore, be described here before showing how their results, in Lavoisier's hands, completed the downfall of the phlogiston theory (p. 22).

Henry Cavendish, 1731-1810.*—A son of Lord Charles Cavendish and a contemporary of Black and Priestley, Henry Cavendish is known for some of the most important researches in the history of chemistry.

His discovery of the quantitative composition of water in 1781, which had such far-reaching consequences, commenced as a result of investigating "the cause of the diminution which common air is well known to suffer by all the various ways in which it is phlogisticated, and to discover what becomes of the air thus lost or condensed." Among methods for "phlogisticating" air, or of burning substances in air, Cavendish included that of exploding mixtures of common air and "inflammable air" (hydrogen) by the passage of an electric spark.* A few years previously Warltire, a friend of Priestley, had performed the same experiment and had observed that a deposit of dew was formed. Cavendish repeated these experiments and definitely stated that water was the product of exploding the gases. Continuing his investigations he determined the relative proportions in which hydrogen and oxygen combine to form water, or as he termed it, when working with air, the relative proportion of "inflammable air" required to phlogisticate completely a given volume of ordinary air.

The first opinion that water was composed of two substances seems to have been due to James Watt, the engineer. Watt's ideas regarding the nature of its components were, however, unsatisfactory, and as the result of a long and extended controversy it is to Cavendish's quantitative synthesis of water that the first true proof of its nature is now usually attributed.

Another important discovery made by Cavendish, in 1784-5, as an outcome of the same investigation, was that of the composition of nitric acid.* Priestley had noticed previously that when electric sparks were passed through moist air an acid was formed. Cavendish had also noticed in some of his experiments on the formation of water from hydrogen and oxygen, that the water had an acidic taste and that the acid product could be absorbed by soap lees (caustic potash) to form nitre (potassium nitrate). He discovered that this "nitrous" (nitric) acid was caused by the presence of "phlogisticated air" (nitrogen) as an impurity in the mixture of gases, and that when more nitrogen was purposely added the quantity of acid was increased. He concluded from this and later experiments that the acid was formed by the combination of phlogisticated air (nitrogen) with dephlogisticated air (oxygen) and eventually he found the relative proportions of oxygen and nitrogen requisite for the formation of nitric acid.

He was finally led to the famous experiment in which he proved that the whole of a given volume of atmospheric nitrogen could be made to combine with oxygen by the continued passage of electric sparks; all, that is, except "a small bubble of air . . . which certainly was not more than $\frac{1}{120}$ th of the bulk of the phlogisticated air (nitrogen) let up into the tube" (Plate VI). Just over a hundred years later Cavendish's residue of gas was rediscovered by Rayleigh and Ramsay,

and was shown to consist of five additional constituents of the atmosphere. The discovery of these gases, of which argon is the chief, is described later (p. 39). The method of producing nitric acid from air discovered by Cavendish forms the basis of one of the modern processes for utilising atmospheric nitrogen on a commercial scale.

Cavendish is remembered as one of the most exact and careful workers of his time. Like Black, he used quantitative methods, though in the researches just recounted the measurements were chiefly volumetric and do not appear to have been confirmed by the balance. Nevertheless a balance of remarkable accuracy was devised by Cavendish, a copy of which is to be seen in the collections.

The New Chemistry.—A most important result of Cavendish's work on the composition of water was its bearing on the phlogiston theory. Allusion has already been made to Lavoisier's views on this subject (p. 28), and when, in 1783, Lavoisier was informed of Cavendish's discovery, he proceeded to verify it and at once perceived its importance. Interpreting it in accordance with his new ideas he directly stated that water was formed by the combustion in oxygen of "inflammable air," which he re-named "hydrogen" (Cavendish's nomenclature was, of course, in terms of the phlogiston theory). Now for the first time Lavoisier directly attacked the phlogiston theory, setting up his own theory of combustion in its place, no longer as a tentative hypothesis, but as a comprehensive system of chemistry. The chemists of the time were divided in opinion regarding the merits of the new theory. Joseph Black and many of the French chemists speedily accepted it. Some, however, both in Britain and on the Continent, were reluctant to abandon the older ideas, and belief in phlogiston continued to exist, although declining, until the end of the century, by which time Lavoisier's theory had become firmly established. Priestley remained a believer in phlogiston until his death in 1804. Cavendish, during his later years, took no part in the controversy between the phlogistonists and the antiphlogistonists; consequently it is not known whether he changed his opinion or not.

Lavoisier accepted Boyle's concept of elements, as substances from which nothing different could be obtained by decomposition, and he compiled a list of elements, or "simple substances," as he termed them, which included the metals, the better-known solid non-metals, the gases, oxygen, hydrogen and nitrogen, and light and heat. Certain substances such as lime, magnesia, alumina, and others now known to be compounds, were counted as elements, for at that time they had not been decomposed.

The adoption of this idea, together with that of the new theory of combustion, created a veritable revolution in chemistry, and the French followers of Lavoisier quickly set themselves the important task of revising the whole system of chemical nomenclature. They did away with the meaningless names previously given to compounds and introduced the rational method of naming them according to

elementary composition. Phlogiston was swept away and chemistry appeared in an entirely new aspect.

Science owes much to Lavoisier and the French School of the late eighteenth and early nineteenth centuries, for it was due largely to their labours that chemistry was placed upon the sure foundation that it occupies to-day. At the same time it is equally indebted to Black, Priestley and Cavendish, whose brilliant discoveries supplied the essential facts upon which this foundation was built.

V. LAWS AND THEORIES OF THE NINETEENTH CENTURY

Reference has already been made to early conceptions of the nature of matter and to the "atoms" or "corpuscles" of which it was supposed to consist. Although these theories were the result of shrewd speculation, and in some instances approached very near to the truth, they were unsupported by actual evidence or experiment and it is not until the beginning of the nineteenth century that a satisfactory chemical atomic theory was founded. About the same time, partly influencing and partly influenced by, this atomic theory, were evolved the fundamental laws of chemical combination, which it will be convenient to summarise briefly here.

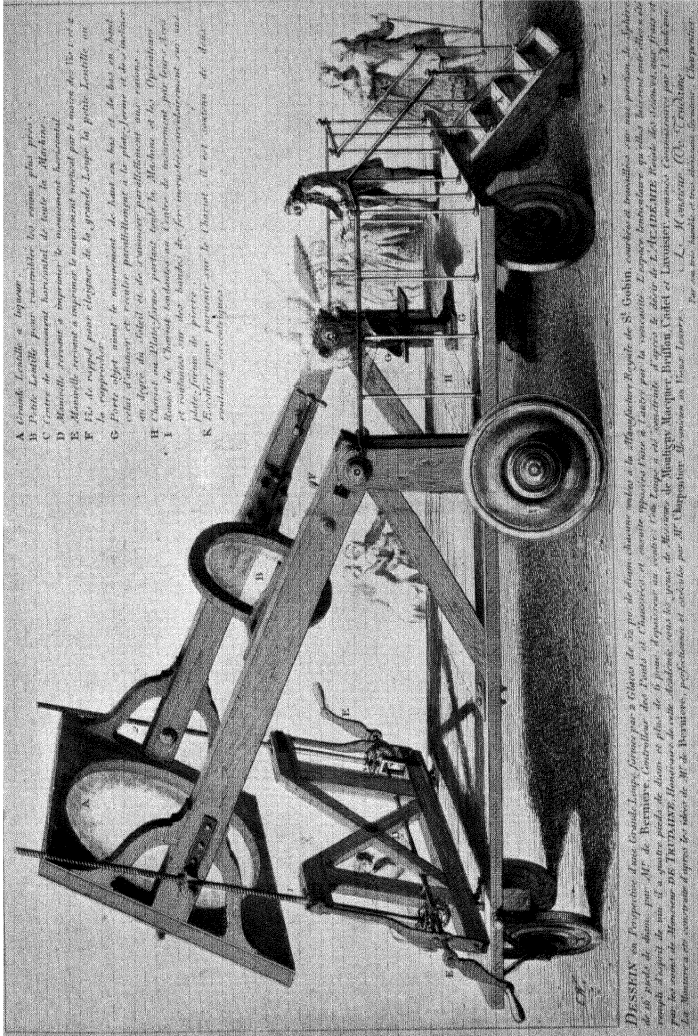
In 1792-4, Jeremias Benjamin Richter (1762-1807), a German chemist, published the results of his work on the neutralisation of acids by bases to form salts. He proved that the quantities of various bases required to neutralise a fixed quantity of a given acid, serve exactly to neutralise a fixed though different quantity of another acid, and vice versa. This "Law of Neutralisation" expressed, in effect, the "equivalent" or combining proportions of acids and bases. Richter did not, however, express himself very clearly, and moreover the publication of his results took place during the controversy between the phlogistonists and the antiphlogistonists. On account of this unfortunate combination of circumstances, his important work was overlooked.

Between the years 1800 and 1808, the two French chemists, Claude Louis Berthollet (1748-1822) and Joseph Louis Proust (1755-1826), engaged in a controversy that excited world-wide interest. The former maintained that compounds are as a rule of variable composition, *i.e.* that the proportions in which the composing elements are present may vary continuously within more or less wide limits. Proust contested this view and was able to prove conclusively by experiment that a particular compound always contains the same elements united together in the same proportions ("Law of Constant Composition") and further, that when two elements form more than one compound the composition changes abruptly, not continuously.

In 1803 John Dalton (1766-1844) enunciated the "Law of Multiple Proportions," which states that when one substance unites with another in more than one proportion, the different proportions bear a simple ratio to one another. (Dalton's work is further discussed below.)

About 1812 Jöns Jacob Berzelius (1779-1848), carried out experiments on the relative combining proportions of lead and iron with oxygen and sulphur, as a result of which he was able to generalise Richter's Law of Neutralisation into the "Law of Reciprocal Proportions or Equivalents," which states that the weights of different elements

PLATE VIII

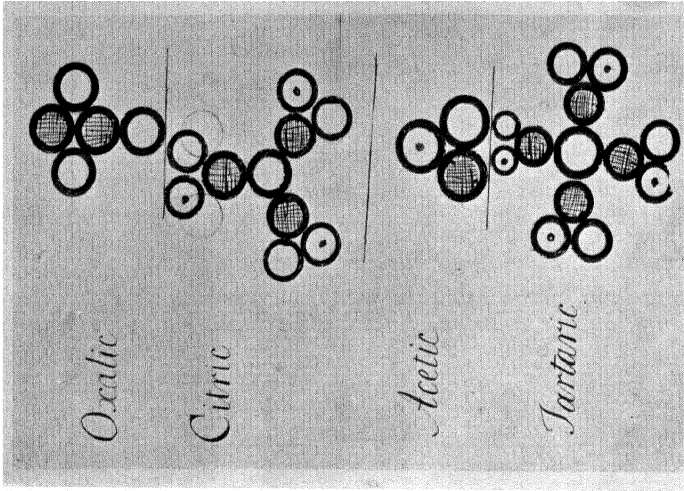


A Grande Lentille à la japon
 B Petit Lentille pour augmenter les rayons plus près
 C Centre de mouvement horizontal de toute la Machine
 D Manivelle pour imprimer le mouvement à la machine
 E Manivelle pour imprimer le mouvement sur la roue de la roue
 F Ce, de rapport pour régler de la grande-Lentille la petite Lentille
 G Grande roue pour imprimer le mouvement de tout en bas et de haut en haut
 H Centre du cadet de la roue par rapport à la plate-forme et de la roue
 I Centre du Manivelle par rapport à la Machine et des Opérateurs
 J Roue de charnière au Centre de mouvement par rapport à la roue
 K Roue de charnière de la roue de mouvement par rapport à la roue
 L Roue de charnière de la roue de mouvement par rapport à la roue
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 X Roue de charnière de la roue de mouvement par rapport à la roue
 Y Roue de charnière de la roue de mouvement par rapport à la roue
 Z Roue de charnière de la roue de mouvement par rapport à la roue

DESSIN de l'Appareil dans lequel on se sert pour faire des lentilles creuses par la machine à vapeur, qui est une machine à vapeur de la force de 10 chevaux, et qui est montée sur un chariot à quatre roues, et qui est entraînée par la machine à vapeur. Les lentilles creuses sont faites de verre de Bohême, et sont employées pour la fabrication des lunettes, des télescopes, et des instruments de physique. La machine est inventée par M. Lavoisier, et perfectionnée par M. Berthollet, professeur de chimie à l'école nationale de chimie de Paris.

Lavoisier's Burning Glass, 1774 (').

Used for submitting numerous substances, including the heat produced by the large hollow lens, filled with alcohol, the rays from which were concentrated by the smaller lens of solid glass.



