
9 Atomic Weights Revisited

Lavoisier had provided the rule for building a table of elements. If chemists could decompose a substance, then that substance was a compound. If they could not decompose it, then it was to be regarded as an element. Its elementary status was, however, provisional and open to challenge, since what chemists could not decompose today, they might well be able to decompose tomorrow. In that case the substance would lose its status as an element and be revealed as a compound.

Then came John Dalton, with his atomic theory. *Atom* is derived from the Greek word meaning “indivisible.” Dalton associated his atoms with elements, each element being characterized by its own unique atoms, with unique properties, including weight, *atomic weight*. For those who fully accepted Dalton’s ideas about atoms and elements, it was hard to think of elements as having merely provisional status. It was tempting to think of them as consisting of true indivisible atoms, which implied that they were ultimately unchanging, except in the combinations that they formed with other atoms. Determining the atomic weights of elements thus meant finding something enduring, and the research programs devoted to determining atomic weights were, for the most part, confident about this aspect of atoms and their weights. In the light of these programs, molecular weights and formulas indicating the atomic composition of compounds also promised to be enduring.

Chemists, like other kinds of natural philosophers, were also attracted by ideas about the regularity and ultimate simplicity of nature. We have seen that Dalton’s atoms were individually simple, although there were a lot of different kinds. The list of elements stood at around thirty when Dalton published his atomic hypotheses or theories. It seemed to some chemists that simplicity and regularity might well result in a set of atomic weights that were all whole numbers.

Keep It Tidy, Keep It Simple: Prout, Gay-Lussac, and Avogadro

This was the view of atomic weights advocated by the English chemist and physiologist William Prout (1785–1850), but he combined it with other ideas

that undermined the idea of indivisible atoms. Prout regarded hydrogen as the "primary" material agent in mineral chemistry, and he believed that it was converted, by galvanic electricity and other means, into all the other chemical elements. There was an original or prime matter, from which all the elements, and thus all bodies, were composed. Heavier elements were built up of multiples of the fundamental unit, the hydrogen atom. It followed that, if the atomic weight of hydrogen was taken as one, the atomic weights of the heavier elements would be integral multiples of that unit. In other words, atomic weights would all be whole numbers.

It is a striking fact that many atomic weights, although not all, *are* close to whole numbers, and the distribution of atomic weights is in general so close to whole numbers that there has to be a reason for it. We know today that the reason is that the heaviest part of any atom is its nucleus, made up of neutrons (uncharged particles) and protons (positively charged particles), which have almost exactly the same weight. Some elements have an atomic weight that is not a whole number, for example, chlorine has an atomic weight close to 35.5. From the discovery of atomic structure around the beginning of the twentieth century, we now know that such elements have two or more isotopes. Different isotopes of a given element are forms of that element having different numbers of neutrons in the nucleus of their atoms, and therefore have different atomic weights, since the atomic weight of an isotope is the sum of the number of protons and neutrons in the nucleus of its atoms.* Atomic weights that are not whole numbers arise from the mixture of isotopes, whose weights average out to a non-integral value. All that Prout knew or could know, however, was that many atomic weights are either whole numbers or very close to whole numbers. In two papers published in 1815 and 1816, he put forward what has become known as *Prout's hypothesis*, that atomic weights are all whole numbers because they are multiples of the weight of the hydrogen atom.

Chemists with more confidence in the regularity and simplicity of nature than in the results of rigorous and painstaking analyses were able to round off even problematic atomic weights to whole numbers, without doing too much violence to the results. Molecular weights could then be calculated from the results of quantitative analysis. The Scottish chemist Thomas Thomson (1773–1852), who had been an early convert to Dalton's atomic theory, publishing an account of it even before Dalton himself, promptly set about showing that

*Electrons, negatively charged particles, are also constituents of matter and contribute to atomic weights. But since electrons weigh only about 1/1,840 of the weight of a proton, they may be ignored for all but the most precise determinations of atomic weights. The sum of the weights of protons and neutrons is close enough.

Prout was right. If you know what the result should be, it is relatively easy to obtain it. Thomson accordingly came up with a set of atomic weights supporting Prout's hypothesis. He was promptly criticized for the unsatisfactory nature of his analyses. Berzelius, a scrupulously careful chemist, was ruthlessly dismissive of Thomson's results. The best that one can say of this aspect of Thomson's work is that he was careless. Prout's hypothesis had received a setback, but it had a way of coming back to life throughout the century, like a phoenix.

