FOUR CENTURIES OF ATOMIC THEORY
An Overview

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1. Introductory Apology. It might seem oddly perverse to give a lecture entitled "Four Centuries of Atomic Theory" at a symposium entitled "200 Years of Atoms in Chemistry." No one questions, of course, that the 19th- and 20th-centuries were the heyday of chemical atomism and historians of chemistry have long agreed that Dalton's work was the starting point for our current quantitative views on this subject. Less well known, however, is the fact that atomism had been slowly seeping into chemical thought for nearly two centuries before Dalton and that, while these earlier variants of chemical atomism did not lead to a significant breakthrough in chemical theory, they nonetheless gradually produced a significant qualitative reorientation in the way in which chemists thought about chemical composition and reactivity – a qualitative reorientation which formed an essential foundation for the rise of a quantified gravimetric atomism based on Dalton's concept of atomic weight.

My task in this overview lecture is to give you both a feel for this qualitative pre-Daltonian foundation and to properly interface this prehistory with the later developments of the 19th and 20th centuries which will be the focus of the other talks in this symposium. I hope to do this by presenting a very broad overview of how each century tended to focus on a different atomic parameter and how this changing focus was reflected in the chemical thought of the period.

2. Ancient Atomism. Before beginning our four-century survey, however, it is necessary to first say a little about ancient atomism – and by ancient atomism I mean the reductionistic mechanical atomism of Leucippus, Democritus and Epicurus rather than the nonreductionistic pseudo-corpuscularism associated with the "seeds" of Anaxagoras or the "natural minima" of Aristotle. Only secondary and often critical accounts of the atomic doctrines of Leucippus and Democritus have survived (e.g. in the writings of Aristotle), whereas four Epicurean documents have survived: three short letters on various topics reproduced by the 3rd-century AD writer Diogenes Laertius in his *Lives of Eminent Philosophers*, and a major Latin prose poem, *On the Nature of Things*, by the 1st century BC Roman author, Titus Lucretius Carus.

Epicurean atomism was predicated on five basic assumptions:

a. There is an absolute lower limit to particle divisibility – i.e., true minimal particles called "atoms" which are not only indivisible but also immutable and thus permanent.

b. There is an interparticle void or vacuum.

c. All interparticle interactions are due to collision followed by mechanical entanglement.

d. The only fundamental atomic properties are size, shape, and motion – all others are secondary psychological responses to various atomic complexes.

e. There is no dichotomy between mind and matter, thus implying that the soul is both material and mortal.

Thus we see that Epicurean atomism was both materialistic and strongly reductionistic. Given that, within the broader context of Epicurean philosophy, this strong naturalistic tendency was also coupled with an overt attack on both religion and superstition, it comes as little surprise that Epicurean atomism was an anathema to early Christianity and that this philosophical school essentially disappeared after 500 AD. Indeed it is remarkable that anything managed to survive at all.

Though often applied to physical processes, such as weathering, evaporation and filtration, there are no examples of the application of ancient atomism to phenomena that we would today classify as chemical and hence our survey of its gradual modification and impact on chemistry does not truly begin until the 17th century.

3. 17th-Century Mechanical Atomism. While printed editions of both Diogenes Laertius and Lucretius were available by the 15th century – the first editions appearing in 1472 and 1473 respectively – it was not until the 17th century that atomism began to seriously impact on European science. A necessary prerequisite for this process was the "Christianization"of Epicurean atomism through elimination of its more objectionable assumptions, much as Thomas Aquinas and the scholastics had done four centuries earlier for the writings of Aristotle. This task was undertaken by the French priest and scientist, Pierre Gassendi, and by his English imitator, Walter Charleton, in the period 1640-1660. Their revised atoms were no longer self-existent entities whose fortuitious collisions led to the creation of both the universe and man himself, but rather were instead created by God and directed by him for his own predetermined purposes. Boyle did much the same by the simple expedient of dissociating atomism from the despised names of both Epicurus and Lucretius and referring to it instead as either the "corpuscular doctrine" or the "Phoenician doctrine."

