Rediscovery of the Elements

The Road to Karlsruhe

Figure 1. This statue of John Dalton is located in front of the Manchester Metropolitan University (John Dalton Building of Science and Engineering), Chester St., Manchester, England (N 53° 28.32 W 02° 14.44). The university is 800 meters south of the city center (Town Hall).

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In Sir Isaac Newton's Principia, physics had come to maturity: with the law of gravity and three laws of motion, the heavens with their celestial motions were no longer so capricious and future events could be predicted. With chemistry, the underlying forces and structure were more mysterious; understanding had to await the atomic theory of John Dalton (1766–1844) (Figure 1) in 1808 and the subsequent general acceptance by the scientific community, which did not occur for another half century.¹

Table of Affinities. In an early attempt to raise the level of sophistication of chemistry, Étienne François Geoffroy (1672–1731) constructed a “Table des Affinités” (Figure 2).¹ Geoffroy (Figure 3) took his concept of “affinity” from Georg Ernst Stahl (1660–1734), the proponent of phlogiston,¹ who believed a relative ordering of “affinities” (the order in which substances displaced each other from compounds) would allow the prediction of other chemical reaction outcomes. Geoffroy's family included a long line of pharmacists (Note 1); Étienne's other strong contribution was his pioneering research on Prussian blue. This concept of the affinity of one substance for another was an extension of the Newtonian idea of mutual gravitational attraction of physical bodies, and was taken seriously as late as the 19th century by Claude Louis Berthollet (1748–1822), the inventor of l'eau de Javel (the French equivalent of Clorox®) and who, with Lavoisier, Fourcroy, and Guyton de Morveau, instituted the new French (i.e., modern) nomenclature of chemical compounds.¹

Dalton's Atomic Theory. Even after a century of use by 18th century chemists, the Table of Affinities did not lead to any enlightenment of the nature of chemical reactions, and clearly a new direction was needed. Instead, the way for understanding was provided by the idea of atomism,¹ conceived shortly after the demise of phlogiston.¹ John Dalton, a naturalist and meteorologist of Manchester, England, thought matter consisted of tiny spheres.¹ His ideas grew from his observations of weather phenomena where he imagined air consisting of minuscule particles in motion. Since he was color-blind, it was natural for him to view these particles as achromatic, featureless spheres, and he constructed models to illustrate his interpretation of atoms (Figure 4). He believed elements of a kind differed from others only by their weight.¹

Figure 2. Predating Lavoisier's Traité des Réactions, the Table of Affinities identified substances by ancient alchemical symbols. Each substance at the top row heads a column which includes the substances in order of affinity, or displacement, as one moves down the column. For example, in the 4th column, top row, vitriolic acid (sulfuric acid) combines most rapidly with phlogiston, and then with alkali (potassium hydroxide), followed by volatile alkali (ammonia), the "absorbent earths," iron, copper, and silver. This crinkled, old painting dates from 1769 and hangs in the library museum of École Normale Supérieure Physique (24, rue l'Hénon, Paris, N 48° 50.57 E 02° 20.82).

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The hypothesis that all atoms of an element had the same weight—the "atomic weight"—was based on Dalton's observation that constant ratios of elements combined to form compounds. According to the Edinburgh chemist Thomas Thomson (1773–1852), the idea occurred to Dalton during his investigations of "olefiant gas" (ethylene) and "carburetted hydrogen gas" (methane) (Figure 5). "It was obvious from the experiments... that the constituents of both were carbon and hydrogen, and nothing else. ... [The] carburetted hydrogen gas contains exactly twice as much hydrogen as olefiant gas does." This caused [Dalton] to view... olefiant gas as a compound of one atom of carbon and one atom of hydrogen [CH], and carburetted hydrogen of one atom of carbon and two atoms of hydrogen [HCH]. The idea thus conceived was applied to carbonic oxide [carbon dioxide], water, ammonia, &c.; and numbers representing the atomic weights of oxygen, azote [nitrogen], &c. ...".