The same could be said about Dalton's atomic theory, but that theory, unlike Prout's, did, in modified form, become a fixture in chemistry. Dalton's ideas had led to a system of atomic weights and also to some rules or laws of combining proportions, including the law of multiple proportions.* Eight parts by weight of oxygen combine with six parts by weight of carbon in forming carbon monoxide; in carbon dioxide, twelve parts by weight of carbon combine with the same eight parts by weight of oxygen. The ratio of the weight of carbon in the dioxide to its weight in the monoxide is $12:6 = 2:1$.

There is of course a problem, which did not arise for Dalton. His simplicity-criterion about the ratios of combining *atoms* works for carbon monoxide and carbon dioxide, but it denies the possibility of diatomic molecules such as H_2 and O_2 . This leads to problems, and it produces headaches when applied to water and hydrogen peroxide, H_2O and H_2O_2 for us, but HO and HO_2 for Dalton. Errors in atomic weights lead to errors in determining molecular formulas, and errors in molecular formulas lead to errors in determining atomic weights. Dalton erred by a factor of two in the atomic weights of oxygen (8, instead of our 16) and carbon (6, instead of our 12). These errors gave rise to confusion and controversy in the ensuing decades.

Dalton wrote down his ideas about atoms in notebooks of 1802. The first public mention of Dalton's atomic theory and laws of combining proportions was by Thomas Thomson in 1807, and only in the following year, 1808, did Dalton publish his own account. That publication coincided with the publication in France of a different law of combining proportions.

Joseph Louis Gay-Lussac (1778–1850) was one of the brilliant generation of French chemists and physicists who came to prominence after the French Revolution. He made balloon ascents to study the earth's magnetism and to collect samples of air. In 1805 he published a paper showing that oxygen and hydrogen formed water by combining in the ratio of 1:2 by volume. Other gas

*Dalton's law of multiple proportions states that when two elements combine in a series of compounds, the ratios of the weights of one element that combine with a fixed weight of the second are in a ratio of small whole numbers (see Chapter 7).

studies soon showed him that there was a *law of combining volumes* for gases that corresponded to the law of multiple proportions for analysis by weight (gravimetric analysis). When gases combined, they did so in volumes that were in a ratio of small whole numbers. Gay-Lussac's gas studies convinced him that regularities in gas composition were more general and simpler than those regularities that Dalton discovered for combining weights. Dalton and Gay-Lussac, the one wedded to gravimetric analysis, the other to volumetric analysis, did not develop any enthusiasm for each other's work, and it was by no means obvious how their laws of combining weights and combining volumes could be reconciled. Neither for the first nor for the last time in the history of chemistry, French and English chemists were rivals when they might better have collaborated with one another. Intellectual pride was reinforced by the hostilities of the Napoleonic Wars.

There was a way in which Dalton's law of multiple proportions and Gay-Lussac's law of combining volumes could be reconciled, but even when it was offered, it was at first not well received. In 1811, the Italian chemist Amedeo Avogadro (1776–1856) proposed an explanation for the regularities described in Gay-Lussac's law. He suggested, in what has become known as *Avogadro's hypothesis*, that equal volumes of gases at the same temperature and pressure contain equal numbers of particles. These particles could be atoms or molecules, simple or compound. They were the smallest particles of oxygen gas, hydrogen gas, carbon monoxide, carbon dioxide, ammonia vapor, and so on. A consequence of Avogadro's hypothesis was that combination by volumes in the ratio of small whole numbers implied the combination by particles in the ratio of small whole numbers. This was a remarkable insight that brought together two empirical laws, Dalton's combining proportions and Gay-Lussac's combining volumes, and one might have expected that it would have been welcomed by the whole chemical community of Europe.

Such an expectation would have been wrong. Avogadro's hypothesis did not find a general welcome and acceptance for a half century. Why not? Let us begin by considering Gay-Lussac's own results for the composition of water. Two volumes of hydrogen combine with one volume of oxygen to give two volumes of water vapor. That implies, according to Avogadro, that two particles of hydrogen combine with one particle of oxygen to give two particles of water vapor. That can happen only if each particle of oxygen is divisible into two parts, as it is in our modern formula for oxygen gas, O_2 . But for Dalton and his followers, diatomic molecules of a single element cannot exist. He was convinced that identical atoms do not and cannot combine directly with one another, as only unlike atoms could combine. And if oxygen was not diatomic,

but monatomic, then Avogadro's hypothesis implied that each atom of oxygen was divisible into two parts, another impossibility for Dalton, since his atoms were by definition indivisible. Avogadro's hypothesis was simply not compatible with the assumptions of Dalton's atomic theory.