In actuality the revival of atomism in the 17th century was quite complex and involved not only the true mechanical atomism of Epicurus, but also various hybridized versions based largely on the reification and atomization of the older Aristotelian and Platonic theories of forms and seminal principles. Within these hybridized versions, atoms could act as the inherent carriers of such secondary properties as color, taste, acidity, hotness and even coldness. These corpuscularized qualities would eventually evolve into the imponderable fluids much beloved of the 18th- and early 19th-century theorist, of which phlogiston and caloric are perhaps the best known examples.

In addition, several new forms of atomism or corpuscularism were also introduced, the most famous of which were Descartes' plenum theory and Newton's dynamic atomism, both of which rejected one or more of the basic assumptions of Epicurean atomism. Thus Descartes rejected both a lower limit to particle divisibility and the existence of an interparticle vacuum or void, as well as insisting on a strong dichotomy between matter and soul, whereas Newton replaced mechanical entanglement with short-range interparticle forces of attraction and repulsion.

It is well known that Robert Boyle was the major proponent of the application of particulate or corpuscular theories to chemical phenomena in the 17th-century, though neither he nor his contemporaries were able to develop a specific form of the theory which could be meaningfully related to quantitative chemical data. As a consequence, the true impact of mechanical corpuscularism on 17th-century chemistry was largely indirect and is best illustrated, as J. E. Marsh observed many years ago, in terms of its impact on the acid-alkali theory of salt formation.

The reaction between various acids and various alkalis or metallic carbonates first attracted the attention of iatrochemical writers as a possible chemical model for the process of digestion. Ignoring the CO_2 gas that was generated, which they misinterpreted as a violent churning or mechanical motion of the interacting particles, they viewed this reaction as a simple addition:

acid + alkali = salt

Acids were thought to have sharp, pointed particles, which accounted for their sour taste and ability to attack or corrode substances, whereas alkalis were thought to have porous particles. Neutralization and salt formation consisted in the points of the acid particles becoming mechanically wedged in the pores of the alkali particles, thus blunting or neutralizing their properties (figure 1).

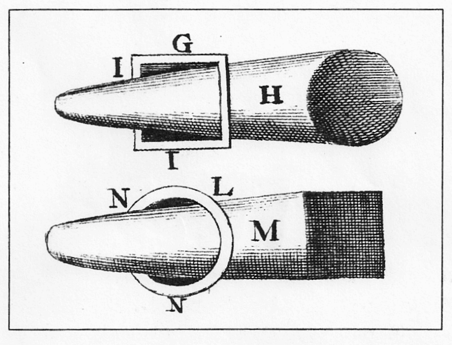


Figure 1. A typical 17th-century representation of an acid-alkali neutralization in terms of points and pores. (From T. Craanen, *Tractatus physico-medicus de homine*, 1689).

The importance of this theory for chemistry, however, did not lie in this mechanical mechanism for neutralization, but rather in the fact that it gradually accustomed chemists to the idea of characterizing salts in terms of their component acid and alkali particles rather than in terms of property-bearing principles and to looking at acid-alkali reactions as exchanges between preexisting material components, rather than in terms of the generation and corruption of alternative abstract forms or essences. This newer way of looking at neutralization reactions can be found in the writings of many 17th-century chemists, including Glauber, Lemery, Sylvius, Tachenius, and especially John Mayow, who would cite a laboratory example of the analysis and synthesis of various nitrate salts interpreted in terms of the separation and addition of their component acid and alkali particles.

4. 18th-Century Dynamical Atomism. As already noted, Newton replaced the concept of mechanical entanglement with the postulate of short-range interparticle forces of attraction and repulsion and applied this model in his *Principia* of 1687 to rationalize Boyle's law relating gas pressure and volume. However, it was not until the first decade of the 18th century that this new dynamic or force model was first specifically applied to chemical phenomena by the British chemists, John Freind and John Kiel, and by Newton himself in the finalized version of the 31st query appended to the 1717 and later editions of his famous treatise on optics, where he succinctly summarized his new particulate program for chemistry:

There are therefore Agents in Nature able to make the Particles of Bodies stick together by strong Attractions. And it is the Business of experimental Philosophy to find them out.

