4 An Enlightened Discipline

Chemistry as Science and Craft

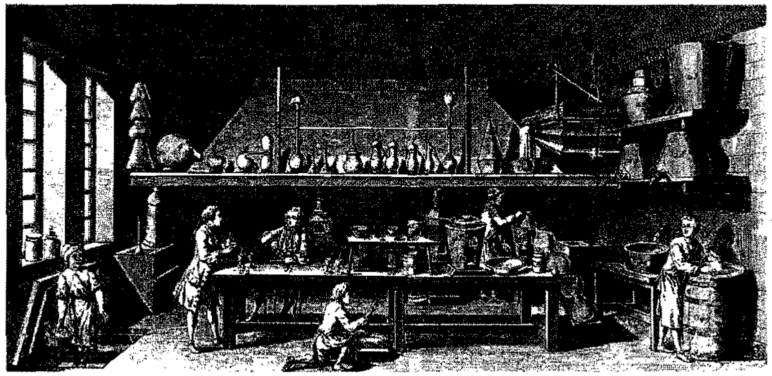
In 1726, Voltaire, an independent spirit who through his lively wit came to embody the French Enlightenment, ran afoul once again of a nobleman whom he had satirized in his writings. The nobleman's response was to have Voltaire beaten up. Voltaire challenged him to a duel, found himself (not for the first time) thrown into the prison of the Bastille fortress, and was released only when he promised to go immediately to England. There he immersed himself in literary life. He studied the philosophy of John Locke and, as far as he could master it, the physics of Isaac Newton. He decided that Locke and Newton, for whom the laws of nature were based on experience, had shown the right way to do science. Memories of his time locked up in the Bastille helped Voltaire to develop an enthusiasm for things and ideas English, to the disadvantage of things and ideas French. He also developed a taste for science that was to lead him, in later years, to install a chemical laboratory in his chateau, where he and his mistress explored the latest developments in chemistry.

In spite of Voltaire's experience, and in spite of the undoubted importance of the work of Isaac Newton, it was France and not England that became the cultural hub of eighteenth-century Europe. This was to be as true in chemistry as it was in most areas of thought and practice. The French took what they wanted from Locke and Newton and combined these ideas with the rationality and organization that epitomized their culture. The resulting intellectual climate was one that Voltaire increasingly represented. It was appropriately called the Enlightenment, because it represented the conscious rejection of authority, superstition, and magic in the light of experience and reason. Progress was to be the watchword—progress in knowledge and society, including its material aspects. Science and its applications, founded on experience, would undergo improvement and in turn would lead to the betterment of the material and moral lot of humanity. Chemistry was to play an important part in this process and progress. It was about to undergo one of its repeated transformations, to expand greatly, and to become, not for the first time, part of the dominant scientific culture of the day.

Voltaire was in many ways a radical, but even the French establishment under the old regime nurtured enlightenment and science. The Royal Academy of Sciences had been founded in Paris in 1666, soon after the Royal Society of London. Chemistry had a role in the Academy from its foundation; and chemists who were members of the Academy at the start of the eighteenth century were expected to contribute to the advancement of their science, assessing and improving its practical applications. There were also two professorships in chemistry, established in the seventeenth century, in the Jardin du roi in Paris. The lectures given by the professors were increasingly well attended by all who had an interest in that science, including philosophical chemists, metallurgists, dyers, apothecaries, physicians, and even some geologists. Chemistry was fully ready to perform as an enlightened science.

The Enlightenment was more than the Academy and the Jardin du roi. If Voltaire was its embodiment in person, then the great *Encyclopedia* of mid-century was its embodiment in print. If one talks about "the" encyclopedia today, different people will think of different encyclopedias. There was no such confusion in mid-eighteenth-century France. Everyone knew that "the" encyclopedia was the work edited by Diderot and d'Alembert, the *Encyclopedia, or Analytical Dictionary of the Sciences, Arts, and Trades.** Gabriel François Venel (1723–75), a pupil of Rouelle, wrote the article on chemistry. He told his readers that it was a mistake to seek to reduce chemistry to physics. Chemists had their own independent science, which could penetrate beneath the surface of things and get to their true nature, their inner essence. Physicists, in contrast, dealt only with external and accidental characteristics of bodies. Chemistry was and had to be an autonomous science, practiced by specialists.