ELEMENTS.

Hydrogen.		1	Strontian		46
Azote		5	Barytes		68
Carbon		5	Iron		50
Oxygen		7	Zinc		56
Phosphorus		9	Copper		56
Sulphur		13	Lead		90
Magnesia		20	Silver		190
Lime		24	Gold		190
Soda		28	Platina		190
Potash		42	Mercury		167

Left : List of Elements, 1806-7. Right : Formulæ showing composition of Organic Acids, 1810-1815.
 (Reproduced from the originals in the possession of The Manchester Literary and Philosophical Society.)

Lecture Diagrams prepared by John Dalton (p. 33) (*).

that combine separately with a constant weight of another element, are either the same as, or simple multiples (or sub-multiples) of, the weights of the different elements that combine with one another.

*Dalton's Atomic Theory.**—The opening years of the nineteenth century were marked by an event of very great importance in the history of chemistry, namely, the enunciation of the Atomic Theory of John Dalton. During the latter half of the previous century the quantitative investigation of phenomena had made considerable progress and an abundance of data had been accumulated. The value of these results could not, however, be properly appreciated, for there was no reliable means by which facts could be explained and correlated in a manner that would lead to a quantitative system of chemistry. The means to do this was at last provided by the Atomic Theory propounded by John Dalton in 1803–8.

According to this theory each element is composed of atoms, all exactly alike and of a definite weight; compounds are formed by the union of atoms of different elements in the simplest proportions. In this way a definite meaning was given to the terms "element" and "compound," affording an intimate insight into the mechanism of chemical change that before had been impossible.

The processes of reasoning by which Dalton arrived at his great generalisation have received various interpretations. One which has gained considerable acknowledgment is that, following the Newtonian doctrine of the atomic constitution of matter, Dalton visualised the atoms of different elements as having different characteristic weights, the atoms of any particular element being exactly alike. From this conception it appears that he was led to picture chemical combination as occurring between numbers of atoms of definite weight, and was able to confirm this by practical observation. He weighed the amounts of various elements which combined together chemically to form new substances and found that not only did combination take place abruptly, in steps, but also that the steps were either equal to, or were simple multiples of, one another. This law of multiple proportions has already been referred to above. Among related compounds which Dalton first investigated were the various oxides of nitrogen, the oxides of sulphur, marsh gas (methane) and olefiant gas (ethylene).

By representing the atoms of different kinds by means of symbols, Dalton enabled chemical relationships to be shown pictorially.* Chemists began to think in terms of visualised atoms and later, also of molecules, and thus to clarify their ideas by forming mental pictures of the changes involved in their experiments. Dalton's symbols consisted of arbitrary signs, which, unlike the symbols in use at present, had no reference to the names of the elements designated (Plate IX). The modern symbols were first used by Berzelius about 1818.

In Part I of his "New System of Chemical Philosophy," published in 1808, Dalton emphasised the importance of knowing the relative weights of the various atoms, and he gave a list of thirty-seven substances with the weights of their ultimate particles as determined by

him, relative to that of hydrogen as unity. These "atomic" weights were not the same as the corresponding values of atomic and molecular weights accepted to-day, the reason for the discrepancies being partly experimental error and partly that Dalton had no means of determining the number of elementary atoms forming the "atom" of a compound. (Dalton used the word atom to denote the unit particles of both elements and compounds. The word "molecule" is now used for compounds, atom being restricted to elements). Dalton therefore made the simplest assumptions possible, *i.e.* that if two elements unite to form only one compound, the "atom" of the latter contains one of each elementary atom, and that if more than one compound is formed, the simplest of them contains one of each elementary atom, the remainder being formed by the addition of one, two, three or more elementary atoms.

Although Dalton's Theory met at once with general acceptance, it proved unsatisfactory at first, owing to its quantitative uncertainty, and some chemists preferred to pin their faith to equivalent or combining weights rather than to uncertain atomic weights. Before long, improvements in methods of analysis enabled more accurate determinations of equivalent weights to be made, but the major difficulty, that of fixing precisely the numerical proportions of the atoms, still remained. Although the principles whereby the problem might have been completely solved were formulated before 1820, it was not until 1858, as explained below, that the true methods were fully appreciated and applied. The early development of the atomic theory was largely due to Berzelius, the great Swedish chemist, whose acumen and uncommon skill as an analyst enabled him to improve upon the work of Dalton and thereby to place the doctrine on a firm footing.

In 1808, Joseph Louis Gay-Lussac (1778-1850), the celebrated French chemist, announced his discovery of the important "Law of Gaseous Volumes." Gay-Lussac observed both in his own work and in that of others, that when gases react chemically they do so in volumes that bear a simple ratio to one another and to the gaseous product, measured under the same conditions. He attempted to explain this law by supposing that equal volumes of all gases under the same conditions of temperature and pressure contain the same number of "atoms," but the explanation broke down. Five years later, in 1811, Amedeo Avogadro (1776-1856) pointed out that if it be assumed that the particles of gases consist not of single atoms, but of combined atomic groups, which he called "molecules," the Law of Volumes could be satisfactorily explained, and he put forward the hypothesis that "under similar conditions of temperature and pressure, equal volumes of all gases contain the same number of molecules." This important generalisation, one of the keys to the completion of the atomic theory, was, however, practically ignored at the time, and not until many years after was its value recognised.

The discovery by Dulong and Petit in 1819 that atoms of various kinds have the same capacity for heat, and Mitscherlich's discovery about the same time that compounds of analogous composition have

the same crystalline form, proved to be of great assistance in fixing the values of atomic weights.

However, the cardinal principle that would have sufficed to settle the atomic weight question, namely, the hypothesis of Avogadro, was ignored. The atomic weights of Berzelius, of which many were approximately correct, were altered by various workers to suit their own ideas, and in consequence the subject became involved in hopeless confusion. In 1858 Stanislaò Cannizzaro (1826–1910), Professor of Chemistry at Genoa University, pointed out in a paper remarkable for its clarity and cogency, that the application of Avogadro's hypothesis would remove all difficulties in the way of establishing a consistent system. The adoption of the principles laid down by Cannizzaro resulted in great benefits to chemistry, for it dispelled the last doubts of the truth of the Atomic Theory, paved the way to the discovery of the Periodic Law (*see* below) and placed the science in all its branches on a much surer theoretical foundation.

*Classification of the Elements.**—Systems for the classification of the elements have been proposed from early times and according to various properties. The alchemists divided the metals into two groups, the noble and the base metals, and Berzelius divided the elements into metals and metalloids, or non-metals. Although several instances suggestive of arithmetical relationships between the atomic weights of similar elements had been noticed, the perception of any general scheme was impossible before about 1860, because many of the accepted atomic weight values up to that time were wrong. In 1858, as has been mentioned, the confusion regarding atomic weights was cleared up by Cannizzaro and soon afterwards the correct chemical atomic weights were assigned to most of the commoner elements.

In 1862 de Chancourtois arranged the symbols of the elements in the order of their atomic weights along a helix or spiral line drawn on the curved surface of a cylinder at forty-five degrees to the axis.* The arrangement was drawn in such a way that the distance of any point denoted by a symbol, from the beginning of the spiral, was proportional to the number representing the atomic weight of the particular element symbolised. De Chancourtois's observation that similar elements fell approximately on the same perpendiculars appeared to indicate that some regular relationship between atomic weight and chemical nature existed.

Three years later, Newlands, an Englishman, prepared a table,* which although overlooked at the time, may be regarded as the immediate forerunner of the "Periodic Law" described below. Newlands showed that when the elements are considered in order of their atomic weights, similar elements occur in periods of eight, from which analogy to the octaves in the musical scale, Newlands called this relationship the "Law of Octaves."

That the properties of the elements are a periodic function of their atomic weights, was again recognised by the Russian chemist, Mendeléeff, and independently by the German, Lothar Meyer, in 1869.

These workers found that if the elements were arranged in order of increasing atomic weight their properties varied periodically in a definite way. This arrangement (Plate X), which was more comprehensive and complete than Newlands's table, and which was termed the "Periodic Law,"* placed the general truth of the theory beyond reasonable doubt. Mendeléeff found that with few exceptions the elements fell with remarkable regularity into eight groups with family likeness. The exceptions failed to shake his belief in the truth of the principle, which as a "natural" scheme of classification of the elements, has been of very great value in interpreting the properties of the elements and in the discovery of new elements. The evidence in favour of the law was so strong that, in spite of the exceptions, its general validity was accepted in anticipation that future research would clear away the difficulties. This anticipation has been fulfilled, for comparatively recent researches, described later (pp. 64-6), have shown that with a slight yet fundamental modification of the premises, the law still holds good.

The Periodic Law gave assistance in the assignment of doubtful atomic weights and it enabled the existence, the properties and the most probable sources of undiscovered elements to be predicted. A striking example of the latter was Mendeléeff's prediction about 1871 of the discovery and chief properties of three elements which at that time were unknown and which he provisionally called eka-aluminium, eka-boron and eka-silicon respectively. The discovery within twenty years, of gallium, scandium and germanium confirmed Mendeléeff's predictions, and it is interesting to note that the properties of these elements corresponded almost exactly with those predicted.

In the light of modern knowledge the Periodic Table has been clarified in a remarkable manner. The discovery of the inert group of rare gases, chemically inactive, and of the radio-elements, which latter has led to a notable revision of ideas on the elementary nature of matter, have both been of the greatest importance. The probing of the atom and the revelation of a complex yet ordered electrical structure within it has afforded an insight into the sequence and character of the chemical elements that has not before been attained. The importance of atomic weight as a guide to the order of the elements has given way to atomic number, "a fundamental quality that increases in regular steps as we pass from one element to the next." Thus has a more complete and perfect view of the elements and their atomic structure been obtained, and what appeared as discrepancies in Mendeléeff's great generalisation have been largely cleared away and harmonised with known facts.

VI. PRACTICAL DISCOVERY IN THE NINETEENTH CENTURY

In the preceding section it has been convenient to deal broadly with theoretical considerations ; the present notes afford a glimpse of the practical discoveries made during the same period, confining the attention chiefly to the famous researches which resulted in the discovery of important new chemical elements. As time progressed the subject of chemistry became sub-divided into several branches, and hence much that might appear under the present heading will be found under "Organic Chemistry" and "Physical Chemistry" (pp. 44 and 54).

Electricity and Chemistry.—Recognition of the relationship between electricity and chemistry, a subject known as electrochemistry, dates from the year 1800, following Volta's construction of the first electric battery, the historic "pile of plates." Using a voltaic battery Nicholson and Carlisle discovered that water is decomposed by the passage through it of an electric current, and that hydrogen and oxygen gases are thereby produced in the ratio of two volumes of the former to one of the latter. This provided, incidentally, a convincing confirmation of the composition of water (p. 29).

During the next ten years Sir Humphry Davy (1778–1829) and Berzelius (p. 32), independently of one another, further investigated the effects of the electric current in bringing about chemical changes and made important discoveries. Davy, in 1807, was enabled by this means to decompose caustic potash and caustic soda, thereby demonstrating the compound nature of these substances and producing for the first time the metallic elements sodium and potassium.* By a modification of the method he also showed that magnesia and the alkaline earths, lime, strontia and baryta, are compounds and isolated from them the metals magnesium, calcium, barium and strontium.

This work was of great importance, not only because a group of new metallic elements was discovered, but also because it extended the scope of electrochemistry and disproved the older idea that the stable metallic oxides were elements. After this, the study of electrochemistry was eagerly taken up, and as knowledge grew the principles of the subject came to be used, especially by Berzelius, as one of the bases of chemical theory. Both Davy and Berzelius propounded electrochemical theories of which that of Berzelius had an important influence far into the nineteenth century. His arrangement of the elements into an "electrochemical" series, with oxygen at one end, as the most electro-negative, and potassium at the other end, as the most electro-positive, followed on his conceptions of the electrical nature of the atoms of an element and the way in which elements

were liberated consequently at the negative or positive poles of a battery when substances were decomposed by an electric current. Although his development of the theory into what was known as the "dualistic system," which regarded all compound bodies as formed of two electrically-different parts, was neglected at the time, the system of chemical symbols which he invented proved of immense advantage and formed the foundation of the present system of notation.

The study of electrochemistry in a quantitative way began about 1834 when Michael Faraday (1791-1867) discovered the fundamental laws of electrolysis. These are referred to more fully on p. 57.