Dalton went on to assign the atomic weights to 20 elements. The values of some seem strange today, e.g., H=1, O=7, C=5, P=9, S=13, Fe=50, Pb=90, Ag=190—but it must be remembered that analytical methods were not as refined as today's, and without the concept of valence, it was impossible to know if some of the derived atomic weight values should be multiples. Since he believed the formulas for methane (CH₄) and ethylene (C₂H₄) were HCH and CH, respectively, then naturally his atomic weights for carbon would be half (viz., 6) of the actual modern value (viz., 12) based upon the respective modern empirical formulas of CH₄ and CH₂.

Today in Manchester, England, the individual locations where Dalton lived and worked are known, but all have changed greatly and few original buildings exist (one of his original homes is now in Chinatown!). A plaque mounted on a building wall is all that remains to remind us of his original workplace, which was destroyed in a World War II bomb raid (Note 3).

Accepting the "Atom." Dalton's theories launched a century-long struggle of chemists to comprehend and even to accept atoms, until the discoveries of Ernest Rutherford in the early 20th century proved beyond doubt that they did exist. A glimpse into this debate is given to us by Thomas Thomson, who describes a discussion during the fall of 1807 among Sir Humphry Davy (1778–1829), William Hyde Wollaston (1766–1828), and himself (Figure 3) debating the viability of atoms. The setting was the Crown and Anchor, a tavern that was the customary meeting place of the Royal Society in London (Figure 6). At this meeting, Thomson and Wollaston were trying to persuade Davy of the logicality of atoms. The argument included data from experiments where...
the proportions of the constituent elements increase in a regular ratio, e.g., not only Dalton's methane and ethylene, but also the two oxides of carbon, the carbonates and bicarbonates, oxylates and bioxylates (i.e., the approximate ratios of 1:2 of potassium in diprotic acid salts). Once convinced, Davy became an ardent atomist; the Royal Society followed, and Great Britain was secured as a haven for the new theory. Acceptance of the theory was slower to come to the Continent—but throughout the 1800s, even those who were not convinced that atoms actually existed nevertheless believed that the world probably behaved as if they did. The last notable diehard was Ernst Mach (1838–1916), who on his deathbed persisted in his conviction that atoms were nonsense.2

Once it was recognized that compounds had constant compositions and that each element had its own "weight," research commenced to determine the atomic weights for all elements. But soon more questions were raised than answered. Although Dalton had assumed binary compounds combined one atom of each, this was by no means an established fact, nor was it generally accepted. While Dalton assumed HO for water (which would lead to an atomic weight of O=8), Davy preferred H2O (O=16). Wollaston retreated from his original position, cautiously warning that "one should not depend upon any theoretical concept" upon an experimentally derived value,2 and he returned to HO for water. To distinguish his values from Davy's "atomic weights," Wollaston invoked a new term, "atomic equivalents." (The meaning of this term is essentially unchanged today.) The idea of equivalent weights became popular among pragmatists, while the theorists clung to the notion of atoms, leading to a half century of debate between the so-called equivalentists and atomists.

The main problem, of course, was that no matter what one chose to call these values, its magnitude depended upon the formula that one assumed for a compound. Water was viewed as either HO or H2O (or sometimes even H2O2); metals were lumped into one broad family and were generally assigned a formula of either MO or MO2, or even an arbitrary mix, depending upon the arguments of a particular chemist. Inconsistencies abounded, and naturally, atomic weights derived by various researchers were generally multiples of each other. For example (on a basis of H=1), O was given 8 or 16; N was given 7, 14, or 28; sodium was given 24, 47, or 94; calcium was 20, 40, or 80; lead was 100, 200, or 400 [original numbers, which vary somewhat depending upon the experimenter, are rounded off here to clarify the trends].2 When one published a paper utilizing atomic weights, it was common practice to preface the article with one's own adopted set of weights.2

Dumas and Vapor Densities. A real impediment to the correct understanding of atomic weight was the commonplace belief that like atoms could not combine with one another. This was the logical conclusion ensuing from electrolysis experiments of metals, historically credited to Davy but, in fact, pioneered by Jons Jakob Berzelius (1779–1848).3 Berzelius (Figure 3) noticed that in a battery, the "alkalis and earths" were drawn toward the negative pole, and that oxygen, acids, and oxidized substances migrated to the positive pole. He was very impressed by the electrical forces needed to rip apart these reactive metals, and he championed the hypothesis of "electrochemical dualism," wherein the forces holding atoms together were positive-like (the metals) and negative-like (the nonmetals).3 Berzelius was thus the first to conceptualize ionic bonding, and he assumed this bonding occurred in all compounds. The idea that hydrogen was H2 and chlorine was Cl2 never occurred to him, and his ideas held sway through the first half of the 19th century.

