A HISTORY OF CHEMISTRY

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Summary

This short history of chemistry is dedicated essentially to a description of the evolution of ideas in chemistry during the nineteenth century. The experimental work in previous centuries, which allowed the transformation of chemistry into science, is also mentioned. In some cases, the evolution of the ideas into the twentieth century is also mentioned. The article is divided into the following thirteen sections: introduction, the birth of chemistry as a science, the definition of the building blocks of chemistry, the elements, thermodynamics, chemical dynamics, the states of matter, valence theory, spectroscopic analysis, stereochemistry, electrochemistry, organic chemistry, and discoveries of new products and less expensive processes.

1. Introduction

The history of chemistry can be divided into four periods:

1. Alchemy.
2. The birth of chemistry as a science.
3. The foundation of chemical disciplines.
4. Modern chemistry.

It is possible to fix the second period, the birth of chemistry, as a science in the second half of the eighteenth century, with only one exception, the contribution of Robert Boyle (1627–1691), who lived much earlier. The third period, the foundation of chemical disciplines, started around the early nineteenth century with the development of chemistry along the different sectors or disciplines that are still characteristic of present day chemistry. The era of modern chemistry began at the close of the nineteenth century, when the history of chemistry coincides in great part with that of the contributions of Nobel laureates. This division based on centuries is not formal but is justified by the fact that at the end of the eighteenth and nineteenth centuries many new revolutionary ideas were developed, which changed the course of chemical thought completely.

The short history of chemistry presented in this article particularly examines the evolution of concepts developed in the nineteenth century. Many of these ideas started just at the beginning of the century and reached a certain maturity by its end. Therefore, an analysis of the developments over the period of just 100 years provides an almost complete picture of the course of the evolution of chemistry. In a few cases (the chemical bond, catalysis, and industrial applications), the fundamental concepts were not developed until the first part of the twentieth century. In these cases, in order to show the evolution of the ideas, we also have to take a step into the twentieth century.

We have also introduced the experimental facts, developed in the previous centuries, that were the basis of later ideas that contributed towards the transformation of chemistry into a science during the second half of the eighteenth century, when only 17 elements where known and the phlogist theory had many followers. In studying the history of chemistry, it is possible to note some common paradigms through the anecdotes that accompany the description of the lives of several scientists: the fact that each new idea had to wait many years before being accepted, the key role played by the discovery of new instrumentation and by ideas developed outside chemistry (which had a cascade effect on innovation), the fact that many discoveries were made by very young scientists (during work on their doctoral theses or earlier), and the roles of chance and mistakes that brilliant minds succeeded in interpreting.

2. The Birth of Chemistry as a Science

In this section we trace the origins of chemistry as a modern science. Without any intention of resuscitating the debate on the defining criteria of science, the term "modern science"—or just "science"—is intended here in its general meaning understood today. Our concept of the meaning of the word "science" was shaped during that crucial period of our history extending over the seventeenth century that is commonly designated with the expression "scientific revolution." This expression conveys the sense of a radical rupture between scientific and pre-scientific investigations, and this is in part the case. Indeed, the birth of modern science required that our investigations of nature enter a qualitatively different dimension from their pre-scientific antecedents. Even so, the transition was not so sharp as the idea of a "revolution" suggests. There are, in fact, elements of continuity between the scientific investigations of one century and those of the preceding and following centuries. This is particularly true in the case of the development of chemistry, which had to wait until the end of the eighteenth century (after a long process of accumulation of data, technical equipment, and critiques of the old essentialist theories of matter) before acquiring scientific status. The aim here is to follow in some detail the most significant moments along this process, which is generally considered to culminate in the discovery of the component elements of air and water by the French chemist Antoine-Laurent Lavoisier (1743–1794). Indeed, it is common to use the term "chemical revolution" to refer to his work in recognition of his fundamental contribution in bringing the scientific revolution to chemistry.

What chemistry acquired with the contribution of Lavoisier was the strict interrelationship between observed facts (experimental data) and theory, which was achieved by astronomy and mechanics a century before with the works of Johannes Kepler (1571–1620), Galileo Galilei (1564–1642), and Isaac Newton (1642–1727). This is the necessary step to close the qualitative gap that divides the pre-scientific from the scientific approach to the investigation of nature. The strict cooperation between observation and theoretical elaboration meant, in fact, that our reflections on the events of nature abandoned the speculative and qualitative dimension to which they had always been relegated by the various mythological, religious, Aristotelian, and magical explanations of those events, to enter the empirical and quantitative dimension of their prediction and control. From that moment, in order to be considered as valid candidates for knowledge, our theories had to refer back to the actual working of nature, as understood from our observations and experimentation, and empty explanations (such as the idea that opium puts us to sleep because of its *virtus dormitiva*) were no longer acceptable. This is the conception of science that the scientific revolution brought about.

