

ALAN J. ROCKE

CHEMICAL ATOMISM AND THE EVOLUTION OF CHEMICAL THEORY IN THE NINETEENTH CENTURY

The development of chemical theory in the nineteenth century has been relatively little studied, compared with other sciences and other periods; much remains still to be explored. One notable example is chemical atomism, and its adjuncts such as valence and structure theory. Nonexistent at the beginning of the century, a generation or two later these ideas had moved to the very center of the science, which they still inhabit. The chemical atomic theory embodies outstanding examples of paper tools that provide not only explanatory and expository functions for what is already accepted as known, but also heuristic guidance in the further construction of a science. It may be of interest, therefore, to attempt an analysis of what some recent studies have revealed about this subject, along with indications of where further historical efforts may yield additional rewards.

Let me start with a set-piece taken from the dawn of the theory: the determination of the atomic weight of nitrogen and of the formulas for the simplest nitrogen compounds. The determination of atomic weights from analytical data requires prior assignment of atomistic formulas for the substances analyzed. Dalton assigned formulas using two different principles, both of them derived from physics: first and foremost, his simplicity axioms, and secondarily and pragmatically, vapor densities.¹ Both of these approaches led Dalton to the N_2O , NO , NO_2 pattern for the three principal nitrogen oxides, and evidence suggests that he was permanently convinced that these were about the most securely established formulas in chemistry.² He also assigned the HO formula to water, which accorded with simplicity, but created an anomaly for vapor densities.³ These formula assignments, combined with chemical analysis, enabled Dalton to determine by an indirect route (through their respective oxygen compounds) that nitrogen atoms weigh about five times as much as hydrogen atoms.⁴ But the same numerical result could also be obtained directly, through a compound of nitrogen and hydrogen. His simplicity axiom led Dalton to think that the formula for ammonia should be NH , and chemical analysis of ammonia gave the right answer, namely that ammonia contains about five times as much nitrogen as hydrogen. In this way, successful retrodiction, or reticulation, of existing empirical data provided a validating instance for the theory as a whole.

Sort of. This particular network of assumptions and evidence was about as leaky as a fishnet. Dalton's simplicity axiom was ambiguous for cases of multiple proportions, and his application of it conflicted with his vapor-density approach for some of the most central cases. His stance toward vapor densities as an indicator of atomic-molecular weight was always inconsistent. The direct and indirect means of

calculating the atomic weight of nitrogen summarized above did not really quite tally, after all, and Dalton was compelled to engage in rhetorical ploys to be able to claim that they did. Another of his tactics was to impugn the analytical data when it suited him to do so; this was often not unreasonable, considering the uncertainties of analysis at the time, but it also called into question the whole enterprise in which he was engaged.

Not everyone let him get away with such sleight of hand. The respected physician John Bostock (1773–1846) pointed out several of these flaws in 1811.⁵ Although he was careful to declare his approval in principle of Dalton's hypothetico-deductive methodology, the details of his critique were telling. Hypotheses need tight empirical validation, he emphasized, and Dalton had not yet provided this. And he was right.

However, even as Bostock was writing these words, that more effective empirical validation was emerging from the laboratory and writing desk of Jacob Berzelius, and from the work of J. L. Gay-Lussac. After 1812, critics such as Bostock could no longer attack the stoichiometry at the heart of the atomic theory. But the new analyses also frustrated Dalton's desire to retain his preferred nitrogen oxide formulas *and* the binary hydride formulas HO and NH, for ammonia now needed to be formulated $\text{NH}_{3/2}$ to agree with analysis—and no atomist could countenance fractional coefficients. Most chemical atomists, of whom there now was emerging a small coterie, chose to write NH_3 , doubling the presumed atomic weight of nitrogen and adjusting the formulas of oxygen compounds accordingly in order to recapture internal consistency.⁶ Curiously, Dalton himself never responded to the dilemma posed by the new ammonia analysis, and it is astonishing how completely he dropped out of the theoretical dialectic after 1810.

This episode exemplifies virtually all of the salient characteristics of the chemical atomic theory for the first decades of its life. Atomists used analytical chemical data, combined with simplicity assumptions and working hypotheses often derived from physical considerations, to arrive at a relatively restricted candidate sample of interlinked atomic weights and molecular formulas. They then applied a kind of bootstrapping technique which we have just illustrated on a small scale, both to extend this limited system to additional elements and compounds, and also to cross-check the partial structure that they had created. This constitutes a fine example of what William Whewell called a "colligation of inductions" and Rom Harré a "reticular theory." Anomalies inevitably appeared in the network. These could be dealt with by several tactics: ignore them, if they did not seem too severe; eliminate them, by appropriate adjustments to the system; or rationalize them away by arguing why they should not be considered anomalies at all. The candidate system needed to be judged as a whole, for its coherence, the plausibility and sophistication of its articulation, and the empirical robustness of testable consequences deduced from it.⁷