One of the first to understand "like"-bonding was Jean Baptiste André Dumas (1800–1884) (Note 4). In his mid-20s, Dumas (Figure 3) was asked to explore the reason why the burning candles in the Tuileries Palace were emitting obnoxious odors.2 He found that these candles had been bleached by chlorine and that the irritating stench was hydrogen chloride. His curiosity piqued, he followed up with much research that allowed him to conclude that either H (positive-like) or Cl (negative-like) could combine with carbon in a similar way, without losing the general physical properties of the compound, (i.e., the compound still acted like an organic substance). There must be an additional type of bonding, which today we recognize as covalent bonding.

Dumas is well known today for his method of molecular weight determination,4 currently utilized in chemistry laboratory curricula (Note 5). Dumas developed this method in an attempt to understand molecular weights, and by 1828, he introduced the terms "molécule chimique" and "molécule physique" to distinguish between the apparent respective weights involved in a chemical reaction and in physical phenomena.11 He came to believe that these "chemical molecules" (i.e., atoms) are subunits of "physical molecules" (i.e., true molecules).5 It was becoming clear that an element may have more than one atom in its natural aggregate. But he was confused by some molecules that were "behaving anomalously"—notably, arsenic, phosphorus, and sulfur, which we know today are variable in their multiformula formulas. Dumas just could not find final answers to the critical questions: How many atoms are there in a molecule of an element? And is this number the same for every element?11

The Need for a Chemical Convention. Friedrich August Kekulé von Stradonitz (1829–1896, Ghent Belgium), the famed discov-
erer of the structure of benzene (1865), in 1860 proposed a convention to promote common understanding and eliminate confusion among chemists. He met with Charles-Adolf Wurtz (1817–1884) of Paris, and Carl Weltzien (1813–1870) of Karlsruhe, and they issued a general invitation in June 1860 for an international meeting of chemists to be held in Karlsruhe on 3 September of that year. In the letter of invitation, it was hoped that “common agreement” could be “facilitated” on “the definition of important chemical notions, such as those expressed by the words atom, molecule, equivalent, atomic, basic; the examination of the question of equivalents and of chemical formulae; and the institution of a notation and of a uniform nomenclature.” Some old-school chemists refused to participate, avowing that “anything decided would be arbitrary” or even “fraudulent,” but on the appointed day, there came assembled at the Ständehaus (Parliament Building), graciously provided by the Archduke of Baden, more than 140 participants from some 12 countries (Figure 7). The chosen site in Karlsruhe, near the French-German border, underscored the internationality of the meeting.

After three days, the discussion indeed appeared to vindicate the old-school pessimists; compromises were proposed, but nothing seemed to satisfy anyone. Then an amazing thing happened: Stanislao Cannizzaro (1826–1910) (Figure 3), a charismatic speaker from Genoa, Italy, distributed a pamphlet, reproducing a paper he had published two years previously, that stopped everyone dead in his tracks. In this pamphlet, Cannizzaro showed how the forgotten and long-ignored work of Gay-Lussac, Avogadro, and Dulong could make sense of everything. This was the same Cannizzaro who discovered the eponymous reaction where benzaldehyde reacts with potassium hydroxide to give potassium benzoate and benzyl alcohol.

