Affinity, That Elusive Dream: A Genealogy of the Chemical Revolution by Mi Gyung Kim

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Theoretical chemistry had reached an impasse in the late 18th century, just as its horizons were expanding. New substances were being discovered, but the fundamental components of chemical substances and how they could be isolated had puzzled chemists for a long time. The ancient Greeks had imagined the four elements—earth, air, water, and fire—to account for the make-up of all matter and to these Paracelsus in the 16th century had added three further substances: sulfur, mercury, and salt. These basic principles, each of which was thought to convey certain chemical and physical properties, persisted through the 18th century, along with methods of analysis introduced by the alchemists, though sharp criticisms about their inadequacy for use by chemists had already been expressed in the 17th century by Robert Boyle.

In practice, 18th-century chemistry was little more than a technical skill used in various industries or subordinated as a mere assistant to medicine. There were no 'professional' chemists and most of those who were interested in the subject pursued it as a hobby. In England, the 18th century saw the rise of pneumatic chemistry with the discovery of many new gases or 'airs', including Priestley's 'dephlogisticated air' (oxygen), while in France chemical philosophy commanded more attention and fresh studies on chemical composition and the concept of affinity were made. There were also attempts to relate chemistry to physics and so develop a more quantitative structure. Lavoisier's synthesis of these developments in the 1780s, his pragmatic definition of the chemical element, and his demonstrations that neither air nor water could be truly considered to be elementary led to the displacement

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of phlogiston by the oxygen theory of combustion; and together with the revision of chemical nomenclature and the introduction of new analytical techniques, these changes culminated in the Chemical Revolution. Subsequent developments eclipsed much of the earlier work. In recent years, historians have reassessed Lavoisier's influence in changing the theoretical basis of chemistry; but we should not lose sight of the long history of the subject prior to the Chemical Revolution, nor should it be forgotten that the radical changes introduced by Lavoisier and his contemporaries grew out of chemistry as they found it.

In what she modestly calls 'an interpretative essay', Mi Gyung Kim sets out to trace ideas about chemical composition in 18th-century France. She discusses the nature of chemical principles (i.e., elements) and the role of affinity; ideas that shaped chemical theory in the 17th and 18th centuries. She compares the work of academic researchers at the Académie des Sciences and practical demonstrators at the Jardin du Roi where, influenced by Boyle, Nicholas Lemery introduced corpuscular explanations together with traditional chemical principles supposedly isolated during distillation analyses. Lemery expressed doubts about the validity of the five principles introduced by Estienne de Clave;[1] and like Boyle he preferred the gentler processes of solution analyses as did others including his contemporary at the Académie, Samuel Cottereau du Clos, and Etienne-François Geoffroy. To demonstrate the potential of solution analyses for elucidating chemical composition, Geoffroy constructed affinity tables; but distillation analysis, which was supposed to isolate the chemical principles, was not entirely displaced until Louis Lemery, son of Nicholas, demonstrated the inadequacy of distillation as an analytical tool. Thus, in the early 18th century, two fundamentally different approaches to chemical composition proceeded side-by-side. On the one hand, distillation analysis was thought to isolate the elementary principles of substances while, on the other, solution analysis, based on relative affinities, revealed the composition of the products.

Kim explores the nature and meaning of Geoffroy's affinity tables, comparing those who regarded them merely as a method of classifying collections of chemical observations with others who used them to explain chemical composition using crude notions of purity. In solution analyses, displacement reactions were crucial to the

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[1] These were water or phlegm, earth, mercury or spirit, sulfur or oil, and salt.

separation of stable chemical compounds and, when Louis Lemery suggested that heat or fire might also act as a 'solvent', the concept of 'displacement' could be applied to those parts of the table that still depended upon distillation analysis.

The German chemist Georg Ernst Stahl had first come to notice through his studies on salts, and Geoffroy used Stahl's data from solution analysis as the basis for an 'order of selectivity' in chemical reactions. Geoffroy also discussed Stahl's ideas about the transference of phlogiston between substances, specially those involving sulfur. It was through this application of fire in Geoffroy's affinity tables that Stahl's 'phlogiston' was introduced into French chemistry. In the 1720s, phlogiston was employed as the basis of a universal theory by Guillaume François Rouelle, a popular lecturer at the Jardin du Roi, and Pierre Joseph Macquer, his most famous pupil. Macquer wrote books promoting chemistry as a public science and seeking to situate it among the other sciences in a position of importance equal to medicine. By the mid-18th century, phlogiston was accepted as a principle that could be fixed in bodies, transferred from one body to another, or released as heat or fire. Thus, phlogiston figured along with the other principles as a component of chemical composition. Growing information on chemical reactions yielded ever more complex affinity tables during the 18th century, culminating in 1775 in the definitive affinity table of the Swedish master of chemical analysis, Torbern Bergman. This work showed experimental chemistry at its best and encouraged chemists to seek the laws of chemical combination.