Dalton had opened the floodgates. Between 1810 and 1816, no fewer than nine separate systems of chemical atomism were proposed by leading chemists in four countries.⁸ Each of these was distinct, but they tended to fall into three broad categories: what became known as the system of "atomic weights" per se ($\text{H}=1$, $\text{C}=12$, $\text{O}=16$, $\text{N}=14$); the French system of "volume weights" ($\text{H}=1$, $\text{C}=6$, $\text{O}=16$, $\text{N}=14$); and the system of so-called "equivalent weights" ($\text{H}=1$, $\text{C}=6$, $\text{O}=8$, $\text{N}=14$). The latter was championed especially by William Wollaston, whose assertion that

he had succeeded in eliminating the hypothetical element from the atomic theory was much credited, even though the logical foundation for this claim was shaky.⁹

The situation became even more complex after 1830, when there was a different atomistic system in use in each of the three largest European countries. Each required an entirely distinct set of formulas for all known chemical compounds—the numbers of which were growing explosively—and this had ripple effects that cascaded through pedagogy, texts and reference works, and research programs. In the course of the 1840s this confusing multiplicity of systems became even more chaotic. The French chemists Charles Gerhardt and Auguste Laurent advocated a fourth atomic weight system, a modification of the Berzelian system that Berzelius himself found intolerable. Their early campaign did not prosper, partly because they were arguing against a new concerted campaign, initiated by Leopold Gmelin, to replace the Berzelian system by the putatively empirical Wollastonian equivalents. At first Gmelin's success in this endeavor was only mixed; however, Baconian empiricism and "textbook positivism" were by then in the ascendant, and Berzelius began increasingly to be viewed as superannuated and overly theoretical.¹⁰ By about 1845 chemists of various nationalities were coming over en masse to the Wollaston-Gmelin flag. At last, it seemed, all European chemists were beginning to agree on a single system, moreover one that was putatively non-theoretical, hence one that could be adopted *permanently*.

About mid-century this enviable goal appeared to be within reach of the international community. Ironically, this was just when a coterie of leading theorists began touting the least popular of the four systems, the Gerhardt-Laurent reformed version, not merely as simpler or more convenient, but as *true*—the one system that *had* to be adopted because of its unique claim to veridical character. There was much implicit and explicit conflict in the 1850s over these issues, all over Europe, until the Karlsruhe Congress was devised to try to create concord. But the reformers went home dissatisfied with the results of the meeting.

One can heartily sympathize with those young chemists, like Marcellin Berthelot and Hermann Kolbe, who were educated in the peak years of discord. Every authority seemed to have his own preferred set of weights, based on his own preferred theories; and the referents of these theories, namely the atoms being specified in the formulas, were utterly beyond direct human perception. There should be little wonder, then, at the appeal offered by the apparent empiricism and permanence of the system of chemical "equivalents."

Here I would like to offer a second set-piece, Berthelot's campaign for equivalentism.¹¹ In the early 1860s Berthelot took on the atomists directly. "The constitution of bodies," he wrote, "can be envisaged in two ways: 1. From the point of view of positive science, i.e., precise relations that exist between facts; 2. From the point of view of speculative science, i.e., constructions imagined by the human mind to represent things." For positive science, chemical constitutions can only express "the totality of the physical and chemical properties of the body, reduced to the simplest and most general relations that experiment establishes."¹² Then Berthelot suggested that chemical compounds be considered as "systems of material particles, exhibiting a definite mass, all maintained at certain distances, and each animated by its own speed and movements of vibration, rotation, translation, etc."¹³ It is ironic that in the very act of derogating atomism for its hypothetical character, Berthelot introduced a conjectural image of the microworld.

Such a physicalist vision and phenomenalist methodology provided the context for Berthelot's animus against contemporary atomistic accounts of chemistry, but there was more to it than that. The atomic theory of his day, he argued, was rife with inconsistencies—some of which atomists conceded. For instance, the so-called law of atomic heats was no law at all, only an approximate relation, and the use of vapor densities could not be made internally consistent. Berthelot gradually built a compelling case for equivalentism and against atomism, and in the anti-theoretical climate of mid-nineteenth-century Paris, many rallied around Berthelot's flag.

However, critical voices were also raised against this position, and in favor of atomistic accounts. Equivalentism, these chemists charged, had its own inconsistencies. A case in point was the elemental weight used for nitrogen by every chemist in the world from 1820 on, and illustrated by our first set-piece. $N=14$ was derived by no single chemical replacement value or gravimetric experiment. The best gravimetric equivalent of nitrogen was surely Dalton's "atomic weight" figure of about 5, for that is the hydrogen-replacement-value of nitrogen for its only known hydride at the time, ammonia. Instead, everyone, including equivalentists, had tripled that number, so that ammonia could be written as NH_3 ; the reason was to coordinate with formulas of other nitrogen compounds.¹⁴ But to decide on a single *unchanging* "equivalent weight" violated all the sense of the empirical definition of the term. Doing so—adopting unique conventionally-chosen equivalent weights for each of the elements, selected to create a single well-articulated system of atomic weights and formulas—signified, willy nilly, an entry into the theoretical realm.¹⁵