A Flasback: The Société de Arcueil. Claude Louis Berthollet (Figure 3)—the very same one who had invented “l’eau de Javel” and collaborated with Lavoisier—accompanied Napoleon during the Egyptian campaign (1798–1801) and returned as Napoleon’s “favorite scientist.” The emperor, realizing the importance of technology in his imperialistic aims (for example, in the production of gunpowder), founded the École Polytechnique and supported science in general. For Berthollet he provided the funds for generous living quarters, and in 1801, Berthollet built a mansion in Arcueil, a village six kilometers south of Paris (Figure 8). In this mansion was included a lavishly equipped laboratory “devoted to quality instead of quantity.” By 1802 Berthollet was attracting some very clever and famous scientists, including Alexander Humboldt (1749–1827), who assembled for regular meetings and discussion of recent research; over a few years the list of official members grew to 12, with many more associate members. Eventually, many international scientists were to visit Arcueil, including John...
facilities at which the primal experiments by Gay-Lussac (gas-volume) and Dulong (heat capacity) were carried out. Humboldt met the young Gay-Lussac and Dulong in Paris (the school still exists, 7 avenue de General de Gaulle, Maisons-Alfort, N 48° 48.76 E 02° 25.38), spent as much time as he could at the Berthollet laboratory. Since Berthollet was interested in chlorine, it was natural for Dulong to pursue research in this area, and soon discovered nitrogen trichloride, a yellow oil prepared by reacting chlorine gas with ammonium chloride (1811). Dulong was oblivious to potential dangers, and he lost a finger and the sight of an eye in an explosion. Berthollet forbade further studies along these lines, and Dulong turned to other areas. Later studies of importance included those in collaboration with Alexis-Thérèse Petit (1791-1820) on the heat capacities of several solid elements. In a paper dated 1819, Dulong (Figure 3) presented the mathematical relationship, since known as the Dulong-Petit law, where he showed that the heat capacity varied inversely with the atomic weight of an element. At the time, this paper was not taken seriously, because in order to establish this relationship, he had to change anything theoretical out of these observations, possibly because Berthollet was an avowed anti-atomist and was still involved in his "old-school" concepts. In particular, Berthollet was bothered that two volumes of hydrogen and one volume of oxygen did not produce only one volume, but instead two volumes of water: "If the theory of atoms is true," he reasoned, "how can $H + O$ give $\text{HOH} + \text{HOH}$?"

The Ignored Research of Avogadro and Dulong—Lost Opportunities. Meanwhile, an Italian named Amedeo Avogadro (1776-1856) (Figure 3) at the University of Turin was not so bashful about making atomist conclusions. He proposed in 1811 that the observations of Gay-Lussac were explained simply by the hypothesis that equal volumes of gases (at the same temperature and pressure) contained equal numbers of molecules ("physical" molecules, in the Dumas sense)—the so-called "EVEN" hypothesis. Avogadro's hypothesis, now a fundamental part of any introductory chemistry text, was far ahead of its time. Because it could not be experimentally verified, and because Avogadro was far from the action in northern Europe, it was generally ignored in scientific publications, although it possibly was discussed in the private conversations of a few farsighted chemists.

It is additionally frustrating to realize that there was not only Avogadro's research on gases that pointed the correct way, but there was also important information on solids—and embarrassingly, it was right under the noses of the scientists at Arcueil. Pierre Louis Dulong (1785-1838), a chemist at the Ecole Vétérinaire d'Alfort, seven km southwest of Paris (the school still exists, 7 avenue de General de Gaulle, Maisons-Alfort, N 48° 48.76 E 02° 25.38), spent as much time as he could at the Berthollet laboratory. Since Berthollet was interested in chlorine, it was natural for Dulong to pursue research in this area, and soon discovered nitrogen trichloride, a yellow oil prepared by reacting chlorine gas with ammonium chloride (1811). Dulong was oblivious to potential dangers, and he lost a finger and the sight of an eye in an explosion. Berthollet forbade further studies along these lines, and Dulong turned to other areas. Later studies of importance included those in collaboration with Alexis-Thérèse Petit (1791-1820) on the heat capacities of several solid elements. In a paper dated 1819, Dulong (Figure 3) presented the mathematical relationship, since known as the Dulong-Petit law, where he showed that the heat capacity varied inversely with the atomic weight of an element. At the time, this paper was not taken seriously, because in order to establish this relationship, he had to change (either double or halve) several of the established atomic weights. Berzelius, who, by coincidence, was at Arcueil in 1818-1819, did not take kindly to having some of his atomic weights changed, and he politely called the ideas of Dulong "interesting" but rejected them.  