A major role in the promulgation and formation of this conception was played by what is known as "mechanical philosophy." This is an idea about the working of the universe according to which the universe and all things in it work like a clock. It is all a matter of mechanical pushes and pulls, interactions between the parts they are composed of. The explanation of all kinds of events, as the explanation of the working of a clock, is exhausted in terms of the shape, size, and weight of their components. Mechanical explanations, therefore, are not answers to questions of "why," but rather they are interested in telling us how things work. This means that they make it possible to get rid of all the obscure forces and final cause to which Aristotelian and magical conceptions of the universe typically turned to in their attempts to explain natural phenomena.

The origins of the Aristotelian and magical traditions, as well as the mechanical philosophy, date back to the beginning of western culture, in its Greek and Hellenic periods. These origins lie in the atomist conception of the world depicted first by Leucippus and his pupil Democritus (around 420 BC) and then made famous by the work of Epicurus (341–270 BC). According to this conception, all the materials of the world are composed of indivisible atoms, and their shape, size, and position account for all the properties of materials. But while by the twelfth century the whole of the Aristotelian and alchemical works had been for the most part recovered from the Arabic world after the period of decadence that darkened Europe from the sixth to the tenth century, the mechanical tradition was not recovered until the first translation of the *De Rerum Natura* by Lucretius in 1473, and of the work of Archimedes and Hero of Alexandria in the mid-sixteenth century. Until this time, and the first mechanical reinterpretations of the corpuscular theory by Galileo Galilei (1564–1642), Pierre Gassendi (1592–1655), and René Descartes (1596–1650), the two dominant accounts of the phenomena of nature remained the Aristotelian and magical ones.

The Aristotelians accounted for all the properties of all the substances in the world in terms of a primary matter impressed with a form. The form of a substance was the hidden cause of its properties. They also accepted the theory of the four elements—earth, fire, air, and water—first stated by Empedocles (490–ca.435 BC), according to which any substance could be explained on the basis of the proportions in which it contained the four elements. Since these elements could be varied in any degree, it was possible to transform any substance into any other. In particular, they thought that in combining different substances a new substance was formed in which the individuality of the former ones was lost. The theory of the four elements, together with Aristotle's theory of the formation of metals—he thought that metals were formed from the imprisonment in the earth of two kinds of exhalations, a moist vaporous and a dry smoky one, which Arabic alchemists identified later with vapors of mercury and sulfur—exerted a great influence on early chemical investigations. These developed around the search for the philosopher's stone, the substance that allowed the transformation of metals into gold, and this was to set the main goal of alchemy for centuries. Another important source of influence on the alchemical approach to nature was represented by the hermetic tradition dating from about the third century, and based on neo-Platonist writings. The hermetic writing formed the basis of the magical tradition in the investigation of nature, according to which the world was populated by mysterious, occult, personalized forces. Control of these forces required special knowledge and methods far removed from our standards of rationality.

The anti-scientific nature of magical disciplines like alchemy and astrology, though, should not make us underestimate the important role they played in the laborious process that prepared the way for the scientific revolution. Indeed, their attempts to exercise control over the events of the world, even if carried out in ways that sound bizarre today, had as a consequence an increased attention to the concrete workings of nature. This, in turn, resulted in the growth of the amount of observable facts known and in the development of technical equipment and devices that were later to form the necessary empirical and technological basis for the growth of modern science.