Meanwhile the particulate approach to chemical reactions, first realized in the 17th-century theory of acid-alkali neutralizations, was applied to chemical reactions in general, which were now being routinely classified as simple additions, simple decompositions, single displacements, and double displacements – an advance difficult to imagine within the older context of the theory of forms and essences which had dominated chemical thought for centuries. In addition, empirical observations concerning the observed outcomes of single displacement reactions were being tabulated, starting with the work of Geoffroy in 1718, in the form of so-called "affinity tables" (figure 2), as well as in a series of textbook statements known as the "laws of chemical affinity" (e.g, Macquer 1749).

It was not long before this empirical concept of chemical affinity became associated with the concept of Newtonian short-range interparticle forces, an identification best expressed in Bergman's 1775 monograph, *A Dissertation on Elective Attractions*, and in attempts, now known to be flawed, by such chemists as Guyton de Morveau, Wenzel, and Kirwin to quantitatively measure these forces – attempts which also culminated in a early precursor of the chemical

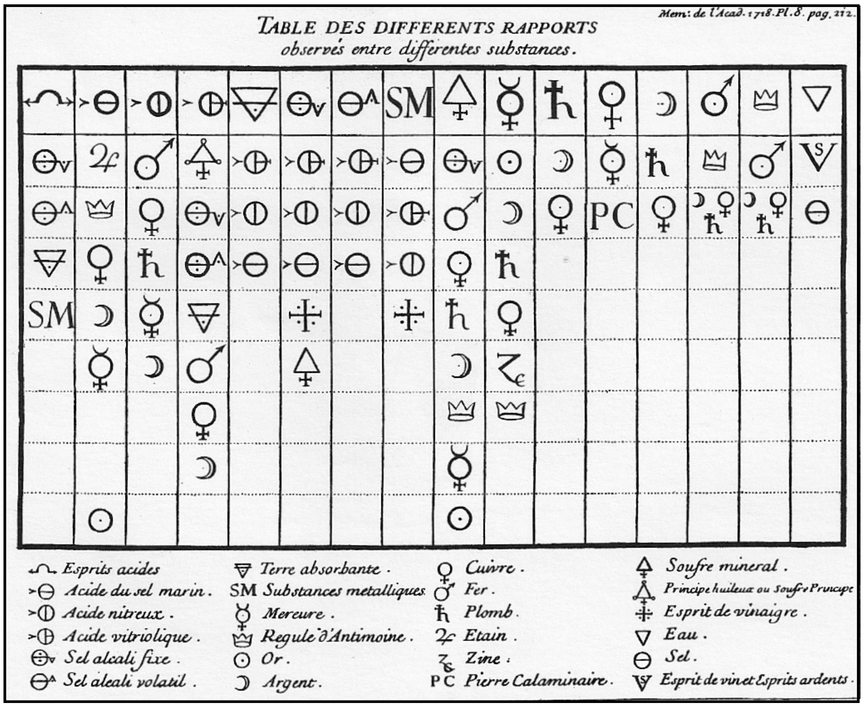


Figure 2. Geoffroy's affinity table of 1718 which attempted to organize single displacement reactions in terms of relative particle interchanges.

equation known as an “affinity diagram” (figure 3).