Venel defined chemistry as "a science concerned with the separations and combinations of the constituent principles of bodies, whether effected by nature or by artifice, with the goal of discovering the properties of these bodies, or to render them suitable for different uses."† This definition still uses the language of principles that we encountered with Stahl and then with Rouelle. Clearly, however, with its talk of separation and combination, it refers to a science of operations, one in which the composition of bodies is seen as related to their properties. Bodies, indeed, are to be defined by their *constitution,* by the *reactions* that lead to their *composition* (or synthesis) and *decomposition,* and by their empirically determined *properties.* Here, in a short space, was a whole program for the theoretical and practical development of chemical science. Chemists were the ones who changed bodies or who combined them so as to make them useful for practical ends, including industry, agriculture, and pleasure. Theirs was an enormously valuable enterprise, vital for society and commerce.



Chemistry in the *Encylopédie*

The *Encylopédie* of Diderot and d'Alembert was the manifesto of the French Enlightenment. It was an ideological statement as well as a wonderfully optimistic account of the role of science and its practitioners in the progress of civilization. *Progress* is one of the key terms in the Enlightenment, and it assumes the perfectibility of humankind and the improvement of material culture. It was at least the incubator of the ideas of democracy and equality, the intellectual precursor of the constructive side of the French Revolution of 1789.

Artisans and craftsmen would, through their empirical practice, reveal to gentlemen-scholars some of the workings of nature, and gentlemen-scholars would, through their theoretical or philosophical understanding, be able to help craftsmen to improve the operations of their trades. This exchange of expertise and insight is shown in the engraving depicting a chemical laboratory. Coats, cravats, and wigs identify the gentlemen-scholars in the laboratory just as aprons identify the artisans.

Note that the apparatus in their mid-eighteenth-century laboratory would not be out of place in an alchemical laboratory of the Middle Ages; the same range of crucibles, furnaces, and distillation apparatus (the last on the long shelf above the laboratory bench) could be found in each.

■ Denis Diderot and Jean le Rond d'Alembert, eds., *Encyclopédie. Recueil des planches.* Seconde livraison, en deux parties (Paris, 1763): Seconde Partie, "Chimie," plate 1.

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*The French phrase translated here as "analytical dictionary" is *dictionnaire raisonné,* but the meaning of *raisonné* cannot be translated literally as "reasoned"; here it means based on critical, rational, analytical principles.

†"Chimie," by G. F. Venel, in *Encyclopédie ou dictionnaire raisonné des arts, des sciences, et des métiers,* ed. Denis Diderot and Jean le Rond d'Alembert, 28 vols. (Paris and Neuchâtel, 1751–72), 3: 408.

The plates illustrating the *Encyclopedia* were an integral part of the work. They showed craftsmen and artisans at work, while philosophers or *savants* (the Enlightenment term for scientists) watched and studied what they did. Some plates portrayed industrial processes and buildings. Others represented the interior of chemical laboratories, with their furnaces, distillation apparatus, and the rest; and yet other plates were devoted to a detailed portrayal of the latest chemical and related apparatus, including the balance. A central message, conveyed by the plates as much as by the text, was that philosophers could learn from the experience of practical men and that practical men in turn could improve their practice by listening to what philosophers had to tell them. Historians generally locate the Scientific Revolution in the seventeenth century and date the Industrial Revolution toward the end of the eighteenth century. The plates illustrating chemistry in the *Encyclopedia* strongly suggest that the Enlightenment enterprise helped to build a bridge between these two revolutions. They also suggest that chemistry was an important part of that bridge.

Scotland was another country in which chemistry thrived and which enjoyed its own age of Enlightenment. Scotland had been in a formal union with England since the early eighteenth century, and an attempt to restore the Scottish-derived house of Stuart to rule both England and Scotland was crushed on the battlefield of Culloden in 1746. But Scotland, or at least its capital city of Edinburgh, had long been closer to European culture than London was. Scottish intellectuals visited France and spoke French; Scottish doctors, in the early eighteenth century, took advantage of Europe's better medical education and studied in the Netherlands, where Boerhaave gave the best chemical lectures of the day as part of the medical curriculum. Those Dutch-educated Scots then returned to Edinburgh and Glasgow, where they gave chemistry a real presence in the universities.