Spectrum Analysis.—It is well known that when white light is passed through a glass prism the resultant play of colours, or spectrum, consists of a continuous band of light showing the colours of the rainbow in the order : red, orange, yellow, green, blue, indigo, violet. Glowing vapours and gases, on the other hand, show a "line" spectrum consisting of a number of coloured lines corresponding to the colour of the light emitted and interspersed by dark spaces. These coloured lines appear in the positions that would be occupied by the same colours in the continuous spectrum, and the position of any given line is determined by the angle through which the light is deviated by passage through the prism. Each element gives a characteristic set of lines in fixed positions, thus forming a sign by means of which its presence may be recognised. Thus, by measuring the position of lines obtained by an incandescent vapour mixture with those of known elements, the elements present in the mixture can be determined. "Spectrum analysis," as this is called, is of great value in chemical investigation owing to the fact that exceedingly minute quantities of chemical elements, of the order of several thousandths of a milligram in some instances up to one three-millionth of a milligram in the case of sodium, may readily be detected by its means.

The scientific application of spectrum analysis as an aid to chemical research was initiated by Robert Wilhelm Bunsen (1811-1899) and Gustav Kirchhoff (1824-1887), who in 1860 detected the presence of two elements, previously unknown, in the mineral water of Durkheim and in the mineral lepidolite, in Germany. These elements, to which the names "caesium" and "rubidium" were given, have properties very similar to those of potassium. They occur in nature only in very small quantities, though widely distributed, and on account of their rarity and their similarity to potassium it is probable that, had it not been for the spectroscopic method, their discovery would have been delayed many years. In 1846 Plattner had analysed the rare mineral, pollux, a substance containing a large amount of caesium, but had failed to discover the individuality of the element on account of its similarity to potassium in chemical properties, and not until four years after its discovery in the Durkheim water was it identified by Pisani as the metal of pollux.

In 1861, Sir William Crookes (1832-1919), discovered a metal previously unknown, in the solid deposit formed in the lead chambers

of a German sulphuric acid works. The residue remaining after the removal of selenium from the deposit was examined by means of the spectroscope, and its spectrum was found to contain a bright green line that could not be assigned to any known substance. In 1862 Crookes isolated the metal, to which he gave the name "thallium," and determined its chief physical and chemical properties. The notebook recording the discovery and the original specimens of thallium and its compounds are to be seen in the collections.*

For many years Crookes was the leading British authority on spectrum analysis. He prepared a "library" of spectra, still in existence, in which photographs of the spectra of the elements then known are to be found.

The discovery of indium by Reich and Richter in 1863, and of gallium by Lecoq de Boisbaudran in 1875, resulted from the spectroscopic examination of zinc ores. These metals, which resemble aluminium chemically, are very rare. One of the richest known sources of gallium is Middlesborough pig-iron, of which thirty tons contain about one kilogram of gallium. Indium occurs notably in the metallic zinc produced at Freiberg, of which a ton contains about a kilogram of indium.

The gaseous element helium was discovered by Sir William Ramsay in the mineral cleveite. Ramsay examined the spectrum of the gas that is evolved when cleveite is heated, and noticed a bright yellow line that could not be attributed to the presence of any known terrestrial element. It was shown, however, by Crookes that the line was identical with one observed by Janssen and also by Sir J. Norman Lockyer in 1868 in the spectrum of the sun, and accordingly the name helium, derived from the Greek, *helios*, the sun, was given to the newly discovered gas. (*See also "Inert Gases" below.*)

In connection with the discovery of new elements it is of interest to recall the work of William Hyde Wollaston (1766-1828), who in 1803-4 discovered and isolated palladium and rhodium, of which specimens associated with him personally, including gifts to Faraday, are to be seen in the collections. Both these metals now have various uses. They were discovered by Wollaston whilst inventing an improved method of working platinum. Under his supervision platinum apparatus became readily obtainable for operations in chemical analysis and also, as large stills, for the distillation of sulphuric acid, an important event in the sulphuric acid industry.

The Inert Gases.—One of the most important discoveries of recent times is due to the late Lord Rayleigh (1842-1919) and Sir William Ramsay (1852-1916), through whose labours a complete series of new elements, known as the inert, or rare, gases was discovered. These gases are present in small quantities in ordinary atmospheric air and their discovery excited very great interest, for it was universally considered that the composition of the atmosphere had been completely determined before the end of the eighteenth century. It is of considerable historic interest to remember that Cavendish had noticed

that a small inert residue was left in some of his experiments on combining atmospheric nitrogen with oxygen by the passage of electric sparks through the mixture of gases (p. 29), and it is a matter for surprise that no one had troubled to investigate it. As it happened, this small residue consisted of the very gases subsequently discovered by Rayleigh and Ramsay.

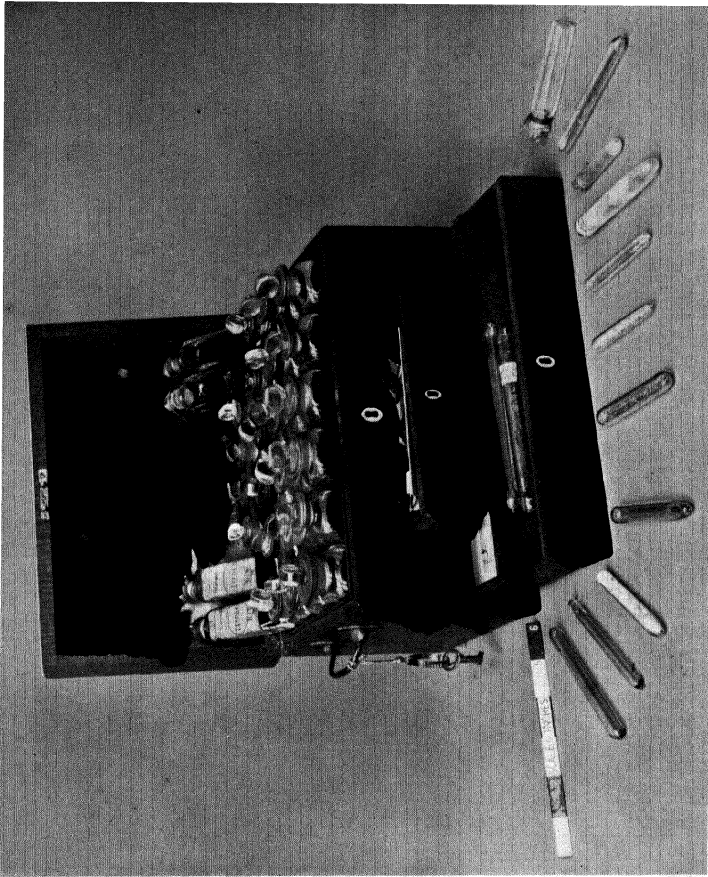
Rayleigh in the course of experiments on the density of nitrogen made the unexpected discovery, in 1892, that this gas when prepared from purified air by absorbing the oxygen was distinctly denser than when made from ammonia by decomposition. As the discrepancy could not be explained, Rayleigh was led to repeat Cavendish's experiment in order to find whether there was present in the atmosphere some undiscovered constituent that could influence the density of nitrogen prepared from it. As a result, in 1894, he rediscovered Cavendish's residue and, as it appeared to be neither oxygen nor nitrogen, he concluded that it was a new gas, which was later called argon. Ramsay had also been working at the same problem, with Lord Rayleigh's permission, and discovered the gas about the same time by a different method. Eventually the discovery of argon was communicated to the world as a joint announcement.

Ramsay's method, unlike that of Cavendish and Rayleigh, made use of the fact that nitrogen can be removed from air by absorbing it with magnesium metal. By first removing the oxygen and impurities and then repeatedly passing the remaining gases over red-hot magnesium, in the form of turnings, there was ultimately left only the small quantity of gas already mentioned. After removing the last traces of nitrogen the residual gas, amounting in volume to $\frac{1}{84}$ th part of the original atmospheric nitrogen, was found to be twenty times as dense as hydrogen, or nearly fifty per cent. denser than pure nitrogen.*

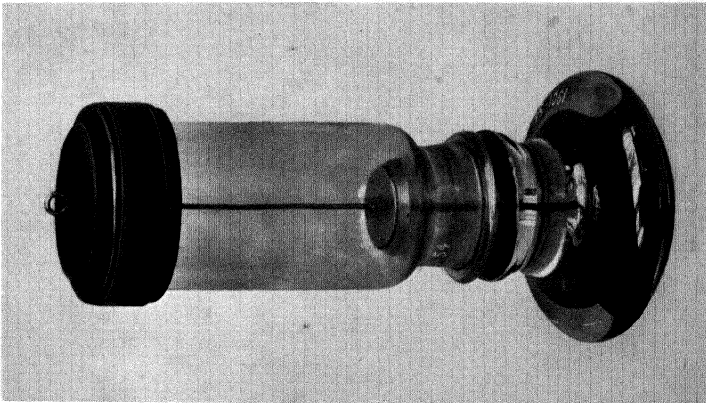
Further examination of this gas indicated that it was inactive chemically and on this account it received the name of "argon," from the Greek, meaning "idle."

Between 1895 and 1898 Ramsay and Travers discovered no less than four more new constituents of the atmosphere in the portion which had originally been thought to consist only of argon. To these gases, which resembled argon in being inactive, were given the names helium, neon, krypton and xenon.* Helium was discovered by Ramsay in the mineral cleveite, in 1895, before he found it to be a constituent of the atmosphere. The gas which is evolved when the mineral is heated had been noticed previously by Hillebrand, who had supposed it to be nitrogen. Ramsay, however, realised by its spectrum that it was a new gas and Crookes, whose expert knowledge of spectroscopic work was well known, identified its spectrum with that of an element which had previously been known to be present only in the sun, and to which the name helium had been given.

The discovery of the rare gases ranks as one of the outstanding events in the history of chemistry and the way in which each gas was brought to light, one after the other in rapid succession, was no less



Michael Faraday's Chemical Cabinet (p. 38) (*).



Apparatus for Decomposing Potash and Soda,
c. 1810.

than dramatic. Their separation from one another involved the handling of quantities of liquid air and liquid hydrogen, which at that time were not so well known as to-day and which, in the latter case, was prepared by Travers with considerable risk for, so far as he then knew, the first time. Actually Dewar had prepared liquid hydrogen in quantity some time before, but had not published his results. Crude argon is now obtained on a large scale by the fractional distillation of liquid air and is used for filling "gas-filled" metallic filament electric lamps. Helium, a very light gas, only twice the density of hydrogen, the lightest substance known, is sometimes used, partly on account of its non-inflammability, as a substitute for hydrogen for filling the gas bags of airships. The chief commercial source of helium is the natural gas which is found in many parts of the United States of America.

Neon, next to argon the most plentiful of the inert gases in the atmosphere, is of commercial value in the electric lighting industry. When a high tension electric discharge is passed through a glass tube containing rarefied neon a fine red light is emitted. Neon lamps constructed on this principle are very useful as guide lights owing to the fact that the light penetrates fog more effectively than any other known light. They are also extensively used in the construction of illuminated shop signs.

An account of the inert gases would be incomplete without the inclusion of the radioactive element, niton, or "emanation." As, however, this is intimately concerned with the general history of radioactivity and the radio-elements, it will be convenient to describe it in connection with the latter.

The Radioactive Elements.—The discovery of these substances marked an event of no less importance than that of the rare gases. Their history, as such, commences with the observation by Niepce de St. Victor in 1867 that certain salts of uranium have an effect upon photographic plates similar to that of light, the action taking place without direct contact and in the dark. In 1895 Röntgen discovered some highly-penetrating non-luminous rays, known as the X-rays, which proceeded from the phosphorescent parts of the tube in which they were produced (Crookes' tube). This led Becquerel in 1896 to see whether the phosphorescence of certain minerals was connected with the emission of similar rays. Becquerel repeated Niepce de St. Victor's experiments on uranium salts, some of which are strongly phosphorescent, and found first that a certain uranium salt, potassium uranyl sulphate, and later, that metallic uranium and all its compounds emit rays that are sufficiently penetrating to affect a sensitive photographic plate wrapped in opaque black paper.* The discovery of these rays, known as "Becquerel rays," was an event of great importance, for it opened up an entirely new line of investigation.

Marie Curie examined a large number of minerals containing uranium and found that some of them emitted Becquerel rays much more strongly than would be expected from the amount of uranium

contained in them. She therefore concluded that they contained an unknown substance more active in ray emission, or radioactive, than uranium. This was noticeably so with pitchblende, which was about four times as radioactive as uranium metal. A ton of the residues remaining from the extraction of uranium from the pitchblende of Joachimsthal, in Austria, was therefore obtained and subjected to a long and systematic process of separation. In this way M. and Mme. Curie, in 1898, obtained a substance containing a powerfully radioactive element which was named "polonium." In the same year they obtained a salt over a million times as radioactive as uranium and to the new element in the salt responsible for this extraordinary activity they gave the name "radium."