Dalton's was not the only atomic theory at the time. Berzelius had also proposed an atomic theory, but with divisible atoms. Berzelius, however, was also unhappy with Avogadro's hypothesis. Divisible atoms might be all very well, but diatomic molecules containing two identical atoms violated Berzelius's developing ideas about the electrical nature of atoms and the relationship between electrical character and chemical affinity. Substances that had affinity for one another, and were therefore disposed to combine together, had to have opposite or at least significantly different electrical characters, as was the case with electropositive hydrogen and electronegative oxygen or electropositive sodium and electronegative oxygen. By allowing for the possibility of diatomic molecules of oxygen, hydrogen, and other gases, Avogadro was making claims that ran counter to Berzelius's electrochemical dualism.

There were other, less theoretical but no less persuasive objections. Some substances, such as ammonium chloride, dissociate in the vapor phase. That is, a single particle of vapor turns into two or more particles. Two or more particles occupy two or more times the volume that one particle does. That wreaks havoc with measurements of gas volumes and provides empirical evidence that fails to obey Gay-Lussac's law, making apparent nonsense of Avogadro's hypothesis. It was not until the phenomenon of dissociation was understood, and interpreted in terms of reaction kinetics, that this objection could be countered. Similar objections were raised against Dalton's laws of combining proportions, which work only for compounds of fixed composition. Metallic alloys and salt solutions, to take two of the most obvious exceptions, do seem to share some of the characteristics of chemical compounds, but they do not fit Dalton's laws. The simplest way to avoid that objection was to say that only those substances that did fit Dalton's laws were true chemical compounds, but that is a circular argument that did not convince critics.

In the decades when Avogadro's hypothesis was mostly gathering dust, Berzelius's electrochemical dualism was the most successful chemical theory in Europe. It explained the properties of elements and compounds, especially the chemical reactions they underwent, and Berzelius, looking at those properties and reactions, derived his own formulas for compounds. But, as Berzelius's critics from organic chemistry pointed out in the 1840s, different reactions suggest different formulas for one and the same substance, and that is not very satisfactory. What is more, the kinds of problem arising from Dalton's simplicity

criteria, leading many chemists to err by a factor of two in determining a variety of atomic weights, meant that there would continue to be major disagreements about fundamentals, including atomic weights, molecular weights, and molecular formulas. Prior to 1860, chemists who avoided these problems were in a minority.

Among that minority, Gerhardt and Laurent, thorns in Berzelius's side in the final decade of his long life, succeeded in confronting and resolving many of the problems concerning atomic and molecular weights. The route they took was not widely shared, but it did involve them in adopting a rule corresponding to Avogadro's hypothesis. Once again, they were in the minority at the time, but their molecular formulas tended to have the right number of atoms, two in a hydrogen molecule, two in oxygen, three in water, and so on.

They were in a minority because most chemists at the time derived atomic weights from relative combining *weights* and equivalents. Laurent and especially Gerhardt looked instead to combining gas *volumes* and to a whole group of various other properties, including the physical property of specific heats.* Those who worked from combining weights used simplicity rules, including the main one that atoms combined with one another in the simplest proportions by weight and number. This was a fruitful hypothesis, but it was just a hypothesis, and so, as Gerhardt and Laurent pointed out, atomic weights based on it were also hypothetical. They also pointed out that the use of proportional numbers combined with simplicity rules often led to fractions of atoms, as for example in ferrous oxide, where the proportional numbers require two-thirds of an atom of iron to one of oxygen. This was not very satisfactory. Of course, one could always triple the numbers and arrive at two atoms of iron to three of oxygen, but that seemed arbitrary.