Scots of the next generation were able to study at home. They maintained and strengthened chemistry in the universities from the middle of the eighteenth century on, in the years of the Scottish Enlightenment. Philosophers, lawyers, economists, literary men, chemists, and natural philosophers all contributed to the intellectual ferment in Edinburgh, and, as in France, theory and practice combined. Ironworks and agriculture were just two of the practical areas where academic chemists contributed to the passion for "improvement," the Scottish term for material progress. The leading figure in Scottish chemistry in the second half of the eighteenth century was Dr. Joseph Black, who had written an M.D. thesis on a possible chemical cure for bladder stones. That thesis involved the study of a salt, an examination of the nature of heat and its role in a chemical reaction, the use of the balance as a tool for chemical analysis, and the identification and characterization of a gas as a chemical species. In almost every aspect of this work, Black contributed significantly to key problem areas in the rapidly developing science of chemistry. In the next chapter we shall return to Black and see why his work was important. First, however, we need to look at two central areas of chemical investigation in the eighteenth century: the elucidation of the chemistry of salts, important for pharmaceutical and mineral chemistry alike, and the development and application of a new concept of chemical affinity.

Salts of the Earth, and the Classification of Substances

Paracelsus had introduced Salt as a principle in his chemical classification. For Stahl, salt was not so much a principle as a category, and his laboratory skills enabled him greatly to expand knowledge about salts. In 1723 he published a book on salts, in which he argued that they were produced by a combination of earths, alkalis, or metals with water. The book was reprinted, and a second edition followed, as did a French translation. Stahl's theory of salts, and his experiments and observations on salts, were thus available to European chemists throughout the middle fifty years of the 1700s. Stahl had an influential view of the constitution or composition of salts. He and other chemists recognized that an acid was involved in the composition of each and every salt, and, as a chemical philosopher, he regarded this acid as the most important part. But he saw that salts were of commercial as well as philosophical interest, and in their commercial aspect, other parts also needed to be identified (e.g., the "metallic" part).

Stahl's work became known in France. Meanwhile, French chemists within the Academy worked separately and independently on the chemistry of salts. As the eighteenth century progressed, German and French understanding of this area of chemistry came steadily closer together. The French translation of Stahl's book on salts marks the effectiveness of that union. The leading student of salts in Paris at the opening of the eighteenth century was Wilhelm Homberg (1652–1715), a widely traveled chemist who made Paris and its Academy his home. He developed an elaborate classification of salts. Composition and experiment were the keys. He found the definition of any given salt to be threefold. It depended on (1) the properties of that salt that the chemist could detect through the senses of sight, smell, taste, and touch; (2) the laboratory operations that led to the preparation of the salt; and (3) the substances of which the salt was composed. The chemist in his laboratory could, for example, combine one of the mineral acids (hydrochloric, nitric, or sulfuric acid) with an alkaline earth, such as the one found in lime, to form a salt.

The implication of Homberg's approach, which became widely accepted, was that a salt, or any other chemical substance, was defined by three things: the substances that composed it, the operations by which it was prepared, and the totality of its empirical properties. The practical correlation of operations in the laboratory with chemical constitution was of great significance because it led to a new understanding of composition. This was more complex than the older ideas of elements and principles and more useful than they had been in demonstrating the differences between chemical substances. And it was the work of Homberg and his colleagues that was absorbed into Venel's definition of chemistry that we encountered in the *Encyclopedia.*

The definition of substances in terms of their properties was philosophically problematic, although the problem was far from being a new one in chemistry. Some salts were produced by a vigorous combination of acid and alkali—a union of substances of chemically opposite character, in violation of the old idea of affinity as the cause of the union between like substances. But the salts produced were neither acidic nor alkaline. Chemical indicators such as litmus, which turn red in the presence of acids and blue in the presence of alkalis, showed clearly that most salts composed of acid and alkali had the properties of neither parent. Corpuscular explanations, harking back to the seventeenth century, were brought forward. Homberg, for example, suggested that we could think of acids as having pointed corpuscles, like daggers, while alkalis were the sheaths. Combining the two would then be like sheathing a dagger, concealing its sharp point.