As the concept of the Newtonian force atom came to dominate 18th-century chemical atomism, the parameter of atomic shape, so important to 17th-century mechanical atomism, faded and chemists and physicists came to more and more think of atoms as spherical – a view which reached its most extreme form in

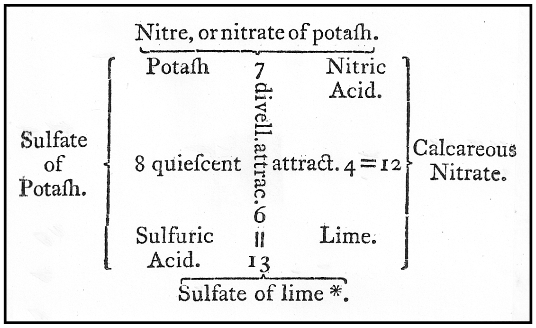


Figure 3. A typical 18th-century affinity diagram for a double-displacement reaction involving the reaction between a solution of potassium sulfate and a solution of calcium nitrate. (From A. Fourcroy, *Elements of Natural History and Chemistry*, 1790).

Roger Boscovitch's 1763 monograph, *Theoria philosophiae naturalis*, in which the atom was reduced to an abstract point for the convergence of a series of complex centro-symmetric force fields (figure 4).

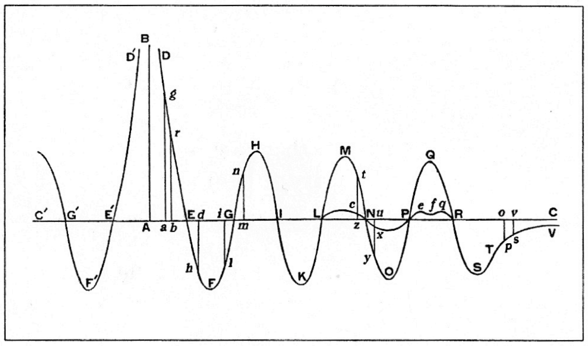


Figure 4. An 18th-century Newtonian force atom (from R. Boscovitich, *Theoria philosophiae naturalis*, 1763).

5. 19th-Century Gravimetric Atomism. This background now allows us to more fully appreciate the uniqueness of Dalton's contribution, when, in the period 1803-1808, he shifted, for the first time, the focus of chemical atomism from the atomic parameters of shape and interparticle forces to a consideration of relative atomic weights, with a concomitant emphasis on characterizing the chemical composition of individual species rather than on the classification and rationalization of chemical reactions.

By the end of the 18th century it was possible to characterize the chemical composition of a species at the molar level in terms of its composition by weight, or, in the case of gases, by its composition by volume. Thus one could speak of water as being composed of 11.11% hydrogen and 88.89% oxygen by weight or of 66.67% hydrogen and 33.33% oxygen by volume. With the introduction of the atomic weight concept, however, one could now characterize the composition of a species at the molecular level in terms of the relative number of component atoms and so speak of water as composed of molecules containing a ratio of two hydrogen atoms to one oxygen atom.

Key to Dalton's compositional revolution was the ability to link atomic weights at the molecular level with gravimetric composition measured at the molar level using his so-called "rules of simplicity." These, however, were soon shown to be operationally flawed and nearly a half century would pass before this problem was finally solved in a satisfactory manner by Cannizzaro in 1858 and accepted by the chemical community following the Karlsruhe conference of 1860. This final resolution of the problem of chemical composition was, of course, soon brilliantly elaborated by the rise of chemical structure theory and classical stereochemistry during the last quarter of the 19th century. The story of these advances is, of course, far more complex and nuanced then suggested by this brief summary and aspects of it will no doubt be covered in greater detail by other speakers in this symposium.

6. 19th-Century Kinetic Atomism. If the gravimetric Daltonian atom was the chemist's primary contribution to atomic theory in the 19th century, then the kinetic atom was the physicist's primary contribution. Atomic motion was, of course, always a part of the atomic theory from ancient atomism onward. However, it functioned primarily as a way of explaining diffusion and providing a means for bringing about sufficient contact between particles to facilitate either mechanical entanglement or the engagement of short-range forces of attraction and repulsion. Aside from this minimal function, motion played little role in explaining the properties of things in either 17th-century mechanical atomism or in 18th-century dynamical atomism.