Analogy had always been a guide to theory and practice in chemistry. It was therefore reasonable to assume that elements with similar specific heats had similar atomic weights. Two other French scientists, Pierre Louis Dulong (1785–1838) and the short-lived Alexis Thérèse Petit (1791–1820), explored the relation between atomic weights and specific heats. They found that, for most elements, the product of these two quantities (the "atomic heat" of elements) was approximately a constant. This, known as *Dulong and Petit's law*, was published in 1819. But the law held only if chemists doubled some of the atomic weights arrived at by the use of Dalton's rules. Dalton, naturally, was not pleased with this suggestion, and few chemists took any notice of what they regarded as an essentially physical rather than chemical result. Disciplinary

*The specific heat of a substance may be defined as the amount of heat required to raise one gram of the substance by one degree Celsius.

boundaries can keep ideas out as well as in. Laurent and Gerhardt, however, working with chemical and physical analogies in arriving at their formulas, made good use of the specific heat data and of analogies in physical as well as chemical properties in determining atomic weights and molecular formulas.

There were problems with specific heats as a guide to atomic weight. Some elements, such as sulfur, existed in different allotropic forms having different specific heats. Did this mean that such an element had more than one atomic weight? Again, volumetric work on vapors revealed that different allotropes of sulfur occupied different volumes. In such cases, even Laurent and Gerhardt had to fall back on proportional weights to arrive at atomic weights.

The fundamental rule that Gerhardt and Laurent adopted was Avogadro's volume hypothesis, which stated that equal volumes of gases contained equal numbers of particles. In order to make sense of this hypothesis, Laurent proposed that "each molecule of an element can be divided into two or more parts that we call *atoms*; these molecules can be divided only in the case of chemical combinations."* So, for example, molecules of gaseous hydrogen and oxygen contained two atoms apiece. When they combined, experiment showed that one volume of oxygen combined with two volumes of hydrogen to form two volumes of water vapor, and this could be represented by the equation $2\text{H}_2 + \text{O}_2 = 2\text{H}_2\text{O}$. Gerhardt and Laurent used superscripts rather than subscripts, so that they represented a diatomic molecule of oxygen as O^2 . But their formulas, corresponding to the formation of two volumes of water in the above equation and conforming to Avogadro's hypothesis, were otherwise more often than not the same as the ones we use today. They called them "two volume" formulas, and Gerhardt in particular used the words *volume* and *atom* to represent the same thing.† This can be confusing for us today.

In practice, Gerhardt, and Laurent with him, agreed with Berzelius's atomic weights for many bodies, but, for example, Gerhardt's use of the two-volume hypothesis led him to adopt atomic weights for the metals that were half the generally accepted atomic weights. The result was a set of molecular formulas that were simpler than Berzelius's, that brought out physical and chemical analogies between different compounds, and that did not depend on any par-

*Quoted in W. H. Brock, *The Norton History of Chemistry* (New York: Norton, 1993), 229. The Italian chemist Stanislao Cannizzaro proved in 1858 that Laurent was mistaken in thinking that all elements had diatomic molecules. Gaseous nitrogen, hydrogen, chlorine, and oxygen are among those elements whose molecules do contain two atoms apiece, but most nongaseous elements do not have diatomic molecules.

†One molecule of oxygen, O_2 , corresponds to one measured volume of gas, in accordance with Avogadro's hypothesis, but for Gerhardt the molecule represented two "volumes," meaning two atomic weights' worth of oxygen.

ticular or privileged chemical reaction, where different reactions could lead to incompatible formulas for the same substance. For the first time ever, the mineral acids and their metallic salts were given molecular formulas generally agreeing with ours today. But, as we have seen, Dalton, Berzelius, and following them many other chemists not only lacked the benefit of our hindsight but had good theoretical reasons for dismissing Avogadro's hypothesis. Because Gerhardt and Laurent proposed formulas based on the acceptance of that hypothesis, their formulas were at first rejected by most chemists. And besides, Berzelius's authority in particular remained strong through the 1840s, and it was not until well into the next decade, after Berzelius had died in 1848, that Gerhardt's and Laurent's ideas met with cautious acceptance. Avogadro's hypothesis had to wait even longer before it was accepted.

Confusion and Resolution of Atomic Weights: Cannizzaro Sets a Standard

Failure to agree whether the atomic weights of metals should be half of what Berzelius advocated was one of the reasons there was little agreement about what formulas, and even what kind of formulas, should represent molecular composition. But there were other issues that led to lively debate about atomic weights. These issues arose from reflecting about some remarkable numerical patterns and regularities in atomic weights, from thinking about allotropy, and from the steady growth in precision in quantitative analysis.