In 1899 a third radioactive element, actinium, was found in the same pitchblende residues by Debierne. Not only uranium was found to contain a radioactive material, but also the element thorium and its compounds.

Following these discoveries the study of radioactivity was quickly taken up by scientific investigators in other countries, especially in Great Britain. Madame Curie had found that the rate of emission of the rays from a radioactive substance was apparently unalterable, for all the methods that she tried, both chemical and physical, with the object of accelerating or retarding the emission, failed to have the slightest effect. This observation led to the conclusion that radioactivity is an atomic property uninfluenced by chemical change. Before long it was discovered that not only were the Becquerel rays composed of radiations, later termed α , β and γ rays (*see below*), but also that the phenomenon of radioactivity was invariably accompanied by the generation of elementary substances previously non-existent as such in the radioactive bodies. Thus it was shown that thorium, radium and actinium evolve radioactive gases in small quantities and that these gases or "emanations," of which that from radium was called "niton" by Ramsay, belong to the inert group, resembling argon in their chemical inactivity (p. 40). Further study of the emanations revealed that their existence was only temporary, for in a relatively short time they disappeared, solid radioactive substances taking their place, and the discovery was made that one of the final, inactive, products of the changes, was helium gas.

These discoveries led Rutherford and Soddy in 1903 to propound their famous Disintegration Theory, according to which radioactivity is due to the spontaneous breakdown or disintegration of unstable elementary atoms.* Ten years later the whole course of radioactive change had been worked out almost completely, mainly by the efforts of these two workers. It was established that the elements uranium and thorium give rise by atomic disintegration to two well-defined series of radioactive elements, the final inactive products of the degradation being lead and helium gas. A third series contains actinium as the most important member and is probably a branch of the uranium series.

When the radioactive series are tabulated in proper order, each

member appears as the parent, by disintegration, of the next member beneath. The change from one element to the next is accompanied by the expulsion of exceedingly small particles of matter, α -particles (the nuclei of atoms of helium gas), or β -particles (particles of negative electricity, or electrons), the latter being accompanied by the emission of radiation known as γ -rays, resembling X-rays in their properties. This may best be understood in terms of modern conceptions of the structure of atoms, which are believed to consist of a nucleus, bearing a positive electrical charge, surrounded by a system of negatively-charged particles, or electrons, held in equilibrium by the positive charge on the nucleus (p. 64). The nucleus of a radioactive atom is unstable and is continually breaking up, α - or β -particles being shot out with enormous velocity and energy. (The way in which a β -particle is ejected from the nucleus of an atom is, as yet, not known with certainty.) The loss of such a particle involves a radical change in the nature of the atom; in other words, the original element is transformed into a second element. If this second element is radioactive, *i.e.* if its atomic nuclei are unstable, it disintegrates and a third element is generated, and so on until an inactive or stable element is produced. The relative stability of the radioactive elements, measured by the rate at which they disintegrate, varies from extreme slowness to inconceivable rapidity. The fact that many of them are chemically identical, yet differ in their atomic structure, will find explanation later (*see* "Isotopes," p. 65).

VII. ORGANIC CHEMISTRY

Origin.—In early days it was found that chemical substances obtained from animal or vegetable sources appeared to be quite different from those of mineral origin. Accordingly they were divided into three main branches corresponding to, and named after, the three Kingdoms of Nature, animal, vegetable and mineral. This distinction was made as far back as the ninth century by the Persian Rhazes, and we find it made also by Nicolas Lemery (1645–1715) in his *Cours de Chymie*, published in 1675. A similar method was followed by Hermann Boerhaave (1668–1738), a Dutch physician-chemist, in his *Elementa Chemicæ*, published in 1732. At the time of making, and for long after, the distinction was not an unreasonable one. The relatively crude practical methods available in those days were entirely unsuited to the investigation of organic substances; in consequence the true nature of the latter was not at all understood and they seemed to fall naturally into classes by themselves.

About the end of the eighteenth century the distinction between animal and vegetable chemistry was dropped, as it was gradually realised that the same chemical compounds were to be found in both. Thereafter the subject was considered under two main headings, Inorganic and Organic, the term “organic” having reference to the fact that substances in this class were obtained from “living” or organised bodies, of which the chief constituents consisted of carbon compounds, as distinct from unorganised or mineral bodies. The distinction appeared to be all the more reasonable in view of the fact that it had not then been found possible to prepare organic substances artificially in the same way as mineral products, and that their only known source lay in things having life.

To account for the difference the belief arose that substances of animal or vegetable origin could be obtained only by the peculiar action of some “vital force” or agency. This theory, put forward by Berzelius, had much influence in its day and was not entirely given up until after the middle of the last century. Further reference to it is made later.

Composition of Organic Substances.—That the chief elementary constituents of organic substances are carbon, hydrogen and oxygen was first recognised towards the end of the eighteenth century by Lavoisier (p. 28), who held the opinion that all compounds of organic origin contained these three elements. Soon afterwards, however, nitrogen was added to the list, and later still, sulphur, phosphorus and other elements were recognised as occasional components. Lavoisier also first devised means for the quantitative analysis of organic substances, whereby the relative proportions of the composing elements

might be determined, but owing to the inaccuracy of the method used and to the fact that the quantitative composition of water and carbon dioxide were not precisely known, the results obtained were only roughly approximate.

The revolutionary theoretical ideas which Lavoisier introduced into chemistry led to greatly increased inquisitiveness regarding the nature of organic substances and moreover, following the enunciation of Dalton's Atomic Theory in 1803, it became important to know whether organic compounds were subject to the law of multiple proportions or not (p. 32). Consequently during the first quarter of the nineteenth century many attempts were made to evolve accurate methods of quantitative organic analysis. Among the early workers were Thénard, Gay-Lussac and Berzelius, whose methods, though not highly accurate, were sufficiently reliable to lead to discoveries of very great importance. In later years it became recognised that the general fundamental laws of chemistry hold good for organic compounds, as they do for every other substance. It was also realised that all carbon compounds would have to be included in the subject, and so the old organic chemistry grew into the "chemistry of the compounds of carbon." This branch is now so large, including well over a quarter of a million different compounds, and the structure and reactions of the compounds subject to so much more certain interpretation than those of inorganic substances, that it constitutes a very distinct division of chemistry.

Theory of "Vital Force."—Reverting to the theory of "vital force," in 1828 the historic and fundamental discovery was made by Friedrich Wöhler (1800–1882) that urea, one of the products of animal change, could be prepared in the laboratory, artificially, from ammonium cyanate, an inorganic substance. This discovery was of the greatest importance, for not only did it overthrow the theory that a "vital" agency was necessary for the production of organic substances, but it also established the doctrine of "isomerism," which states that two substances can have the same elementary composition yet differ in their properties, chemical and physical (*see* below).

Apparently both Wöhler and Berzelius accepted the fact that the vital force theory was no longer tenable, but it appears that Liebig retained the view that it was necessary, for some time afterwards.

At the present day the vital force theory is known to be untenable in its aspect that an organic substance cannot be prepared artificially; but in so far as Nature's simple methods of building up living materials are considered, it may be said to be true. Complex organic substances may be built up from simpler bodies in the laboratory, with great ingenuity and far-reaching results, but as compared with Nature the methods employed are laborious and clumsy. This, however, in no way detracts from the importance of continued and inspired effort in the elucidation of the substances and processes that occur in living things, and ultimately of understanding more fully the "Chemistry of Life," a subject known as Biochemistry.

*Isomerism.**—Wöhler's discovery that urea and ammonium cyanate have the same chemical composition though they differ in their properties had been preceded by two other instances of this phenomenon. In 1823 the tacit assumption that the properties of a compound depend only on its chemical composition, was contradicted by the discovery of Justus von Liebig (1803–1873) that silver fulminate has exactly the same composition as silver cyanate. For two years this remained an isolated example and although Gay-Lussac readily accepted the fact disclosed, accounting for it on the supposition that the difference between the two substances was due to some difference in the mode of combination of the atoms, the majority of chemists remained sceptical of its significance. In 1825 during an investigation of the nature of the "oil-gas" supplied by the Portable Gas Company, Michael Faraday (1791–1867) discovered the important substance, benzene,* and isolated another hydrocarbon having the same composition as olefiant gas (ethylene), but differing therefrom in density. In 1832 Berzelius, still doubtful of the meaning of these discoveries, found that tartaric and racemic acids, two physically different but chemically identical substances, have precisely the same composition. After this there was no further doubt that two distinct substances could have the same composition, and to the fact thus expressed Berzelius gave the name "isomerism," from the Greek, pointing out at the same time that it could be explained only by assuming that isomeric substances differ in the manner in which their constituent atoms are combined, *i.e.* in their structure.

To the revelations of Wöhler organic chemistry owes its inception as a special branch of chemical science, for they stimulated great interest and in consequence close attention began to be paid to the investigation of organic compounds.

*Structure Theories.**—Owing to their complexity the organic compounds could not be brought into line with the early theories and schemes of classification, and therefore in the early days of scientific organic chemistry one of the most important aims was the formulation of a theory whereby the peculiar facts might be explained and organic substances classified consistently.

The earliest mode of representing organic formulæ made a feature of what was known as "radicals," or groups of constituents analogous to the metal in a metallic compound. This theory originated in the fact that many inorganic compounds might be regarded as composed of two typical constituents (*e.g.*, according to Lavoisier's theories: base=metal plus oxygen; acid=non-metal plus oxygen) and this gave rise to the idea that compounds had the same "binary" character. In attempting to apply this rule to organic substances, Lavoisier was led to the supposition that they were binary compounds, not of elements, but of compound groups or "radicals." He had, however, no suggestion to offer regarding the nature of the radicals and the conception remained purely hypothetical. About 1815 as the result of an investigation of the compounds derived from the cyanides, Gay-

Lussac discovered cyanogen and found, moreover, that the atomic group containing one atom each of carbon and nitrogen (the cyanogen radical) was capable of behaving, in numerous reactions, exactly like an elementary atom, in that it could take part in chemical changes as a unit, forming compounds in which, by the ordinary methods of analysis, it was indistinguishable from an element. The importance of Gay-Lussac's discovery of the first known "compound radical" was immediately perceived by Berzelius, who thereupon revived the "radical" hypothesis of Lavoisier and extended it into the first theory of organic chemistry.

Prior to this Berzelius had assumed that organic substances differ from inorganic in being of a higher order than binary, in other words he supposed that they were ternary or quaternary, or composed of three or four typical constituents instead of only two. The discovery of the cyanogen radical, however, led him to modify his views, and in 1820 he reverted to the assumption of binary compounds, the proved conception of compound radicals enabling him to bridge the gap between the two branches of the science. His insistence, however, that the composition of the radicals should conform to his electrochemical theory (p. 37) made it difficult for him to reconcile the two. The development of the radical theory was largely due to Liebig and Wöhler, who in 1832 produced further evidence of the existence of compound radicals by a classical research on the compounds of the radical "benzoyl," in which they demonstrated that this atomic group remains intact during many chemical reactions, changing over like an element from one combination to another.

In spite of the fundamental discoveries that had been made, it was found by about 1836 that the radical theory was insufficient to account for known facts, and by about 1840 it had become untenable. Then followed a period of about a dozen years during which various theories were proposed and in turn abandoned, often after heated controversy. Nevertheless, though knowledge of facts that would lead to a consistent theory was slow in coming, the main trend was in the right direction and there is no doubt that the impetus given by the radical theory to the investigation of organic compounds produced very important results.