Chemists had long relied on a rich imagery of similes and metaphors. Homberg was working in a fine old tradition. And corpuscular explanations, however metaphorically they were intended, did at least offer a way of thinking about the preservation of chemical constituents while their properties were concealed in the properties of the compound. Corpuscular explanations also made it reasonable to envisage the perseverance of a chemical constituent through a series of reactions, so that the same substance was carried from one reaction to the next, and from one substance to another, without undergoing essential change, even though its properties could be masked. Such explanations reinforced the idea that chemical *composition,* embodied in chemical substances and revealed through chemical operations, was the key to chemical *classification.*

An immediate fruit of this new way of identifying different substances was a rapid increase in the number of known salts, and indeed of new substances of every sort. Different alkaline earths were identified, and chemists discovered that there were two distinct caustic alkalis (soda and potash). New acids, new

metals, and new combinations between them threatened an information overload. The only way to handle the rush of information about newly discovered or discerned substances was to devise schemes of classification that would enable chemists to find their way through the ever-expanding knowledge. How else could one bring order to the threatening chaos of new discoveries?

There were critics who thought that chemistry could never be more than a combination of laboratory practice, which they viewed as a kind of cookery, and classification, which they saw as the essence of natural history, including botany and zoology. Those same critics regarded natural history as unscientific, lacking the rigor of mathematical physics or astronomy. Chemistry was indeed far from Newtonian physics. We have already seen the failure of attempts to assimilate chemistry to Newton's program. But to dismiss chemistry for this reason was to adopt too narrow a definition of science and to undervalue the role of classification in the scientific enterprise as a whole. Natural historians have to classify what they observe or collect; so do chemists.

Chemistry was a laboratory science, a science of practice. This had always been so, and Enlightenment pride in laboratory practice merely put a seal of approval on an established fact. But mere empiricism had never been enough in science, had indeed never been possible in science. A major component of science is the organization of knowledge in ways that lead to its refinement and expansion. The organization of knowledge requires some scheme of classification and a language, or at least a set of terms and rules for using them, in order to make the classification fruitful and functional. Classification is essential to science. Eighteenth-century chemists knew that as well as anyone. Chemical operations and an acceptance of the importance of composition to the definition of any compound substance were two of the essential supports of their schemes of classification. A language that embodied these notions was another support (see Chapter 6). Finally, there was a newly reformed notion that gave order to the mass of experiments and identifications: chemical affinity.

Affinities: Classifying Substances and Reactions

The creation of tables of chemical affinities was an attempt to encapsulate all possible reactions between the constituents of chemical compounds. The goal was not only to provide a summary and key to known reactions but also to predict reactions that had not yet been observed. Tables of affinities thus had both a descriptive and a predictive role; they could be used as a shorthand for a description and classification of observed reactions, and they could function as instruments of discovery. It was also possible, although not necessary, to use affinity tables as a clue to the mechanism of chemical reactions. It was along such lines that Isaac Newton had urged natural philosophers to reason from observed phenomena to the forces that caused them, and then to the laws that governed those forces.

The first affinity table to be published was that of Etienne-François Geoffroy (1672–1731), who had joined the Academy in Paris in 1699 as a student of Homberg and soon became an associate member of the Academy. By the time he presented his table of affinities to the Academy in 1718, he had an international reputation and had been elected as a foreign member of the Royal Society of London. It is important to recognize that Geoffroy was careful to call his table one of relations (*rapports*), not of affinities. He rejected old ideas of affinity as the sympathy of like for like. He was also anxious not to be identified with the Newtonian camp, where affinities were interpreted as the result of chemical attractive forces. The danger of such an interpretation was made clear by Bernard le Bovier de Fontenelle (1657–1757), who had been permanent secretary of the Academy since 1697 and was described by Voltaire as the most universal mind of his age. Fontenelle, for many years the official book and article reviewer for the Academy and writer of the Academy's annual *History,* speculated about what might be the cause of Geoffroy's *rapports.* "It is here," he wrote, "that sympathies and attractions would be altogether relevant, if only they existed."*

Geoffroy carefully avoided Newtonian attraction in writing his paper. He began with an account of the selectivity of chemical reactions. Different bodies had certain relations that led them to combine readily with one another. These relations, he asserted, existed in different degrees and obeyed their own laws. Experiments showed that in a mixture of substances, one substance would always combine with another particular one, in preference to all others. Displacement reactions, where one substance drove another out of a compound and took its place, provided an insight into this selectivity.