In the second quarter of the 18th century, French chemists were influenced by the philosophical chemistry of the Dutch physician-chemist Hermann Boerhaave. Rouelle introduced Boerhaave's concept of 'instruments' of chemical change and held that the four ancient elements could each be both principle and instrument in turn, but that the most important instrument was phlogiston. About 1630, it was observed that when certain metals are calcined they gain in weight. This anomaly, overlooked by many chemists, became a problem for interested amateurs. In particular, it raised a difficulty for those who wished to bring chemistry into line with the quantitative physical methods introduced by Newton. Many fanciful attempts were made to account for this gain in weight, including the idea that phlogiston might show levity instead of gravity. The problem could not be solved satisfactorily, but the overall effect of such arguments was to introduce quantitative measurements into theoretical chemistry.

In a lengthy discussion of Lavoisier's work, Kim demonstrates his interest in affinity as well as his opposition to phlogiston. The 'Arsenal Group' led by Lavoisier included Claude Louis Berthollet, Antoine François de Foucroy, and Guyton de Morveau, the authors of the new chemical nomenclature. In addition to their support for the antiphlogistic theory, these four also sought to develop the notion of chemical affinities, to discover a means of quantifying this concept, and to establish a comprehensive chemical theory based on affinities and constitution rather than on principles. Among these four chemists, the joint authors of the Chemical Revolution, Kim singles out Berthollet as offering 'the best guide to tracing its successes and failures' [393]. She devotes her final chapter to a detailed investigation of Berthollet's intellectual development, his success in turning the study of chemical composition away from the isolation of principles and towards the study of affinities, and his failure to complete his program in the absence of a satisfactory method of quantifying the concept of affinity.

Berthollet, who began by studying the affinities of acids, alkalis, and salts following Macquer's ideas on affinity, had a broader understanding of chemistry than Lavoisier. He was involved in many different aspects of the subject—industrial, experimental, and theoretical. He supported the phlogiston theory until 1785, when the decomposition of water made it impossible any longer to identify phlogiston with inflammable air. He then accepted Lavoisier's system and began to argue as strongly in favour of it as he had formerly argued in support of phlogiston. Napoleon I sought to use Berthollet's chemical expertise and his reputation grew until he was able to purchase a mansion furnished with a chemical laboratory at Arcueil, near Paris. Here he gathered a research group in his aim to establish a theory of chemical composition based on the joint action of affinity and heat. The Society of Arcueil became the center of French chemistry in Napoleonic France. However, Berthollet's affinity still lacked quantification and his program failed to satisfy chemists. He disagreed with Bergman's notion of 'elective affinity' that was based on total displacement reactions between salts in solution, as he thought that this introduced inaccuracies into the results of chemical analysis by suggesting that precipitants from reactions in solution were pure and uncontaminated. Berthollet, knowing that this was not true, also discredited affinity tables and set out to construct an improved model of chemical action more firmly based on the laws of mechanics. Believing that the mass of a given substance present in a reacting mixture must affect the direction in which the reaction would proceed, he introduced a form of 'mass action' in which the concept of affinity could play an important, though still unquantified, role. Kim places the Chemical Revolution in direct relation to all these ideas and argues that it was through attempts to quantify the affinity approach to chemical composition that the laws of chemical combination were seen to be essential: for,

> if the principles contained in bodies determined their properties, including affinities, it should be possible to conjure up an infinite variety of compounds with minute shades of difference in their composition. The specificity of affinities curtailed this realm of speculative possibilities. [436]

The new theories introduced by the Chemical Revolution, including the corpuscular ideas introduced first by Boyle and later by Dalton, may then be seen as developments in a long continued endeavor to understand the complexities of chemical constitution: as Kim asserts,

> In order to elucidate the relationship between the chemical revolution and the chemical atomism, then, we must trace the revolutionaries' articulation of the affinity program rather than their antiphlogistic path. [436]

By concentrating upon the development of chemical ideas in 18th-century France, Kim has provided a detailed 'genealogy' for the French roots of the Chemical Revolution. However, she touches only lightly upon German chemistry, where the new ideas emanating from France were slow to take root. Swedish analytical chemistry of the period also receives scant attention, and she makes only passing reference to chemical advances in England and Scotland which also played an important part in the Chemical Revolution. Consequently, her claim to provide 'a genealogy of the chemical revolution' is only partially fulfilled. Nevertheless, her richly annotated discussion provides a fresh account of the rise of 18th-century chemical thought in France. She offers an important alternative context for studies of the Chemical Revolution in which the contributions of Lavoisier and his contemporaries are portrayed as evolving out of long-held ideas.

Affinity in chemistry, like vital force in physiology, energy in physics, or natural selection in biology, was an ambiguous notion that changed constantly depending on the methods used to investigate it. Nevertheless, she argues that broad concepts such as these serve to define disciplines in general terms and deserve the attention of historians of science for that reason. They are concepts that serve a limited purpose and are discarded when they can no longer be reconciled with developments and cease to serve a useful purpose; nevertheless, Kim suggests that their life-cycles have much to teach us about the growth of scientific disciplines.

Extensive bibliographical references, notes, and comments, located all together at the end of the book and covering over 70 pages, range widely across chemical and other relevant studies, and reveal the extent of the author's research into this subject. Similarly, in a wide-ranging bibliography, all the important works with a bearing upon this study are cited. The list includes reference to many relevant original manuscripts, primary and secondary sources, books, and single articles; and it bears eloquent witness to the breadth and depth of scholarship which mark this important study. Future works on the Chemical Revolution will need to take account of such a detailed, well-documented study and of its seminal revisionist approach to the intellectual history of 18th century French chemistry.

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