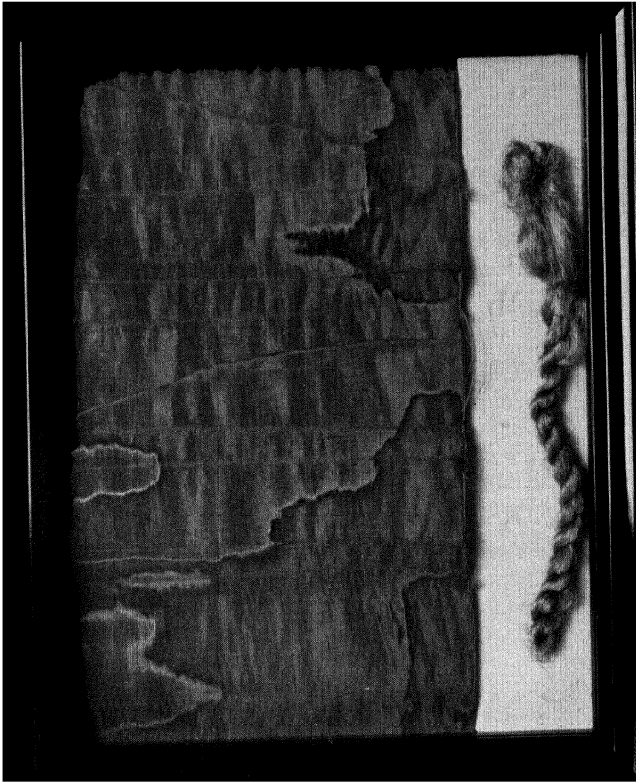
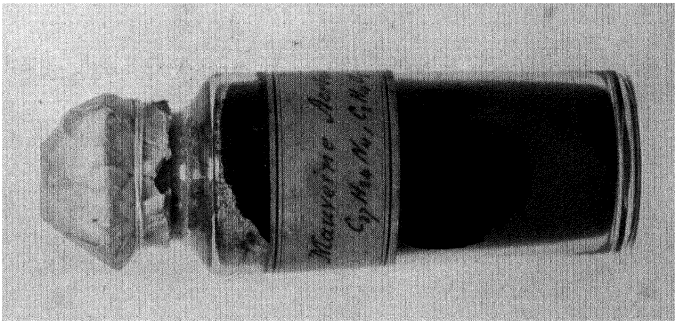
It must not be overlooked that during the period 1830-1832 great progress was made in organic analysis and this, too, had no little effect on the investigation of organic compounds. In 1831 Liebig perfected his method of analysis whereby the carbon or hydrogen contents of an organic substance could be determined with far greater accuracy than had previously been attained, and about the same time Jean Baptiste André Dumas (1800-1884) devised an accurate method for the estimation of organic nitrogen. The new methods of analysis, of which the excellence may be gauged by the fact that with small modification they are still in use, provided incomparably fine weapons for attacking the abstruse problems encountered; and by their aid and by that of the theoretical conceptions of compound radicals and isomerism, the new branch of chemical science began to make the wonderful progress

that has resulted within a hundred years in the immense fabric of modern organic chemistry.

An important advance in the interpretation of organic structure was made in 1850-1852, when Alexander Williamson (1824-1904) published the results of his researches on the formation of ether. Williamson's conclusive proof of the true relationship between ether and alcohol led Charles Frederic Gerhardt (1816-1856) in 1853 to formulate a "New Theory of Types," an improved modification of the older Theory of Types elaborated by Dumas some years previously. According to the new theory, organic compounds could be classified according to a limited number of simple types, such as water and ammonia. Thus, hydrocarbons were of the hydrogen type, alcohols and ethers of the water type, and so on. Between 1852 and 1858 the New Theory of Types, greatly developed and extended by various famous workers, grew into a fairly comprehensive system for the classification of organic compounds, and thus developed it contained the germ from which the modern Structure Theory was evolved.

The Structure Theory, by means of which the formulæ of organic compounds could be represented graphically, owed its origin to the ideas of "valency," a fundamental and important conception, introduced in 1852 by Sir Edward Frankland (1825-1899). As a result of his work on the organic compounds of metals Frankland recognised a fact that had not previously been perceived, namely that the combining capacity, or what he termed the "saturation-capacity," of individual elements is definitely limited with regard to other elements with which they may unite chemically. He noted, for example, that the elements nitrogen, phosphorus, arsenic and antimony tended to form compounds containing either three or five atoms of other elements. Although there was still much confusion between atomic weights and equivalents, nevertheless Frankland's work indicated that the combining capacity of an element is parcelled out in aliquot portions, each of which may hold another atom in combination.

"Valency" was the term afterwards applied to express the capacity of an atom of one element to combine with that of another element, and in order to fix a standard of reference the unit of valency was assigned to hydrogen, an element with the lowest atomic combining capacity then known. With reference to this standard the alkali metals, lithium, sodium and potassium, also have unit valency, or are "monovalent," since an atom of one of them may replace one atom of hydrogen in a compound. Calcium, strontium and barium are "divalent," for they can combine with or replace two atoms of hydrogen; boron and aluminium are trivalent, and so on. Although some elements have a definite and constant valency, this is not always true, for there are also many that exhibit two or more well-defined valencies; for example, oxygen is sometimes divalent or tetravalent; nitrogen, phosphorus, arsenic and antimony are trivalent in some compounds and pentavalent in others; and sulphur may be divalent, tetravalent or hexavalent. Modern ideas of valency and its mechanism are of particular interest in the light of electrical theories of the structure



[Courtesy of Professor and Mrs. A. G. Perkin

1856.

Discovery of the First Coal-tar Dye, Mauve (mauveine), by Sir William Perkin, 1856. Right: a silk skein dyed immediately after the discovery, and part of the first piece of material dyed on the large scale, a dress length of which was presented to Queen Victoria.

of matter (p. 64). Space does not, however, permit an account of them to be given in this short survey.

The conception of valency did not at once help to elucidate the nature of organic compounds; on the contrary it may have produced at first the impression that greater confusion than ever was imminent, for carbon forms such a large number of compounds that it might appear to have an indefinite number of valencies. In 1858, however, Couper, and independently Kekulé, placed the whole subject in a clear light by assuming first that carbon is always tetravalent, and secondly that carbon atoms have the capacity, highly developed, of uniting with one another to form chain-like molecules. Kekulé's theory, based on these assumptions, proved adequate to explain most of the known facts and relationships of organic chemistry; but in one notable instance it broke down, for benzene and its derivatives, usually known as the "aromatic compounds of carbon," could not be fitted into the scheme. This important exception raised a difficulty that was not overcome until 1866, when Kekulé showed that benzene could be brought into line with other organic compounds by assuming that the six carbon atoms in each molecule are united in the form of a closed chain or ring.*

The work of Kekulé, and also of Couper, who first used graphic formulæ, laid the foundation of the Structure Theory, the chief utility of which is the representation of the molecule of a substance by a structural formula, a diagram in which the atoms are depicted by their symbols, and the affinities or bonds uniting them, by short lines or hyphens. In this way the structure or constitution of the molecule, *i.e.* the mode of arrangement of the atoms, is within limitations, conveniently indicated.

*Stereochemistry.**—The limitations of plane structural formulæ lie in the fact that they do not always represent the constitution of an organic substance clearly on paper, and so it was not long before the important conception arose of depicting the structure of organic compounds in three dimensions. This space-, or stereochemistry, as it is known, was developed chiefly as a result of the historic work of Louis Pasteur (1822–1895).* In 1848 he discovered that the sodium ammonium salt of tartaric acid existed in two distinct varieties of crystal, aqueous solutions of which had opposite effects on polarised light, that is, one variety twisted the plane of polarisation to the right, while the other, in a solution of the same strength, produced an equal twist to the left. It was found that the structural formulæ of the two substances were identical when written out on a plane surface and for some time this instance of isomerism (p. 46) defied explanation. In 1874, however, Le Bel and van't Hoff independently put forward the theory of the tetrahedral carbon atom, one of the most fruitful ever conceived and the basis on which the whole science of organic chemistry has been developed. It was noticed that two of the carbon atoms in tartaric acid are each united to four different atoms or groups, and that if the formula is constructed as a three-dimensional model, in which each

of the two special carbon atoms are represented as occupying the centre of a tetrahedron, with the remaining groups attached to the corners, it is possible to obtain arrangements that differ from one another only as an object differs from its image in a mirror, or a right-hand glove from a left-hand glove. Le Bel and van't Hoff stated that this peculiar "asymmetric" structure constituted the difference between the two substances and was the cause of the difference in optical activity. It is now known that any compound of which the structure is asymmetric in this way is theoretically obtainable in two isomeric optically-active forms.

The impetus given by adopting the idea of a tetrahedral carbon atom enabled great advances to be made, especially in the artificial production or synthesis of new substances. Structural formulæ are now of great importance and on this account their determination is one of the chief aims of organic chemistry. Their value lies in the fact that in the mind of the expert they not only epitomise the nature of the substances represented, but also suggest means by which syntheses may be effected.

Since the formulation of the theory, efforts have been directed along well defined main channels. First the study of the chemical reactions peculiar to organic compounds; secondly the application of these reactions to the synthesis of new compounds not known to occur in nature; thirdly the determination of the structure of both natural and artificial compounds; and fourthly the synthesis of naturally-occurring substances.

Synthesis and its Applications.—The synthesis of new compounds has resulted in the production of an enormous number of purely artificial substances. Some of these compounds have important practical applications as, for example, dyes, drugs, photographic materials, explosives and perfumes. The great majority, however, would at first sight appear to have no value; but this is not so, as their preparation forms the chief method by which the structure of organic compounds may be determined.

The study of reactions, of which a large number has been discovered, has shown that in general, similarly constituted bodies react in a similar way to the same reagents. Therefore when it is wished to produce a substance of predetermined constitution this fact is of considerable help. Guided by the structure theory, ingredients are carefully chosen and treated in the way most likely to produce the desired result. Though many alternative trials may have to be made and the unexpected may quite well happen, a large measure of success is frequently attained. The unexpected is not always unfortunate, for the investigation of the substances produced may lead to the discovery of something new.

The determination of the structure of naturally occurring compounds has presented many a difficult but attractive problem, to be solved only after years of patient research. The method adopted is to break up the compound by regulated decomposition, not into its

elements, but into simpler compounds of which the constitution is either known or determinable. The structural formulæ of the fragmentary portions are then combined in the most likely configuration as deduced from the reactions of decomposition, giving a provisional structure of the original compound. Finally the provisional formula is tested by synthesising the compound that it represents, and if the synthetic is found to be identical with the natural compound, it may be safely inferred that the latter is truly represented by the formula.

In this way many highly complex bodies formerly obtainable only by extraction from natural sources have been made synthetically and several have proved of the greatest value to industry. Two historic instances are provided by the artificial production of indigo dye and of alizarin, the colouring principle of madder root.* Alizarin, prepared in 1869 by Perkin in England, and independently by Caro, Graebe and Lieberman in Germany, was the first natural dyestuff to be synthesised. The colours produced by alizarin are amongst the fastest shades known to-day and can be varied by the use of suitable mordants. The early Egyptians more than 5,000 years ago were well acquainted with the tinctorial properties of the natural product, madder root, and the famous "Turkey Red" or "Adrianople Red" of the Turks was due to the same product. The constitution and artificial preparation of indigo, one of the most valuable of blue dyes, was first accomplished by von Baeyer about 1880 after lengthy research. Not until ten years later, after much further work, was a successful method for its commercial production discovered by Heumann, and even then, so great were the difficulties to be overcome, several years elapsed before the artificial product could be successfully launched on the market. These researches represent one of the finest achievements in organic chemistry, the establishment of the synthetic product on a commercial basis having been one of the most costly in recent times.

No less important has been the discovery and synthesis of the coal-tar dyes, which forms a romance in itself. It was Sir William Henry Perkin (1838-1907) who in 1856, whilst working under August Wilhelm von Hofmann (1818-1892), in London, discovered the first artificial "coal-tar," or "aniline," dyestuff, "mauve." The result was that Perkin initiated the manufacture of artificial dyes in this country (Plate XII).

In the same year Natanson prepared magenta, or "rosaniline," as it was termed later by Hofmann, who followed in 1863 and onwards with the preparation of a blue and a violet dye, both produced from aniline, by which his name is now perpetuated.* The work by which Emil Otto Fischer in Germany established in 1876 the constitution or structure of rosaniline and proved that it was derived from triphenylmethane, the parent of a number of valuable dyestuffs, ranks as an outstanding achievement. Since then other important classes of dye have been discovered, of which the azo-dyes form one of the largest; the synthetic dye industry has developed to enormous proportions and many hundreds of new dyes have been prepared in great variety of colour and shade.

Other notable instances of synthesis are represented by camphor, rubber, the "alkaloids" or drugs obtained from opium and other sources,* and the group of carbohydrate substances known as the "sugars." Camphor was first prepared artificially by Komppa in 1901 and, using a different method, by W. H. Perkin and J. F. Thorpe in 1906. The labours involved in unravelling the structure of this substance, and the patience and skill employed, can only be fully comprehended by those who have followed the work step by step in published accounts.

The closely allied study of the essential oils and turpentine of plants, by which many of their odoriferous principles have been made known and prepared artificially, has resulted in the development of an important artificial perfume industry. As early as 1868 Perkin had artificially obtained coumarin, the sweet-smelling principle of woodruff and hay; and vanillin, the scented constituent of the vanilla pod, was synthesised by Tiemann and Haarmann in 1875. About 1900 the systematic study of the group was commenced by Wallach, Tiemann and others with the consequence that many of the constituents of the essential oils of plants are now known and have been prepared artificially. Work with turpentine not only laid the foundation of synthetic perfume manufacture, but also enabled Sir William Tilden in 1892 to prepare the earliest samples of artificial rubber.* Since then many attempts have been made to produce a commercially successful synthetic rubber and quite recently a promising article has been obtained in Germany.