That there were striking regularities in atomic weights had been known for some time. We have seen that Prout's original hypothesis had been prompted by the fact that most atomic weights appeared to be either whole numbers or very nearly whole numbers, and so might be built up of units corresponding in weight to the hydrogen atom. It surely could not be merely by chance that so many atomic weights were close to integers. Thomas Thomson's careless but attractive analyses had reinforced this view. But there were simply too many atomic weights that were not whole numbers, and Prout's hypothesis failed to win acceptance by most chemists. Subsequently, Prout was to contemplate the notion that there might be building blocks smaller than the hydrogen atom, corresponding to perhaps a half, perhaps a quarter of that atom.

Meanwhile the German chemist Johann Wolfgang Döbereiner (1780–1849) observed, between 1817 and 1819, that there were several sets of groups of three elements (triads) where the atomic weight of one was very nearly halfway between the atomic weights of the other two. These triads were of recognizably similar elements, including the halogens (chlorine, bromine, and iodine) and the alkaline earth metals (calcium, strontium, and barium). Döbereiner

also identified the triad of sulfur, selenium, and tellurium, and later added the alkali metals lithium, sodium, and potassium. Elements within such families were related in a way that involved regular increases of atomic weight from one element to the next.

These regularities might suggest, as they did to some chemists, that atoms were made of building blocks, one element in a triad differing from the next by the possession or lack of a certain number of such building blocks. Something like Prout's hypothesis might after all prove to be on the right track. Allotropy also suggested that atoms might be compounds, but somehow compounds of identical building blocks, a difficult and unfamiliar concept when Laurent and others first proposed it. The existence of triads, the existence of families of elements, and the phenomenon of allotropy all contributed to a revival of Prout's hypothesis. But since atomic weight determinations had clearly shown that any building block had to be smaller than an atom of hydrogen (how else could one explain atomic weights that were not whole numbers?), the original hypothesis clearly would not do. Instead, the revival was based on smaller units, fractions of the atomic weight of hydrogen. Going back to one of the most obvious problems for the original version of Prout's hypothesis, chlorine had an atomic weight of 35.5. If the subatomic building blocks of prime matter corresponded to half an atom of hydrogen, then chlorine's atomic weight would not be a problem after all. Prout himself had thought along these lines.

Berzelius, who died in 1848, wrote a critique of Prout's hypothesis in 1845. He noted that transmutation had never been observed in the laboratory. If Prout's hypothesis was right, transmutation would be at least a theoretical possibility, and failure to observe it argued against Prout. The experimental data about atomic weights that best supported Prout's hypothesis were those of Thomas Thomson, and Berzelius had nothing but scorn for Thomson's abilities as an analyst. Clearly, Berzelius regarded it as merely a coincidence that many atomic weights had either whole-number or half-whole-number values.

There were, however, increasingly accurate atomic weights, determined with great precision by laboratory chemists whose practical skills were more impressive than Thomson's. The German-trained Swiss chemist Jean Charles Galissard de Marignac (1817–94) was a superb laboratory chemist who by 1843 had already shown that chlorine was not the only element with an atomic weight approximating to an integral multiple of half the weight of hydrogen. He was sure that there was some truth in Prout's hypothesis. His most incisive critic was the Belgian chemist Jean Servais Stas (1813–91), also a fine analyst, who stressed that atomic weights were not generally either whole numbers or

half numbers, but only near approximations to such numbers. By 1860, Mari-gnac was publishing results to the third decimal point, and he had to admit that his numbers were not exactly what Prout's hypothesis required. Still, he argued, too many of them were too close to integers for Prout's hypothesis to be completely wrong. The numbers just had to mean something, and the idea of a prime matter was as tempting to many nineteenth-century chemists as it had been to medieval alchemists.

Before chemists could fully appreciate regularities in atomic weights and propose hypotheses about the distribution of atomic weights that would be acceptable to other chemists, they still needed to solve troubling problems. These problems had been raised by Dalton's simplicity criteria when applied to atomic weights, and by Berzelius's emphasis on reactions and the electrical nature of atoms as the guide to formulas. They remained unresolved throughout the 1850s, and even at the end of that decade chemists were still disagreeing about the atomic weights of many metals—not about decimal points, but about whether weights should be halved or doubled. In other words, they needed to adopt the solution that Gerhardt and, supporting him, Laurent had already proposed: the adoption of Avogadro's hypothesis and of "two volume" formulas.