Not only was there no empirical "higher ground" for the system of equivalents, Berthelot's critics charged, it also failed the crucial test of *heuristic*. The theory of chemical structure was born about 1858 in the atomist camp. Founded as it was on the notion of atomic valence, this theory could *only* have been recognized by those who distinguished between atomic weights and genuine gravimetrically-determined (hydride) equivalents, for valence is nothing more than the ratio of these two quantities. And here is the point: within a handful of years of its creation, it was becoming clear that structure theory was having significant success explaining the crucial (and increasingly important) phenomenon of isomerism in organic chemistry. The justification of the Gerhardt-Laurent system, promoted for twenty years on ontological and not conventionalist grounds, was initially made purely on appeals to coherence and economy of thought. Now, in the 1860s, it was proving its heuristic worth as a paper tool.

Berthelot recognized and discussed this problem in a monograph on isomerism (1866).¹⁶ Particularly for "isomers in the strict sense"—such as benzyl versus cresyl alcohol, or benzoic acid versus salicylaldehyde—Berthelot cited the same explanation, qualitatively speaking, that had proven so useful for structuralists. Such pairs of compounds, he wrote, prove "that there can exist several different arrangements in the interior of each of the elementary groups that constitute a definite compound."¹⁷ Berthelot once again posited a materialistic, microphysical, and qualitatively structuralist explanation, but his pen stuck on the words "atom" and "molecule," and he was unwilling to hazard guesses about what precise submolecular arrangements might explain particular cases of isomerism. The reason for this hesitancy appears to arise, as we have seen before, in a physicalist analogy. Perhaps, Berthelot mused, the fundamental matter out of which substances are

formed represents a mathematical function, and simple bodies its determined values, or the former an equation and the latter its various solutions.¹⁸

Adolphe Wurtz, the apostle of atomic theory in France, responded to Berthelot. Of the many examples he cited, perhaps closest to his heart were the isomers of amyl alcohol, on which he himself had worked.¹⁹ Writing in 1879, Wurtz noted that six isomers of this substance had been discovered by organic chemists using structure theory, with two additional isomers predicted by that theory which had not yet been prepared, but which could be assigned structural names (secondary butyl carbinol and neopentyl alcohol). Regarding the six then-known isomers, Wurtz wrote: "The theory predicted them; experiment has brought them to light. And this fidelity of theory, this happy coincidence between predicted and observed facts, has been tested in hundreds of cases."²⁰ By contrast, Berthelot barely mentioned the existence of five of these isomers in the first edition of his textbook of organic chemistry (1872).²¹ Berthelot's isomer numbers worked as of that date, but not much longer, as the sixth, seventh, and eighth amyl alcohols were successively discovered. Structure theory had always predicted precisely eight possible isomers, and indeed no ninth one has ever appeared.

Another issue was August Kekulé's extraordinarily successful benzene theory. There is indeed a clear description of Kekulé's theory in the second (1881) edition of Berthelot's textbook, written in conjunction with his former student Émile Jungfleisch.²² One of the merits of Kekulé's theory had been to explain why each di-derivative of benzene has exactly three isomers. Jungfleisch and Berthelot offered an alternative explanation; however, in their theory there are in fact six different ways for two groups to apportion themselves, and they did not explain why they implicitly excluded half of the possible isomers.

Kekulé's theory had also predicted only one isomer of every monoderivative and one isomer of every pentaderivative of benzene. During the late 1860s and early 1870s these predictions had not always seemed reliable. For example, since 1860 Hermann Kolbe had believed that he could identify a second isomer of benzoic acid. However, by 1875 even Kolbe had reluctantly convinced himself that there was only one.²³ Jungfleisch had also apparently contradicted Kekulé's prediction in 1868 by preparing a second isomer of pentachlorobenzene, and this work had been repeated and verified by a German chemist two years later.²⁴ However, Albert Ladenburg, a student of both Wurtz and Kekulé, contested the existence of this second isomer, and by 1874 he had convincingly demonstrated his position.²⁵ Such examples could be multiplied.²⁶ Structure theory, and the benzene theory based upon it, looked ever more securely established by innumerable predictions that seemed to be nearly invariably confirmed by empirical evidence. Both of these theories were outgrowths of chemical atomism.

Now that I have sketched the fortunes of chemical atomism *per se*, I would like to discuss two broader aspects related to this story: first, explicitly to focus on the use of the theory as paper tools; and second, to attempt to embed the theory into broader patterns of theorization in nineteenth-century science. Atomic notation is a prime example of paper tools, and for that very reason it is curious how little this subject has been explored by historians. Ursula Klein has provided a pioneering study demonstrating what this kind of approach can accomplish, exploring how organic chemists in the 1830s used atomic theory, including symbols and formulas, to guide and even transform actual laboratory practice.²⁷ This work opens a rich

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