No less important than the study of essential oils has been the elucidation of the structure and the synthesis of many important alkaloids, products of a crystalline or oily nature which are obtained from plants and which exert a marked physiological action, some being violent poisons.* Of the greatest importance are the opium alkaloids, of which the principal are morphine, codeine and narcotine. Equally important are the quinoline alkaloids, the best known of which are quinine and strychnine; nicotine, the principal alkaloid of the tobacco plant; and the tropine alkaloids, including atropine and cocaine. The history of the isolation of these substances forms a subject in itself. That they are invaluable in everyday life goes without question, and not a little of their intelligent use in medicine has been due to the patient labours of those who have unravelled their structure and so enabled their relations with one another to be determined.

Of all researches those of Emil Fischer and his co-workers on the "sugars" are often described as some of the most brilliant and are held up as model examples to later workers. Fischer not only artificially prepared the naturally-occurring sugars, glucose (grape-sugar) and fructose (fruit sugar), but also a long list of new artificial sugars, of which the first was prepared in 1887. The result has been to gain a clearer vision of one of the most important groups of compounds connected with the functions of vegetable life and to add a completely new chapter to organic chemistry.

Much more might be said about the extraordinary advances that are being made in organic synthesis, notably on the proteins and other substances derived from living matter, but this would go beyond the limits of the present survey. Truly are we only at the beginning of a period during which the complicated mechanism of life itself may be more completely understood and eventually, perhaps, regulated in a manner beyond all expectation.

VIII. PHYSICAL CHEMISTRY

This branch of chemistry may be described as dealing with the mechanism of chemical change and with physical methods of investigating chemical phenomena. As might be anticipated the subject is a large one and covers a wide field ; it is essentially associated with other divisions of chemistry and in fact overlaps them considerably. Formerly the subjects included in this branch were considered as a part of general chemistry and it was not until comparatively recently that their systematic study was pursued separately. During the last fifteen years of the nineteenth century rapid progress was made in physico-chemical discovery, new and important lines of investigation were begun, and the subject increased so rapidly both in volume and in difficulty that its segregation became essential.

In addition to the general properties and laws regulating the behaviour of gases, liquids and solids as such, there are included the more special subjects, such as those dealing with the nature and mechanism of solution, chemical equilibria, by which the effects of various conditions on chemical reactions are explored, electrochemistry, catalysis, by which is meant the acceleration of chemical reactions by "foreign" substances or "catalysts," which themselves remain unchanged in chemical composition at the end of a reaction ; photo-chemistry, chemical crystallography, and colloid chemistry. There are also those subjects to which allusion has already been made in relation to the general development of chemical science, *i.e.* the optical behaviour of chemical substances, such as the production of spectra (p. 38) and optical activity (p. 49) ; radioactivity (p. 41) ; molecular structure (p. 46) ; and modern atomic theory (p. 64).

The fact that physical principles have an important bearing on the interpretation of many chemical problems, and vice versa, was clearly recognised in the early part of the nineteenth century. For some time before this it had been realised that there was a certain connection between chemistry and physics, but the importance of the relation had not then become so apparent. In 1808, however, Gay-Lussac stated his "Law of Volumes," expressing the simple relationships in which gases combine by volume under similar conditions of temperature and pressure (p. 34) and to this, in 1811, was added "Avogadro's hypothesis," which stated that equal volumes of gases, under similar conditions, contain the same number of molecules (p. 34). These two discoveries had a considerable effect on the development of physical chemistry. Avogadro's hypothesis has been of the greatest importance in the determination of the relative weights of the molecules of gases and vapours, for it is evident that if their relative densities be determined, they will be proportional to the molecular weights.* The value of this is that the determination of molecular weights is an

important preliminary to finding the relative atomic weights of the elements.

Thus a definite lead was given to the study of the relations that exist between the physical and chemical properties of substances and from this work followed a number of important generalisations. In 1819 Dulong and Petit showed that the specific heats of many of the elements (their capacity for heat in terms of standard measurements) were inversely proportional to their atomic weights. The value of this relation as providing a method for checking atomic weights was soon appreciated. Eilhardt Mitscherlich's observation, also made in 1819, that substances of similar chemical constitution often crystallised in the same form, or were "isomorphous," was, too, of considerable importance in showing the relationships existing in groups of analogous elements, the members of which can replace one another without apparent change of crystalline form. This "Law of Isomorphism" not only afforded support for the Periodic Law (p. 35), but also provided a valuable guide in atomic weight determinations.*

The famous work which Thomas Graham (1805-1869) carried out between 1829 and 1863 on the diffusion of gases and liquids was also of great importance.* His "Law of Diffusion of Gases," often known as Graham's Law, defined the rates at which different gases travel, or "diffuse," and the extension of his researches to liquids and solutions paved the way to the distinction of "crystalline" from "colloid" bodies, which latter are described more fully later (p. 61).

"Osmosis," the term applied to the diffusion of liquids through semi-permeable membranes (which allow of passage of some liquids and substances in solution, but not of others) was also being studied about this time, notably by Traube and by Pfeffer. By enclosing a solution in a porous pot impregnated with a semipermeable membrane of copper ferrocyanide, and immersing the pot in the pure solvent, Pfeffer in 1877 was enabled to measure the hydrostatic pressure which was developed in the solution to balance the entry of the solvent. The discovery that this "osmotic pressure" was proportional to the concentration of the solution proved most fruitful in the hands of the Dutch chemist, van't Hoff, who, in relation to Pfeffer's observations, was enabled to advance a theory of solution in which the state of substances in highly dilute solution was likened to that of a gas. The outcome of this is referred to later (p. 58).

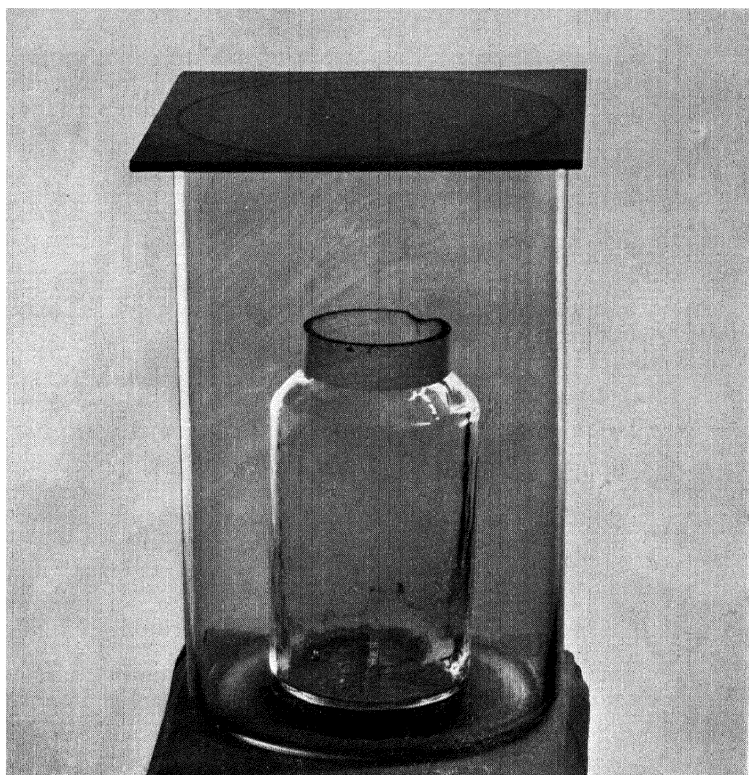
From this date the rapid development of physical chemistry began, and with it the scope and complexity of the subject increased. The limits of this survey preclude any attempt to deal in detail with every branch and attention is therefore confined to tracing the general history of some of the more interesting aspects of the subject. It must not be forgotten that developments in the electronic theory of the structure of the atom in recent years have had an important influence in explaining physico-chemical problems and the reader is referred to the excellent treatises on this subject for further information.

Chemical Affinity—Thermochemistry.— Among the problems of general significance in chemistry one of the earliest to be studied was that of the affinity, or “driving force,” of a chemical reaction. The fact that many chemical reactions proceed spontaneously indicates that a force of some kind is at work, impelling the particles of one substance to react chemically with those of another; and it is natural to enquire first respecting the nature of the force and the laws governing its operation, and secondly respecting the measurable phenomena that may be assumed to depend upon its action. The scientific men of the seventeenth and eighteenth centuries followed Newton in attributing chemical attraction or affinity to some unknown force resembling, but not identical with, gravitation. The electrochemical theories of the early nineteenth century, however, led to the abandonment of this hypothesis and to its replacement by the theory that chemical affinity is electrical in origin.

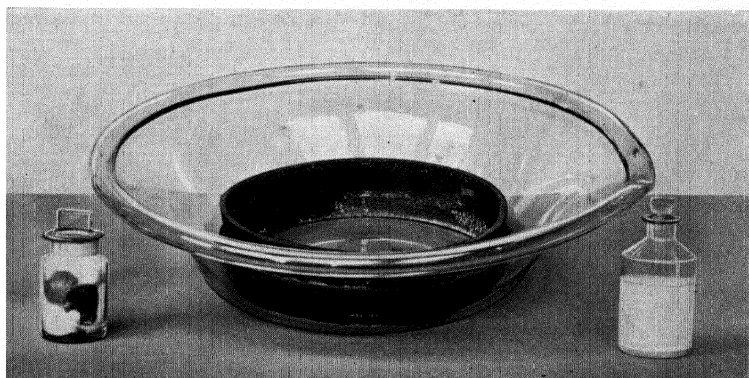
The investigators of the eighteenth century, especially the Swedish chemist, Torbern Bergman (1735–1784), came to the conclusion that in a given instance and under similar conditions the magnitude of the chemical force involved in a reaction is constant. This statement implied that the relative quantities of the reacting substances and the products of reaction were without effect on the course of a reaction. About the end of the century Bergman's views were denied by Claude Louis Berthollet (1748–1822), who showed that the course of a chemical reaction may be modified or even reversed by introducing one of the products of reaction in excessive quantity, *i.e.* the direction in which a reaction proceeds is dependent on the relative quantities of the substances involved. Owing to certain defects Berthollet's theory was not immediately taken up and the earlier view of Bergman was generally accepted until just after the middle of the nineteenth century. About this time, however, as a result of the work of Williamson on chemical equilibria, and of Wilhelmy and others on reaction velocities (the rates at which chemical changes proceed), the Scandinavian chemists, Guldberg and Waage, recognised and stated quantitatively the effect of concentration and thus reinstated in more comprehensive form the doctrine of Berthollet (p. 59).

Meanwhile a new weapon had been brought to bear on the problem of affinity, namely, that of thermochemistry, or the study of the heat effects associated with chemical change. It is well known that in many chemical changes heat, a form of energy, is evolved or absorbed; in 1840 it was found by Hess that for any given chemical change in which the same amounts of two substances react freely to form the same final product, the amount of heat developed is always the same and is independent of the route or stages by which the change is effected.

The development of thermochemistry between 1850 and 1860 was due largely to the work of Julius Thomsen, who measured the amount of heat developed, or the “heat of reaction,” in a large number of instances. The fact that substances having great affinity for one another have large heats of reaction led Thomsen to conclude, erroneously, that the total heat evolved during a spontaneous chemical reaction was

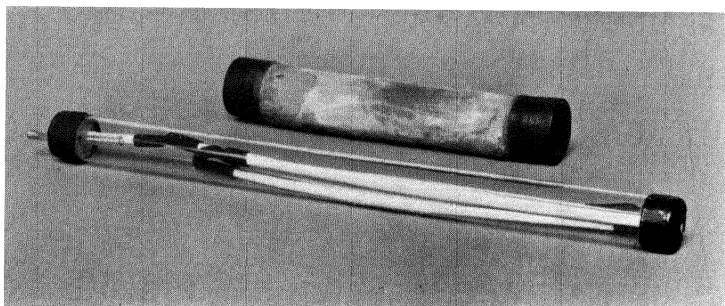


Graham's Diffusion Cell, 1850 (p. 61) (*).