It is easy to use hindsight to criticize the community of chemists who would not "think outside the box"—all they had to do was to combine the ideas of Dalton and Avogadro to current data. Yet there are other examples in history where one did not hesitate to make imaginative leaps, e.g., speculations regarding the neutrino in the early 1930s, which were "fanciful" and yet turned out to be correct.

The Contribution of Organic Chemistry—the Divalent Nature of Oxygen. Berzelius' ideas of electrochemical dualism dominated chemical thinking for many years, and only gradually did chemists appreciate a new type of bonding in carbon compounds. The organic research by Dumas briefly described above only hints at the large body of research contributed by organic chemists, which allowed understanding of covalent bonding. Perhaps an example of a watershed experiment illustrating how organic research clarified the situation is...
embodied in the synthesis of ether by Alexander Williamson (1892–1904), a professor at the University College, London. A common belief in the 1840s was that alcohols and ethers were hydrated forms of radicals, where the organic portion was bonded to the oxygen atom. It was thought that alcohols and ethers had the general formulas RO or RRO, respectively, where the organic radicals were linked together in an obscure way. Williamson (Figure 3) reacted an organic halide with an alkoxide, which formed an ether (his well-known eponymous reaction). When Williamson attempted a mixed synthesis, where he reacted ethyl iodide with potassium ethoxide, he obtained an asymmetric ether. To him this could only be interpreted by the following formalism: \( 	ext{CH}_3	ext{I} + 	ext{C}_2	ext{H}_5	ext{OK} \rightarrow \text{CH}_3	ext{OC}_2	ext{H}_5 + 	ext{KI} \) (in the convention at that time, the polyatomic enumeration was superscripted). At a meeting of the British Association on 2 July 1851, Williamson concluded that throughout both inorganic and organic chemistry, a single model would be sufficient to explain the structures and the chemistry. "It is that of water, represented as containing 2 atoms of hydrogen to 1 oxygen, thus HOH." This clearly showed that oxygen was divalent, but chemists of the time were not ready to put everything together. In fact, many scientists believed that inorganic and organic chemistry were different and should use its own set of atomic weights! It would take several more years before the valency of oxygen was commonly recognized.

Back to the Karlsruhe Convention. On the last day of the Karlsruhe Convention, Cannizzaro distributed his 1856 papers, which culled out the pertinent features of Avogadro, Gay-Lussac, and Dulong, and how they pertained to the latest atomic weight data (Figure 9). The logic was clear and precise: Since two volumes of hydrogen react with one volume of oxygen to give two volumes of water gas, then hydrogen must be \( \text{H}_2 \), oxygen must be \( \text{O}_2 \), and water must be \( \text{H}_2\text{O} \). Through the papers, Cannizzaro took up each element in turn, through the nonmetals carbon, oxygen, chlorine, sulphur, bromine, iodine, nitrogen; through the metals from lithium and sodium to mercury and lead; always reassigning atomic weights where necessary on the basis of Avogadro's hypothesis and Dulong-Petit's law; and showing there were no ambiguities whatsoever. Berzelius, who had died 12 years earlier, would have been euphoric had he been present to witness the vindication of atomism.

The audience was convinced. One member of the audience, German scientist Lothar Meyer of the University of Breslau, Silesia, Germany (now Wroclaw, Poland) read and reread the pamphlet: "The scales fell from my eyes, doubts vanished, and a feeling of calm certainty came in their place." A Russian scientist named Dmitri Ivanovich Mendeleev, a poor scholar from St. Petersburg, Russia, who fortunately could attend the meeting because he was on a two-year sabbatical with Robert Bunsen of Heidelberg, only 50 miles north, was likewise favorably impressed. He wrote home to his mentor in St. Petersburg, A. A. Voskresenskii, "The chemical congress which just finished in Karlsruhe is such a remarkable event in the history of our science that I consider it an obligation to describe to you... the sessions of the congress and the results it achieved." He later related, "I well remember how great was the difference of opinion, and how a compromise was advocated with great acumen by many scientific men... in the spirit of freedom... a compromise was not arrived at, nor ought it to have been, but instead the truth..."