If two substances had an affinity for a third substance, then the one with the higher *rapport* for that third substance would be the one to combine preferentially with it. The idea of classifying substances by the degree of their tendency to combine with one another was not new. Stahl had hit on it, and so in a different way had Newton. There were, however, two important novelties in Geoffroy's formulation, besides his avoidance of the language of Newtonian attraction and the language of Stahlian affinities between like substances. These were, first, the potential universality of the tables of *rapports,* and, second, the predictive power of these tables. Universality was a goal that the mak-

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*Fontenelle, *Histoire de l'Académie Royale des Sciences* (Paris, 1724), 35–37.

ers of tables of affinities never achieved, but they believed that if they could make the tables complete and universal, then all possible reactions could be deduced from them. Some predictive power was readily available, even using incomplete tables. If one knew the initial conditions, and if the reactants and their constituents were ranked in a table of *rapports,* then one could predict the chemical outcome.

As Geoffroy wrote, chemists would find in his tables "an easy method of discovering what happens in several of their operations, even when these are difficult to disentangle." Chemists would also discover "what *must be* the result of the mixtures that they make from different mixt bodies." Here, without causal explanation, Geoffroy was offering an interpretative scheme for chemistry that would have all the force of the laws of physics. Place a substance *C* in a mixture (generally in solution, i.e., dissolved in a liquid, usually water) of compound *AB;* if *C* has a higher *rapport* for *B* than *A* has, it will displace *A* from its union with *B.* At the end of the reaction, *BC* will be the resulting compound, and *A* will have been expelled from its combination with *C.* For example, the second column in Geoffroy's table ranked metals in order of their reactivity with the acid from sea salt (our hydrochloric acid). Tin was placed above copper, because it could displace copper from its combination with that acid.*

Geoffroy's table was important, but it did not have many successors in the first half of the eighteenth century. There was one in 1730 and another in 1749. Perhaps French reluctance to identify *rapports* with attractions lay behind this lukewarm response. The second half of the century, however, saw a resurgence of interest in affinity tables, stimulated by an extremely influential textbook of 1749, Pierre Joseph Macquer's *Elements of Theoretical Chemistry,* which devoted a whole chapter to affinities:

> All the experiments which have been hitherto carried out, and those which are still being daily performed, concur in proving that between different bodies, whether principles or compounds, there is an agreement, relation, affinity or attraction (if you will have it so). This disposes certain bodies to unite with one another, while with others they are unable to contract any union. It is this effect, whatever be its cause, that will help us to give a reason for all the phenomena furnished by chemistry, and to tie them together.†

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*Geoffroy, "Table des différents rapports observés en chimie entre les différentes substances," *Mémoires de l'Académie Royale des Sciences* (1718): 202–12.

†P. J. Macquer, *Elements of the Theory and Practice of Chemistry,* trans. A. Reid, 2 vols. (London, 1775), 1: 12.

Newtonian ideas about chemical combination made inroads in France in the second half of the century, and affinity tables proliferated. By 1778, Macquer (1718–84)had decided that there were no separate laws of chemical affinity and that the law of universal attraction would suffice to explain the whole of chemistry, if only we could learn about the shape of the particles of bodies. In the same year, the second edition of the *Encyclopaedia Britannica* asserted that all theories of affinity were conjectural, "neither is it a matter of any consequence to a chemist whether they are right or wrong."* Here was a recognition that the utility of a scientific theory need not depend upon its truth. Affinity tables were above all *useful,* in providing a summary of existing knowledge about chemical reactions as well as a tool for predicting new reactions.