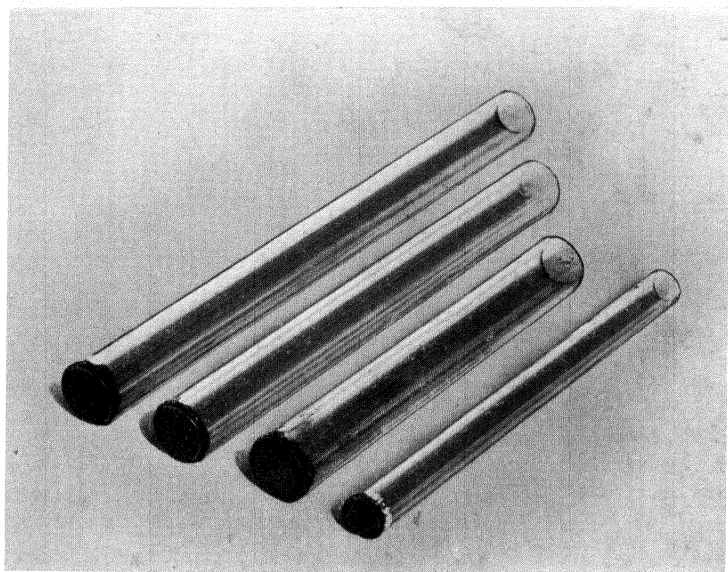


Graham's Dialyser, 1861 (p. 61) (*).

PLATE XIV



Graham's Tube Atmolysers, 1863 (*).



Graham's Diffusimeters, 1863 (*).

a measure of the chemical affinity. In some reactions, however, heat is not evolved, but is absorbed, and thus Thomsen's theory would produce a "negative" affinity; hence the total heat change cannot be a measure of affinity. However, since chemical affinity or force must be a manifestation of chemical energy, Thomsen was right in principle in seeking to measure affinity by an energy change.

The true solution of the problem came not from thermochemistry, but from thermodynamics, by which is usually understood the quantitative relationships between the various forms of energy (electrical, mechanical, chemical, etc.), and of the laws governing the transformation of one form of energy into another. Chiefly as the result of the work of van't Hoff in 1883 it has been shown that the chemical affinity involved in a reaction is proportional not to the change in "total" energy, but to the change in "free" or "available" energy of the reacting system, by which is meant the energy of a reaction which is available for the performance of the maximum external work.

Electrochemistry.—That a relationship exists between chemistry and electricity has already been referred to in connection with Nicholson and Carlisle's decomposition of water into hydrogen and oxygen by electricity in 1800; and also in Davy's isolation of the metals sodium and potassium in 1807, by decomposing caustic soda and potash with the aid of an electric current. Following these discoveries the foundations of electrochemistry were laid by Michael Faraday (1791–1867) in 1832–4 when he discovered the quantitative laws governing the decomposition of substances by an electric current, a process known as "electrolysis." Substances which conducted electricity and suffered simultaneous decomposition were termed "electrolytes." Faraday found that the amount of decomposition in such cases was proportional to the quantity of electricity passing through the electrolyte and, further, that the amounts of substances liberated during decomposition by the same quantity of electricity were proportional to their equivalent, or combining, weights.

Faraday recognised that the phenomena of electrolysis must be due to the migration of electrically-charged material particles which convey the current through the electrolyte. To the electrical boundaries (plates, rods, etc.) through which the current enters or leaves he gave the name "electrodes," and to the particles that convey the current, the general term "ions." Those particles that move towards the electrode through which the current enters (the positive electrode or "anode") he termed "anions," while those that move towards the other electrode (the negative electrode or "cathode"), were called "cations." In the case of a solution of cupric chloride, for instance, the current is conveyed through the solution by blue copper cations carrying a positive charge of electricity and moving towards the cathode, and by colourless chlorine anions carrying a negative charge and moving to the anode.

The work of Daniell, and of Daniell and Miller, between 1839 and 1844, resulted in considerable discoveries regarding the nature of ions.

It was shown that ions are formed by the splitting up of the molecules of a substance in solution, and that under the same conditions different ions move at different speeds. Between 1853 and 1859 Hittorf succeeded in measuring the relative speeds of different ions in solution and was able to calculate the proportions of the total current carried by anions and cations respectively, values known as the "transport numbers" of the ions.

About this time it was generally believed that the molecules of an electrolyte were unchanged by the mere act of solution and that splitting into ions was brought about by the application of the electric current itself. In 1857, however, the German physicist, R. Clausius, showed that if this were so an appreciable minimum electrical potential or pressure (E.M.F.) would be required to tear the ions of the molecules apart. He showed that since electrolytes follow what is known as Ohm's Law (1827), the current passing being strictly proportional to the electrical potential, even when this latter is very small in value, no definite potential was required to form ions; hence ions must already be present in solutions of electrolytes before an electric current is applied, and therefore the bonds by which they are united must be very weak. Hittorf went further in supposing that the molecules of an electrolyte or mixture of electrolytes, in solution, are continually exchanging ions, and this conception went far in explaining the mechanism of electrolytic conduction and of reactions between electrolytes.

For nearly thirty years after Hittorf's publications the chief advances in electrochemistry were confined mainly to extensions of its scientific and industrial applications. The next important step in theory came in 1887 when Svante August Arrhenius put forward the suggestion that the molecules of electrolytes are "dissociated" or split into ions to a greater or less extent when dissolved, that is, that solutions of electrolytes contain "free" ions. The proportion in which an electrolyte was present in solution in this form of "free" ions, or the "degree of dissociation," mainly determined the electrical conductivity of the solution at any particular concentration, the undissociated molecules taking no part in conveying the electric current. This conception, known as the Theory of Electrolytic Dissociation, soon proved its worth in affording simple explanations of many phenomena that had previously been obscure. About the time when Arrhenius first thought of electrolytic dissociation van't Hoff was having some difficulty with his new theory of solution (p. 55). Whereas non-conducting solutions obeyed the laws deduced from the theory very well, solutions of electrolytes failed in varying degree to conform, and consequently he was unable to generalise his important conclusions. However, the receipt of a letter from Arrhenius communicating the idea of dissociation at once gave van't Hoff the means to explain the discrepancies, and enabled him to develop his theory on comprehensive lines.

Modern conceptions, though they have not displaced Arrhenius's theory, have modified it, more especially in respect of what are known

as "strong electrolytes," or those substances that are dissociated into ions to a comparatively large extent when dissolved at normal concentrations. In 1923 it was found by Debye and Hückel that the change in electrical conductivity of these substances was determined not so much by the degree of dissociation (*see* above) as by the mobility of the ions, this depending on the electrostatic forces between them.

In explanation of the chemical reactions between electrolytes in solution, and of the action of galvanic batteries, the dissociation theory has proved of inestimable value. According to the theory, the characteristic properties of acid and alkaline solutions are due to the presence of free hydrogen ions and hydroxyl (OH) ions respectively. In some scientific and technical operations the exact measurement of slight acidity or alkalinity is a matter of importance, and to this end methods have been evolved whereby the concentration of free hydrogen or hydroxyl ions in a fluid may be precisely determined. (Exhibits illustrating these methods will be described in Part II of this handbook.)

Equilibrium and Rate of Chemical Reactions.—About the end of the eighteenth century it was shown by Berthollet that certain chemical reactions may be reversed by suitable modification of the experimental conditions. And it was known also that under certain conditions certain reactions do not proceed to completion. After going on for a time they gradually slow up and finally stop and apparently no further change takes place, the final product being a mixture of the original substance or substances and the products of the reaction. It was generally assumed that this final state was due to the total cessation of chemical change and that the system was in a state of static or restful equilibrium. In 1850 A. W. Williamson suggested that such equilibria are more probably dynamic or mobile, the apparent absence of change being due to the fact that the forward and reverse reactions are taking place simultaneously, the effect of one exactly balancing that of the other.

Many reactions take place with such great rapidity that they seem to be instantaneous and no useful attempt can be made to measure their speed. There are, however, reactions that proceed much more slowly, and in such instances the velocity can be determined by experiment. In 1850 Wilhelmy made measurements of the speed at which cane sugar is converted by mineral acids into a mixture of glucose and fructose, and showed that the rate of change at any given stage of the reaction is proportional to the amount of unchanged cane sugar present. Wilhelmy's results indicated that reaction velocities, far from being haphazard, are governed by definite laws. An important application of this clearer concept was recognised by Malaguti, who in 1853 advanced the opinion that a chemical system is in equilibrium when the velocity of the reverse reaction becomes equal to part of the forward reaction.

In 1862 the French chemists, Berthelot and Péan de St. Gilles, demonstrated the reversibility of the reaction between an alcohol and an organic acid which results in the formation of an ester and water. They showed moreover that under given conditions a definite equilibrium mixture is formed, containing acid, alcohol, ester and water, and that the composition of this mixture is independent of the direction of the original reaction. Thus when equivalent proportions of alcohol and acid are treated together the same equilibrium mixture is produced as when equivalent proportions of ester and water are heated together.

Thus the influence of the relative amounts of reacting substances on the course of a chemical reaction was clearly indicated. The outcome was the enunciation by Guldberg and Waage in 1867 of the law that governs equilibrium in chemical systems that are homogeneous in nature, that is, uniform in physical properties and chemical composition. This law, known as the "Law of Mass Action," stated that the rate of chemical action taking place in a system is proportional to the "active masses" of the reacting substances, the term "active mass" denoting, in general, the concentration of the reacting substances (strictly speaking, the product of concentration and affinity).

In the treatment of equilibrium in systems of a heterogeneous nature, that is, systems formed of parts having different physical properties, the generalisation known as the "Phase Rule" has been widely employed. This rule, which was first deduced theoretically on a thermodynamic basis by Joseph Willard Gibbs, an American physicist, in 1878, has been applied with great success to the investigation of systems in great variety. The rule embodies in simple mathematical form the relationship between the number of "phases" (physically distinct parts of a system), the number of "components" (chemically distinct substances necessary and sufficient to build up the system), and the number of "degrees of freedom" (possible variations in temperature, pressure and concentration), of a heterogeneous system in equilibrium. It is especially of value in providing a simple method for the classification of such systems, and in graphical form its results present, as it were, a complete picture of the life and character of the substances under investigation. ✓

In this way have been ascertained the nature and conditions for the formation of the different "allotropic" forms of phosphorus, sulphur and tin, which can each exist in a number of different crystalline forms. The peculiar substances known as "liquid crystals," first observed by Reinitzer in 1888, which exhibit certain properties of both liquids and crystalline bodies, have been similarly studied; and the application of the Phase Rule to many molecular compounds and metallic alloys has provided much information, as, for instance, in the case of alloys of iron and carbon by which steels of various hardness are produced. An example of noteworthy interest, too, was the work of van't Hoff and his pupils in 1898-9 on the salt bed deposits of Stassfurt in which exists a substance known as carnallite, a double salt

of potassium and magnesium chlorides. The peculiar conditions of concentration necessary for the formation of this substance, and therefore the conditions under which the deposit was formed naturally, were elucidated.

Colloid Chemistry. -- The origin of the subject of colloids is to be found in a series of famous researches of the Englishman, Thomas Graham (1805-1869), on the diffusion, or spontaneous intermixture, of gases and liquids. In 1829 Graham commenced to study the diffusion of gases. This led eventually to his discovery of the law, known by his name, which states that "the rate of diffusion of a gas is inversely proportional to the square root of its density." About 1850 he began to investigate the diffusion of substances in solution, using a simple open-mouthed glass bottle in which the solution was contained and which was placed in a jar of water. On standing, the dissolved substance gradually spread, or diffused, into the water until the concentration became uniform throughout. From these experiments he found that the rate of diffusion was proportional to the concentration of the "solute," or dissolved substance (Plate XIII).*

Later, Graham found that by allowing diffusion to take place through a membrane of parchment paper, it was noticeable that some substances in solution passed, or diffused, freely through the parchment, while others did so at an extremely slow rate or not at all. In this way he was led to distinguish between two types of substance: the members of one type which diffused readily, such as salts, sugar, etc., were, in general, found to be easily crystallisable and were termed "crystalloids"; those substances which diffused relatively slowly, such as gelatin, albumen, gums, caramel and starch, were termed "colloids," from the Greek *Kolla*, meaning glue. In 1861 Graham described a simple apparatus in which he made use of this difference of behaviour to separate a crystalloid from a colloid, a method of separation which he called "dialysis" (Plate XIII).*

The peculiar nature of certain solutions had already been noticed and investigated before Graham's time. Silicic acid jelly was known to the alchemists; J. B. Richter in 1802, and Faraday in 1857, had investigated solutions of metallic gold; and about 1845 Selmi had studied the peculiar solutions of sulphur and prussian blue. The researches of the earlier workers had not, however, been of general interest, and it was left to Graham to perceive the wide importance of colloidal phenomena.