2.1. From Alchemy to Chemistry

A turning point in alchemy was the appearance around the first decade of the fourteenth century of the books attributed to the Arabic alchemist Jabir ibn Hayyan (ca.721–ca.815), known to us as Geber. In them we find evidence that the speculations of the alchemists were indeed actually based on a large amount of practical knowledge. Geber furnishes detailed descriptions of laboratory equipment and work, such as the purification and preparation of substances. For instance he describes methods of distilling mineral acids (for instance, mixtures of sulfuric, nitric, and hydrochloric acids) that manifest an advanced state of the art of distillation. A crucial contribution for the improvement of such art was the invention by Thaddeus Alderotti in the thirteenth century of the water-cooled condenser, which permitted the production of alcohol, the first organic solvent known. Distillation soon became central in the activities and theory of alchemists, who identified in the product of distillation the quintessence of the substances distilled and suggested its use in medical treatment, thus starting the application of chemistry to medicine, namely "iatrochemistry." In 1500, for example, a very influential book appeared by Hieronymus Brunschwygk (ca.1450–1513), known as *The Little Book of Distillation* (an enlarged edition followed) that focused attention on the description of the production of medical agents from distillations of plants.

These works influenced one of the most important figures in the pre-revolutionary history of chemistry who was also the leading practitioner of iatrochemistry, Philippus

Theophrastus Bombastus von Hohenheim (1493–1541) who called himself Paracelsus to indicate his superiority to the second century Roman medical writer, Celsus. He saw himself mainly as a medical reformer and claimed that the principal aim of medicine was the preparation of remedies, *arcana*, through the separation of what is useful from what is not in a substance by transmuting it to its ultimate essence. This was part of the activity of alchemy, to which Paracelsus gave a wider meaning than the transmutation of metals into gold; alchemy included all the processes of transformation of a substance to fit a purpose. He considered *arcana* as being mainly inorganic in nature; in particular he recommended the use of metallic salts in medical practice. In this connection his works show a good knowledge and mastering of contemporary mineralogical and metallurgical chemistry.

In the first half of the sixteenth century there was a considerable growth of interest in the various aspects of chemistry that were to play an important role in the path towards the chemical revolution. It should be noted that the main contributions were not due to investigations made by scholars, but rather came from the direct experience of men involved in the concrete practice of mining and assaying. The advanced state of this practice can be appreciated in the accurate and clear descriptions of quantitative methods of mining and assaying and of the preparation of chemical substances that we find in three books that appeared in the mid-sixteenth century: *De la Pyrotechnia* by Vannoccio Biringuccio, *De re Metallica* by Georg Bauer (also known as Agricola), and the *Treatise on Ores and Assaying* by Lazarus Ercker. Biringuccio was a metallurgist, Agricola a physician in the mining regions of Germany, and Ercker a superintendent of mines for the Emperor. Free from the preconceptions of contemporary theories they could notice things that scholars in chemistry would not have accepted, for example, the existence of more than the seven metals thought to correspond to the seven heavenly bodies.

Paracelsus himself made the only theoretical contribution in this period. He added a third element—salt—to the Islamic sulfur–mercury theory of matter, making a step forward toward the recognition of the three states of matter. Yet, he was still talking in substantialist terms—sulfur was the principle of combustibility, mercury that of liquidity, and salt that of solidity—and still far away from a proper scientific mentality and attitude, as is evident from the quantity of mystical speculations we meet in his works and those of his followers, and from the hermetic, individualist way they were written.

A different approach was that of Andreas Libau, or Libavius, (ca.1540–1616) in whose works the clarity of the exposition and the description of methods and results is striking, thus showing the concern for the communicability of knowledge that would become an essential characteristic of scientific knowledge. His chief work, *Alchemia*, published in 1597, is considered the first textbook of chemistry. In *Alchemia*, Libavius attempted to include all contemporary chemical knowledge, gave a definition of alchemy similar to that given by Paracelsus for medicine as "the art of producing magisteries and of extracting pure essences by separating bodies from mixtures," and recognized its great practical value in daily life. In all his works we find practice emphasized at the expense of theory, and this reflected well the situation of that period in which (almost exclusively) technological and empirical advances occurred while theoretical knowledge stagnated.