Reactions and Operations: Closing Circles and Enveloping Nets

Tables arrange data in significant ways. The terms listed exist in a defined relation to one another. Affinity tables list substances, define them in relation to composition, and embody our knowledge of chemical reactions. They are like dictionaries and encyclopedias that present knowledge and embody the interrelationship of terms. A work of reference such as a simple dictionary or encyclopedia might define a violin as a kind of small cello, and a cello as a kind of big violin. That circularity is fine, as long as we know something about either one of those musical instruments before we consult the work of reference. Chemical substances are also defined in relation to one another. Acids react vigorously with alkalis, some metals dissolve readily in certain acids, while others do not. If a substance is defined in terms of its reactions with other substances, we have a situation only marginally more complicated than the case of the cello and the violin. A network of cross references shows the unity of a set of definitions. The coherence of the network is complete when its set of definitions forms a closed circle. In both cases, we need to bring external knowledge to bear on our reading of the definition. In chemistry, that means we need to understand the conditions in which reactions occur and the operations needed to bring them about.

As a result, French chemists in the Enlightenment developed a double classification—one in terms of affinities and reactions, the other in terms of the conditions of reaction and the operations that caused desired reactions to take place. The classification in terms of affinities was printed in books and papers. The classification in terms of operations and experimental conditions was less formally expressed, but it was equally important. At the level of greatest generality were two questions: (1) Was the experiment to be performed in the wet or the dry way? (2) How should heat be applied to assist the reaction? When chemists wrote of the "wet" way, they meant a chemical reaction in solution or between liquid reactants; the "dry" way involved reactions produced by the mixture of dry reactants. Mixing two salt solutions, or an alkaline and an acid solution, in order to bring about a reaction was the most widely used practice; more reactions took place in the wet than in the dry way. Heating a substance in air (for example, roasting lime to produce quicklime or heating mercury to produce its red calx, which we call mercuric oxide) corresponded to reaction in the dry way. Tables of affinities sometimes indicated that they referred to one or the other of these ways.

Information about chemical theory is easier to come by than information about chemical practice. Nonetheless, we should recognize that when chemists read tables of affinities, they had in mind not only the substances that would be produced but also the ways in which the appropriate reactions could be generated and controlled. So their explicit classification of substances through affinities was joined to an implicit classification of chemical operations. Chemical operations depend on chemical apparatus, some built for that purpose, and some available in any kitchen.

Chemists may have been sparing in describing their practice, but they were even more sparing in describing their apparatus. This may have been partly because most apparatus had changed little over the years, so readers could be expected to be familiar with it. Any eighteenth-century laboratory contained vessels for mixing substances in solution and vessels for mixing them in the dry way. The former group of instruments could include flasks, jars, and cooking pots. The latter group included crucibles and apparatus for bringing about sublimation, the transformation of a solid to a vapor and back again to a solid without the substance passing through a liquid phase. Reactions in the wet way could also involve distillation, and laboratories generally had a variety of apparatus for distilling substances. Distillation, calcination, sublimation, and other processes all depended on the application of heat, in varying intensities. Thermometers were not much used by chemists before the end of the eighteenth century, partly because they were not very accurate. Instead, experienced chemists observed the behavior of reactants to determine how intense a heat to apply, and for how long. They used water baths, in which substances or the vessels containing them were immersed in hot water, steam baths, sand baths, and a wide variety of furnaces. Much of the apparatus in use in 1700 had changed little in a century, and a surprising amount of it was not very different from the apparatus used by Arab alchemists in their heyday. Broadly

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**Encyclopaedia Britannica,* 2nd ed. (Edinburgh, 1778), 3: 1808.

speaking, the laboratory in the first half of the eighteenth century provided a stable but not a static environment in terms of apparatus and its uses. That situation was to change radically in the second half of the century, when chemistry benefited both from its own advances and from advances in the wider field of philosophical or scientific instrument making.

Heat and fire were chemistry's most powerful tools. We saw in Chapter 3 how for Stahl, heat was an instrument and fire a principle or substance. As the eighteenth century progressed, Rouelle's more complex view—in which heat could be here an instrument, there a principle, and sometimes both at once—began to transform chemistry and to bring the science of heat and the phlogiston theory to the forefront of chemical debate. Chemical theory underwent radical change, not for the first time and not without keeping one foot in its past, and chemical apparatus also were altered.