In one respect Graham's work was in advance of its time, for the special study of physical chemistry had not then begun, and the helpful theories and methods of investigation available to-day were then unknown. Consequently during the forty years succeeding, although interesting facts were discovered, scarcely any progress was made in elucidating the nature of colloidal substances. The re-awakening of interest in the subject came about 1900, as a result of the progress made in the study of solutions in general during the

previous fifteen years. The theoretical interpretation of certain colloidal phenomena indicated that the discrete particles of a substance in colloidal solution are very large compared with ordinary molecules. Although these colloidal particles are too small to be seen by ordinary methods of microscopy, the solutions in many instances appearing perfectly clear and transparent, their existence may be detected by the ultramicroscope. This instrument was originally invented by Zsigmondy and Siedentopf in 1903 and has proved of great value in colloid investigation. It consists essentially of a microscope provided with a special form of side illumination by which the presence of colloid particles is revealed by the scattering of light at each particle. A similar effect was studied in 1869 by Tyndall and is observed when a shaft of sunlight enters a darkened room and reveals the particles of dust which float about.

According to modern views the term "colloid" is not restricted to a particular type of substance, but is used rather as defining matter in a certain state, the "colloidal state." Theoretically, matter can exist in either the colloidal or crystalloidal state. The essential feature of a colloid system is that it consists of a continuous medium, liquid, gas or solid, in which are suspended exceedingly small particles, of a certain range of size, of a second substance. The medium in which the particles are dispersed is termed the "dispersion medium" and the particles themselves, the "disperse phase." It is the limits in range of size of the particles forming the disperse phase that define the colloid state; as the particles become smaller they reach the molecular dimensions of the dissolved particles of an ordinary solution; if they are over a certain size the particles become visible as an ordinary suspension. No sharp line of division exists between these states, which merge gradually into one another.

Some well-known examples are the colloidal solutions of metals and metallic compounds, those of gold varying in colour from a bright ruby red to a dull blue, according to the size of the gold particles. The colour of true ruby glass, known to the early chemists, is due to the presence of particles of colloidal gold dispersed in a solid medium of glass.* This incidentally is an example of what is known as a "solid solution." Everyday examples of colloid systems may be seen in mists and smokes, the one representing a system of liquid particles, the other of solid particles, dispersed in a gaseous medium. Such things as emulsions of a certain degree of fineness, foams and jellies all come under the definition of colloid systems. The last-named represents a special type formed under particular conditions. Many other colloid systems exist and applications to industry are numerous.

Chemical reactions in jellies, or "gels," as they are termed, are of considerable interest.* Liesegang in 1896, by choosing suitable reagents and conditions, obtained precipitates in gels in the form of periodic layers or rings and suggested that the bands in the mineral agate were formed in the same way.

During recent years much progress has been made in the elucidation of colloidal phenomena and it has been established that many important

natural processes, including those of life, are essentially dependent upon the properties of colloidal substances. From the modern standpoint colloidal phenomena are intimately bound up with surface phenomena, and this view has already proved fruitful in explanation and suggestion. The subject is, however, one of great complexity and is yet only in its infancy. There can be no doubt that it will prove to be a very wide and important field for future research.

IX. MODERN ATOMIC THEORY

From the time of Dalton until near the end of the nineteenth century it was generally believed that an atom of hydrogen was the lightest particle in existence. Atoms were conceived as indivisible specks of homogeneous structure, the various kinds being fundamentally different in Nature. Towards the end of the nineteenth century, however, it was discovered that the rays known as cathode rays, which are produced when an electrical discharge is passed through a gas under low pressure, consist of a stream of very minute electrically-charged particles, or "corpuscles," travelling at a high velocity from the cathode, or negative electrode, of the tube in which the rays are produced. In 1897-8 Sir J. J. Thomson and others succeeded in determining the mass of a single corpuscle and found that it amounted to approximately one two-thousandth part of that of a hydrogen atom. It was found further that these corpuscles could be obtained by other means, *e.g.* by heating certain substances to incandescence (cf. thermionic valve), by the action of ultra-violet light on metals, or by radioactive change (β -rays), and the remarkable fact was established that the "corpuscles" from all sources were identical. Eventually it became reasonable to suppose that these "corpuscles" were actually unit particles of electricity, and to these particles the name "electron" was given.

Based on this view and on the discoveries in radioactivity, electrical theories of matter were evolved, of which the most successful in explaining observed phenomena was the Nuclear Atomic Theory of Lord Rutherford, put forward in 1911. According to this theory and its later developments, atoms of all kinds are composed of a heavy nucleus, bearing a positive electrical charge, in which virtually the whole weight of the atom is concentrated, surrounded by electrons at a considerable distance away, held in equilibrium by the electrical attraction of the central body. The constitution of the nucleus, according to the views now prevalent, is that of a compact assemblage of particles of unit mass, referred to hydrogen as unity, carrying a unit positive electrical charge (protons), and electrically-neutral particles of similar mass (neutrons), the nucleus thus carrying a positive electrical charge. The number of electrons in a normal atom equals that of the protons in the nucleus. Since the mass of an electron is almost negligible compared with that of an atom, it follows that the mass of the latter must be equal to the sum of the masses of the protons and neutrons in the nucleus; or, in other words, the atomic weight of an element is proportional to the number of particles in the atomic nucleus.

These concepts have been remarkably fruitful in discovery. Linked with, and stimulated by, the work of Moseley in 1913 on the characteristic X-ray spectra of the metals, and also the recognition of the phenomena

of isotopy (see below), it has been established that the chemical individuality of an element depends upon the positive electrical charge on the atomic nucleus. The atomic nuclei of various elements differ from one another first in respect of the total number of protons and neutrons contained, and secondly in respect of the relative proportions in which they are present. The first respect determines the atomic weight, while the number of protons determines the number of electrons round the nucleus and also the chemical properties of the elements. The number of protons, *i.e.* the positive charge on the nucleus, is a fundamentally important quantity known as the "atomic number" of the element. When the elements, starting with hydrogen, are arranged in the order of their atomic numbers they follow one another in the usual order of the Periodic Table, the atomic number increasing by unity in passing from one element to the next. The puzzle of certain pairs of elements (iodine and tellurium, cobalt and nickel, argon and potassium), which did not conform strictly to the order of the Periodic Table (p. 36), has been cleared up, for although the chemical atomic weights of these pairs of elements are in the unexpected order, their atomic numbers are in the proper sequence according to their positions in the Periodic Table as determined by family relationships.

The electrons round the nucleus of an atom are of considerable importance. According to modern theory, the outermost electrons normally condition the capacity of an atom of one element to combine chemically with that of another (termed the "valency" of an element) and according to their number, determine the family group in which the element will fall in the Periodic Table.

The physical cause of valency is believed to be the tendency of the atoms to possess a stable internal structure. The numerical value of the valency appears to be equal to the number of electrons which the atom must gain or lose in order to obtain this stable arrangement. The inert gases (p. 39), for instance, on this theory, owe their chemical inactivity to the fact that their atoms already possess stable arrangements of electrons, and in consequence their valency is nil and they show no desire to enter into chemical combination.

Briefly stated according to modern ideas, there are three types of valency, depending on the different ways in which two atoms may be associated in a molecule, which in turn depend upon the manner in which certain electrons are shared between the atoms. The three types are known as co-ordinate valency, covalency, and electrovalency. The conception of co-ordinate valency was introduced by Alfred Werner as early as 1891 to account for the structure of certain complex inorganic compounds: these structures of Werner have been amply confirmed by the application of electronic ideas. Covalency represents a very common mode of association of the atoms in organic molecules. Electrovalency pictures the mode of attachment of atoms carrying an electric charge ("ions," p. 57).

Isotopes.—Between 1907 and 1913 it was remarked that among the radioactive series of elements certain members that have different atomic weights are chemically identical. For example, radium, thorium-X and actinium-X cannot be distinguished from one another by any known chemical means. Soddy called such elements “isotopes” (from the Greek *iso*, equal; *topos*, place) in allusion to the fact that they occupy the same place in the Periodic Table, and hinted that isotopy might later be found to be of more general occurrence. This suggestion has been amply confirmed by the work of Aston, who has shown that the great majority of the chemical elements consist of mixtures of isotopes. Thus chlorine, of which the atomic weight determined by chemical methods is 35.46, consists of atoms of two kinds having identical chemical properties but different atomic weights, namely, 35 and 37. Some of the elements, such as iodine and sodium, consist of only one atomic species, while others, for example, krypton, xenon and tin, show greater variety, the last named element consisting of as many as eleven isotopes. Thus the chemical atomic weight of an element can no longer be regarded as a natural constant; it is merely the average of the atomic weights of its constituent isotopes. In other words what have been regarded as the chemical elements are now known to consist, in many cases, of several different kinds of atoms, chemically identical with one another, but differing in nuclear structure and mass. These considerations, of the greatest importance in the understanding of the structure of matter, do not, however, affect ordinary chemical reactions, for which the older conceptions of the atom and atomic weight still hold good.

It is of interest here to recall the unitary hypothesis of matter put forward by Prout in 1815, not many years after the enunciation of Dalton's atomic theory. Prout pointed out that many of the chemical atomic weights approximated to whole numbers and suggested that if they were determined more precisely, all atomic weights would be found to be exactly whole numbers. On this basis he constructed the theory that hydrogen is the primal substance and that the atoms of all other substances consist of combinations of hydrogen atoms. This hypothesis was vigorously contested by Berzelius and others, and before long it was abandoned owing to increasing evidence that many chemical atomic weights are undoubtedly fractional. We now know that deviations from whole numbers of chemical atomic weights are mainly due to the presence of mixtures of isotopes in the elements concerned. The atomic weights of individual isotopes are themselves nearly whole numbers; the small deviations can be ascribed almost entirely to the close packing of protons and neutrons in nuclei (resulting in the breakdown of the law of conservation of mass). Therefore the whole number part of Prout's hypothesis was not very far from the truth. A hydrogen atom consists of a single proton accompanied by one electron. Other atoms consist of protons and electrons in equal numbers, with a certain number of neutrons; hence, bearing in mind the relationship of neutrons and protons, Prout's conception of matter as composed of hydrogen was remarkably close to the facts.

Transmutation.—As long as the electrical charge on the nucleus of an atom remains intact, the atom preserves its chemical individuality. It may lose temporarily one or two of the outer electrons, in which case, as a whole, it becomes positively charged, or “ionized” (p. 57), or it may gain electrons from some external source, assuming a negative charge. Although an “ion” has properties different from those of the atom or atomic group from which it is formed, its structure is almost the same, and the original electrically-neutral atom or group is readily reproduced. If, however, the nucleus of an atom is broken up, in such a way that its charge is altered, a new element is produced. This is what happens spontaneously to the atomic nuclei of radioactive elements, either β -particles (electrons), or α -particles (consisting of nuclei of helium atoms), being lost by the nucleus. Radioactivity thus provides actual instances of transmutation, but as previously pointed out, no means of controlling the changes taking place has yet been discovered.

Lord Rutherford in 1919 was the first to bring about transmutation among the common non-radioactive elements, by bombarding them with the most highly energised bullets known, namely, the swift α -particles expelled by radioactive bodies. As these particles have an initial velocity of about ten thousand miles a second their energy of motion is very great and any small target struck by one of them is almost certain to suffer damage. It would appear that if such a bombardment is to bring about transmutation, direct hits on the atomic nuclei are necessary. The shooting is, however, very difficult, for the nucleus is a very small particle (the nuclear diameter of a hydrogen atom is about one-ten-thousandth of the atomic diameter); moreover as both the nucleus and the α -particle are positively charged they repel one another and thus the chance of a direct hit is further reduced. In practical investigation various elements have been subjected to a shower of α -particles numbering millions, and there is evidence that under these conditions a few of the latter (two or three in a million), score direct hits upon nuclei, knocking out a proton from each target hit. The production of protons is the only indication that a change has taken place, the extent of transmutation being exceedingly minute.

In 1932 Cockcroft and Walton succeeded in breaking the nuclei of various light atoms by using swiftly-moving hydrogen atoms, which though they travel at a lower speed than α -particles, and therefore possess less energy, are effective because they can be used in much larger quantities than the α -particles. Other kinds of swift particles have also been used for breaking up nuclei, but transmutation is, as has been said, on an extremely small scale. Recent developments indicate that such changes may be used for the artificial preparation of unstable radioactive bodies, possibly on a scale sufficiently large to be of medicinal use in the treatment of such diseases as cancer. However this may be, the main problem of alchemy is still very far off, if it is ever solved.

(In connection with the above account it should be borne in mind that developments in knowledge of the structure of the atom are taking place so rapidly that what is thought to be the truth at any particular time may soon require modification. Although the details of atomic structure and its mechanism may need revision the general principle of an atomic nucleus surrounded by outside influences appears to be well established.)

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