Thus, within the context of the Newtonian force atom and the caloric theory of heat, solids, liquids, and gases were all viewed as organized arrays of particles produced by a static equilibrium between the attractive interparticle forces, on the one hand, and the repulsive intercaloric forces, on the other. The sole difference was that the position of equilibrium became greater as one passed from the solid to the liquid to the gas, due to the increasing size of the caloric envelopes surrounding the component atoms (figures 5 and 6).

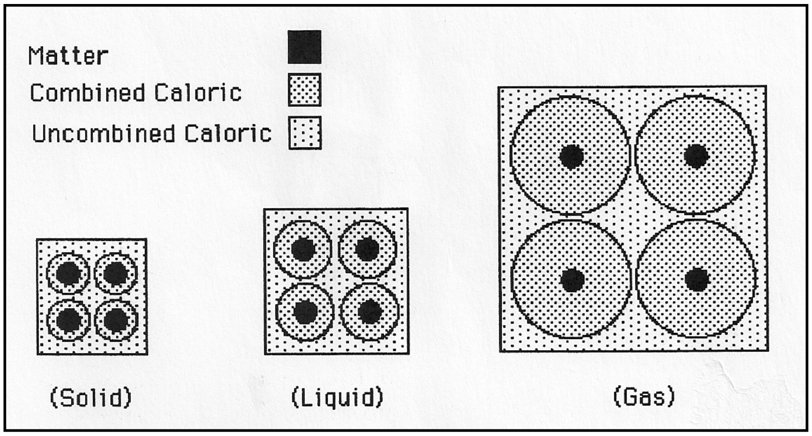


Figure 5. The author's attempt to visualize the caloric model of the three states of matter.

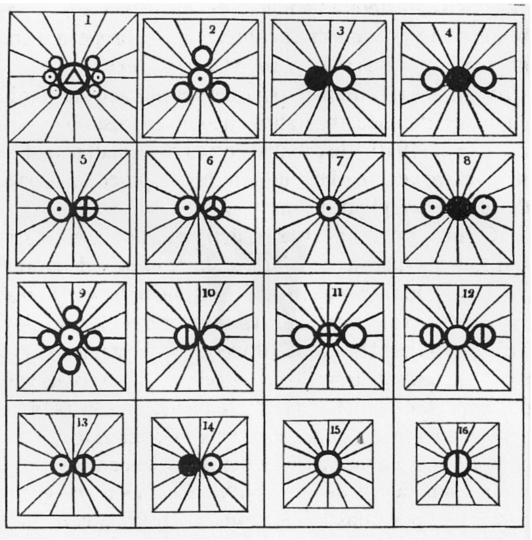


Figure 6. Daltonian atoms and molecules with their surrounding atmospheres of repulsive caloric (from J. Dalton, *A New System of Chemical Philosophy*, Part II, 1810).

Likewise, Berthollet's original concept of chemical equilibrium, introduced in the years 1799 - 1803, was also based on the concept of a static equilibrium between those forces favoring the formation of the products versus those favoring the formation of the reactants. As is well known, this static model made it very difficult to rationalize the law of mass action without coming into conflict with the law of definite composition. This static view of both states of matter and chemical equilibrium, viewed as a competition between chemical affinity and caloric repulsions, continued to dominate chemical thought throughout the first half of the 19th century.

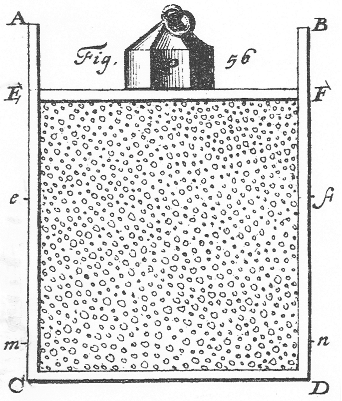


Figure 7, The first known attempt to envision gas pressure in terms of a kinetic model of atoms and molecules (from D. Bernoulli, *Hydrodynamica*, 1738).