The chemist who most contributed to setting the theoretical advance in motion was Jan Baptista van Helmont (1577–1644). He rejected the four elements and three principles theories of matter. He thought there were only two elements: water and air. Fire was not a form of matter but a means of analysis of substances; earth was instead formed from water. Neither water nor air was convertible into the other, and air could not be turned into any other material. Everything was therefore formed from water. To prove this point he set up a series of experiments. That earth is formed from water he thought to be proved by the fact that when sand is fused with alkali, water-glass is formed which liquefies when exposed to air, and this liquid (water) can be reconverted by treatment with acid to the same amount of sand as formerly used. But his most famous experiment is that of the willow tree, by which he thought to prove that all plants are formed from water. He planted a willow tree weighing five pounds in a pot containing 200 pounds of dried soil. For five years he added only rain or distilled water. He then recovered the willow and found that it weighed 169 pounds. But drying out all the soil again, he discovered that it weighed only two ounces less than it did at the outset. From this fact he concluded that the increase in weight of the tree was due to the water. Although he generally derived wrong conclusions from his experiments, as from the two mentioned, their quantitative and controlled nature (for example, he covered the vessel in the willow-tree experiment to prevent the intrusion of dust) make them the forerunners of the application of the experimental method to chemical phenomena. Helmont's scientific awareness can also be appreciated in the assumption of the indestructibility of matter that we find at work throughout his investigations. He not only made extensive use of the balance but also was one of the first to notice that metals could be recovered from their calxes. Yet his most important contribution to the theoretical advancement of chemistry lies in his attention to air-like substances. He coined the term "gas" for them and tended to see them as a new class of substance. He realized there were gases with different properties, but not having any apparatus to collect them he could not distinguish them chemically.

Notwithstanding these remarkable empirical advances, mainly because of the increased use of the balance, and the first recognition of important theoretical facts, such as the law of conservation of mass and the existence of gases, there was not yet a satisfactory chemical theory. The various theories available were, in fact, still heavily endowed with mysterious and occult aspects in the terms of which chemical explanations were given.

2.2. The Skeptical Chemist

The person who first seriously attempted to criticize the vacuity of these explanations and to show that chemistry was a subject worthy of the attention of mechanical philosophy was Robert Boyle (1627–1691). His book *The Sceptical Chymist*, published in 1661, is regarded by many as the founding act of modern chemistry. In it he criticized Aristotelian, Paracelsian, and Helmontian chemistry and generally all the theories that explained the properties of substances based on the substantiation of preexisting essential forms, qualities, or principles. The typical defense of the four-elements theory was the experiment of burning a green wood stick. There could be observed, in fact, that the element air flew away in the form of smoke, then the water escaped from the ends of the stick, and finally the earth remained as ashes, the fire having evidently made its way out. Boyle, however, raised a series of objections to the validity of this experiment as proof of the theory. First, he observed that the four products of burning green wood were not truly elements, and then he criticized the use of fire as a reliable method of resolution of substances into their elementary constituents. The results of fire analysis may in fact vary with the conditions of its execution (for example, in a closed vessel or in open air), and in general there is no guarantee that the products of a reaction tell anything about the original substance. He also complained of the obscure and enigmatic language of the alchemists, and attributed the confusion and vagueness of their language to a corresponding lack of clarity in their own thoughts about their principles and elements. Boyle did not think that the properties of the substances in the world were due to the possession of some mysterious substantial form or principle. Wanting to do away with these vague notions, he turned to mechanical explanations of chemical phenomena, making use of the old corpuscular theory that had been recently elaborated by Pierre Gassendi (1592–1655). The properties of the various substances in the world were due to the effects of the size, shape, and motion of the corpuscles they were composed of. The primary matter of the universe consisted of different kinds of atoms moving in the void. Nevertheless, in spite of his criticism of fictitious entities, his corpuscular theory remained too abstract to be of use to the practical chemist; his definition of element lacked that pragmatic attitude necessary to make of his atoms a useful concept.

> I now mean by elements, as those chemists that speak plainest do by their principles, certain primitive and simple, or perfectly unmingled bodies; which not being made of any other bodies are the ingredients of which all those called perfectly mix bodies are immediately compounded.
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> (Boyle, 1661)

Yet, he never said which bodies he regarded as satisfying his definition or how to tell if a body satisfied it or not. Although materials such as gold could not be resolved into simpler elements, he thought they were agglomerations of particles of primary matter. And although he turned to Gassendi's solution of introducing seminal virtues to account for the different chemical species, ascribing to gold and similar entities the status of *minima naturalia*, he never saw the benefit of treating them pragmatically as elements.