As both Meyer and Mendeleev returned home, they realized they had much to do—they had to rewrite their lecture notes, incorporating all of the changes required by the new atomic weights. Both realized that, in fact, new textbooks must be written incorporating the new chemistry... To be continued.

Acknowledgments

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References.


20. A. Avogadro, J. phys., 1811, 73, 58-76. Three years later, André Marie Ampère wrote a parallel paper, A. M. Ampère, Ann. chim. 1814, 90, 43-86, which realized greater distribution. Henceforth, the "equal volume equal number" (EVEN) hypothesis has often been ascribed to both Avogadro and Ampère.


Notes.

1. We met Geoffroy's family of pharmacists in a previous HEXAGON article, during a visit to the Salle des Actes (Hall of Portraits) in the Faculté de Pharmacie in Paris. Geoffroy's 1719 table was originally called "Table des Affinités," with the name changed to "Table des Rapports" in 1730.3

2. Thomas Thomson wrote a hefty two-volume History of Chemistry (1830), covering the period from prehistoric chemistry to the early 19th century, which is a valuable historical tool presenting not only dry statistics, but also lively descriptions of scientists and situations. Thomson was progressive, perhaps the first British proponent of Lavoisier's antihelgyric ideas and an early advocate of Dalton's atomic theory. He wrote a very successful textbook of chemistry in which he brought Dalton's theory to the broad attention of the scientific world (System of Chemistry, Edinburgh, multiple editions 1802-1831).

3. There are 18 sites associated with Dalton that have been identified by the Manchester Council, including all of the numerous workplaces, homes where he lived and tutored, meetings houses, and even the inn where he "played bowls." The more notable sites include (1) the "Blue Plaque," mounted at 36 George Street on a brick wall of Devonshire House (N 53° 28.76 W 02° 14.38), 350 meters east of Town Hall, which is inscribed: "John Dalton 1766-1844—Founder of the atomic theory—President of Manchester Literary and Philosophical Society had his library here"; (2) New College site, Dawson Street (now Mosley Street), which is now a flower garden (N 53° 28.72 W 02° 14.56). Here he was a teacher, 1793-1800; (3) Mechanisms Institution, Cooper Street (20 m north across the street), where he taught and was vice president, 1825-1857; (4) Portico Library, Mosley Street, where he came to peruse newspapers (N 53° 28.78 W 02° 14.44), and which today has a reading room and extensive historical holdings.

4. In 1824 Dumas had a cramped, inadequate laboratory at 1824 at the École Polytechnique (rue de l’École polytechnique, near Panthéon, Paris, France; N 48° 50.83; E 02° 20.90). The buildings still exist, now occupied by various governmental ministries. He improved this laboratory somewhat, but even by 1832 the facilities were only a small laboratory in the annex of the École. In 1829 Dumas was involved in the founding of the École Centrale and made certain laboratories were included there (École centrale, Place de Thérigny, Paris, France; N 48° 51.58 E 02° 21.76); the building still exists and is now an art museum, Musée National Picasso. Although he was an adjunct professor in 1836 at the Sorbonne, there were no adequate laboratory facilities there. He established his own laboratory in his home in 1838 at 35 rue Cuvier (N 48° 50.72 E 02° 21.51), next to the Jardin des Plantes. It no longer exists. These facilities were so grand that "In the 1840s, the route to an academic chemical career in France almost necessarily led through the Rue Cuvier.27 Owing to the disorder of the French Revolution of 1848, he moved that year out of his home and lost his laboratory facilities, and turned to work in ministerial posts.27 He was able to attend the Karlsruhe Congress and there saw vindicated his perceptive concepts of molecules and atoms.

5. The current "Dumas method," commonly utilized in an undergraduate laboratory, is only a crude imitation of Dumas' original method of determining gas density.10 In the current popular method, the experiment is carried out using a flask whose opening is covered with a piece of aluminum foil punctured with a pinhole; hence, the system is always open to the atmosphere, leading to substantial errors and limiting the method to substances with very narrow boiling point ranges. In Dumas' original method, the vapor is sealed in a closed glass bulb, thereby avoiding these errors and limitations; this method is still practiced in a few laboratory curricula which have been designed with an eye on historical and experimental accuracy.