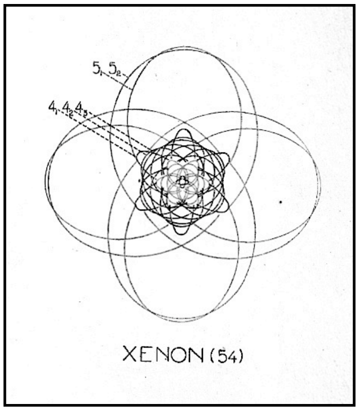
Though a kinetic model of gases had been proposed by Bernoulli as early as 1738 (figure 7) and was unsuccessfully revived by Herapath (1821) and Waterson (1845) in the first half of the 19th century, it was not until the 1850s and 1860s that it began to attract widespread acceptance through the work of Krönig (1856) and Clausius (1857) in Germany and Joule (1851) and Maxwell (1860) in England. Heat was no longer a self-repulsive imponderable fluid but rather a measure of the average kinetic energy of molecular motions. States of matter were no longer the result of a static equilibrium between attractive interparticle forces and repulsive intercaloric forces, but rather the result of a dynamic equilibrium between attractive interparticle forces and disruptive thermal motions. Solids, liquids and gases no longer shared a common structure, differing only in their distance of intermolecular equilibration, but now differed in terms of both their degree of intermolecular organization and their freedom of motion. Chemical equilibrium and mass action were no longer a static equalization of opposing forces, but rather a dynamic equilibrium based on relative collision frequencies and differing threshold energies for reaction – a view first qualitatively outlined by the Austrian physicist, Leopold Pfaundler, in 1867.

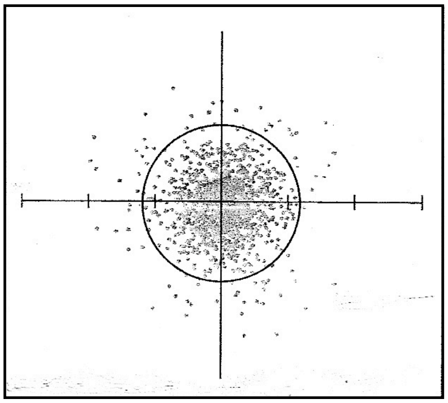
Thus by 1895, the German chemist, Lothar Meyer, would conclude the short version of his textbook of theoretical chemistry with the observation that:

> *Chemical theories grow more and more kinetic.*

a trend which would culminate in the development of classical statistical mechanics by Boltzmann and Gibbs by the turn of the century and which would continue unabated throughout the 20th century.

7. 20th-Century Electrical Atomism. With the advent of the 20th-century we see the solid, impenetrable, billiard-ball atom of the previous centuries replaced by the diffuse, quantized electrical atom (figures 8 and 9). Nevertheless the various atomic parameters emphasized by earlier variants of atomism have all retained their importance in one way or another:





Left: Figure 8. A Bohr-Sommerfeld model of the xenon atom (from H. A. Kramers and H. Horst, *The Atom and the Bohr Theory of its Structure*, 1924). *Right:* Figure 9. A modern statistical or probability model of the hydrogen atom.

Like 17th-century mechanical atomism, modern atomism also recognizes the importance of shape – at the level of individual atoms in terms of the concept of orbital hybridization and directional bonding – and at the molecular level in terms of the lock and key model of intermolecular interactions.

Like 18th-century dynamical atomism, modern atomism also recognizes the importance of short-range interparticle forces – now interpreted in terms of electrical forces of attraction and repulsion between negatively charged electrons and positively charged nuclei.

Like 19th-century gravimetric atomism, the concept of atomic weight and the laws of stoichiometry are still the cornerstones of chemical composition – albeit now modified to accommodate the concepts of isotopes and relativistic mass effects.

Like 19th-century kinetic atomism, molecular motion still forms the cornerstone of our modern understanding of heat, thermodynamics, kinetics, and statistical mechanics, but now also plays a key role in our understanding of the internal structure of the atom itself, via the concept of quantized electron motions.

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