This pragmatic attitude towards the concept of an element reached full realization only in Lavoisier's *Traité Elémentaire de Chimie* (1789), but it is worth noting that it had already made its appearance in the work of a contemporary of Boyle, Nicolas Lemery (1645–1715). In his *Course de Chymie* (1675) Lemery wrote:

> The world Principle must not be understood in too nice a sense: for the substances which are so-called, are Principles in respect to us and as we can advance no further in the division of bodies; but we well know that they may be still further divided.
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> (Lemery, 1675)

The fact that Boyle missed providing this definition is not reason to underestimate his contributions to the scientific development of chemistry. In fact, his mechanical approach shifted the attention of chemical investigation from finalist questions concerning the reasons for natural phenomena to questions concerning the modality and causes of their happening. Furthermore, he introduced a rigorous experimental method to chemistry, which permitted him to reach important results, the most relevant of which is the formulation in 1661 of what is now known as Boyle's Law, stating that the pressure of a gas is inversely proportional to its volume. Together with his assistant Robert Hooke (1635–1703), who improved the air pump invented by Otto von Guericke (1602–1686), he also conducted experiments on vacuum and combustion, noticing that inflammable material would not burn in a vacuum and that the calx of metals weighed more than the original metal. This phenomenon, which plays a crucial role in Lavoisier's conceptualization of oxygen, was explained by Boyle in terms of fire particles that moving from the fire and passing through the vessel, combined with the metal; thus withdrawing his earlier acceptance of the Baconian account of heat as the movement of particles.

John Mayow (1640–1679), noticing the same phenomenon, explained it in a different way, having recourse to the nitro-aerial theory of combustion developed by Robert Hooke in his *Micrographia* (1665). According to this theory the same process took place in all phenomena of combustion that took place in the explosion of gunpowder; that is, sulfur and nitrous particles reacted. Combustible materials contained a sulfur principle that made them catch fire, reacting with the nitrous particles of air. Mayow maintained that the calx increased in weight during combustion because the metal combined with "nitro-aerial" particles melted in the air. He noticed that a candle in a closed flask would stop burning although there still remained an abundance of air in the flask, thus anticipating the discovery of the compound nature of air.

Phenomena of combustion and calcination therefore became the focus of the attention of chemical investigations together with the study of the affinity between different materials. Those studying the latter tried to follow both Boyle's mechanical philosophy (by replacing the occult forces of love and hate with Newtonian attractive forces between the particles of the reagents), and his quantitative approach to experiments (by using laboratory data as the true guide for their compilation of tables of affinity). The dominant interpretation of the phenomenon of combustion was represented instead by a theory that went back to the postulations of elements and tended to disregard quantitative methods. This was the theory of phlogiston proposed in 1718 by Georg Stahl (1660–1734). Johann Becher (1635–1682), in his *Physica Subterranea* (1667), maintained that all the bodies were formed of air, water, and three types of earth—*terra pinguis*, *terra mercurialis*, and *terra lapidae*—and that *terra pinguis* escaped during combustion. Stahl renamed it "phlogiston" and said it was a very subtle material that could not be known directly but was detectable only when it left the material containing it, in the form of fire, heat, and light. With phlogiston he could explain nearly all the facts known about combustion. Combustion and calcination consisted in a loss of phlogiston. The various substances were made of the ashes or calxes they left after combustion or calcination, plus phlogiston. A metal could be recovered from its calx once heated with charcoal because the phlogiston contained in the latter would move to the calx. Combustion would not take place in a vacuum because the vacuum did not absorb phlogiston and combustion would cease when the air was saturated with phlogiston. To explain the fact that atmospheric air never became saturated, he formulated the hypothesis that, phlogiston was absorbed by plants. Yet phlogiston could not explain the increase in weight of the calxes of metals noticed by Boyle and Mayow. By completely ignoring this fact, the phlogistonists showed that they had not yet fully appreciated the quantitative approach to chemical phenomena. Those who tried to account for it turned to the unfortunate hypothesis that phlogiston had negative weight.

The accuracy of measurements however was still questionable, and it was still not possible to isolate and study gases.

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Biographical Sketches

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Ferruccio Trifirò obtained his degree in chemical engineering in Milan in1963 with a thesis on polymerisation of alpha olefins with Ziegler-Natta catalysts with Prof. G. Natta. Since 1975 he has been professor of industrial chemistry at the Faculty of Industrial Chemistry of Bologna. His main research activity is in the field of heterogeneous catalysis, especially for oxidation and hydrogenation processes. He is the author of 300 publications and of three recent books oin catalytic oxidation technology. He is the director of the magazine *Chimica e L'Industria* of the Italian chemical society. His hobbies include the collection of old books about chemistry, and tennis.