By 1860, chemists had begun to accept the homologous formulas that Gerhardt had proposed. Determination of molecular weights using gas analysis and vapor density measurements made it easier to think in terms of the volumes that Avogadro worked with. Studies of dissociation had explained some of the apparently glaring exceptions to Gay-Lussac's law, removing another objection to Avogadro's hypothesis. Chemists were much better prepared than they had ever been for a reconsideration of Avogadro's hypothesis. An Italian chemist, Stanislao Cannizzaro (1826–1910), had arrived at this reconsideration by 1858, when he wrote a paper showing how Avogadro's hypothesis resolved a lot of problems in the determination of atomic and molecular weights and how it helped to bring together work on atomic heats and vapor densities. He also clarified the distinction between atoms and molecules. His paper, published in Italian, was at first ignored. Then he presented his argument and distributed his paper as a pamphlet at a conference in Karlsruhe, Germany. Some chemists were immediately persuaded, others read Cannizzaro's paper on the train going home and were persuaded by the time they got to their destination; and others, of course, missed the point. That conference was the turning point for the acceptance of Avogadro's hypothesis, almost a half-century after Avogadro first proposed it. Now that hypothesis could bring order to the whole of chemistry.

Mendeléev's Periodic Table

Mendeléev's periodic table was the ancestor of all subsequent periodic tables of the elements. He invented the arrangement of elements in groups (horizontal rows identified in this version of the table by Roman numerals) and periods (vertical columns, identified by Arabic numbers).

Some aspects of Mendeléev's table may at first glance confuse those who are familiar with the modern periodic table. First, here and in his early tables (1869), periods were represented as vertical columns and groups as horizontal rows, the reverse of later practice; Mendeléev subsequently changed to the later form. Second, the inert gases were missing, because they were then unknown. When they were discovered, Mendeléev placed them in group o, at the lefthand side of the table, lacking in this illustration, whereas today we place them in group VIIIA.

We place hydrogen as the first element in the first period, along with helium. When helium was discovered, Mendeléev put it in the second period. We put the triads of iron, cobalt, and nickel; ruthenium, rhodium and palladium; and osmium, iridium, and platinum in group VIIIB, in the middle of the table. Mendeléev put them in group VIII. We also have two long groups, the lanthanides and actinides, that were a headache for Mendeléev.

TABLE II
Periodic System and Atomic Weights of the Elements
(Giving the pages on which they are described)

	1st Series	2nd Series	3rd Series	4th Series	5th Series	6th Series
I.	Li 7	K 39	Rb 85	Cs 133	—	—
II.	vol. I. 574	vol. I. 598	vol. I. 576	vol. I. 576	—	—
III.	Be 9	Ca 40	Se 80	Eu 157	—	—
IV.	vol. I. 618	vol. I. 590	vol. I. 614	vol. I. 614	—	—
V.	B 11	Sc 44	Y 89	La 138	Yb 173	—
VI.	vol. II. 60	vol. II. 94	vol. II. 98	vol. II. 98	vol. II. 98	—
VII.	C 12	Ti 48	Zr 91	Ce 140	7 178	Th 232
VIII.	vol. I. 538	vol. II. 144	vol. II. 146	vol. II. 98	7 Di 149	vol. II. 148
IX.	N 14	V 51	Nb 94	Mo 98	—	—
X.	vol. I. 925	vol. II. 194	vol. II. 197	vol. II. 98	—	—
XI.	O 16	Cr 52	Mo 98	—	—	—
XII.	vol. I. 145	vol. II. 276	vol. II. 290	—	vol. II. 290	vol. II. 297
XIII.	F 19	Mn 55	7 98	—	—	—
XIV.	vol. I. 489	vol. II. 308	—	—	—	—
XV.	—	Fe 55	Ru 102	—	—	—
XVI.	—	vol. II. 317	vol. II. 309	—	—	—
XVII.	—	Co 59	Rh 103	—	—	—
XVIII.	—	vol. II. 328	vol. II. 309	—	—	—
XIX.	—	Ni 59.5	Pd 106	—	—	—
XX.	—	vol. II. 353	vol. II. 309	—	—	—
XXI.	—	1st Series	2nd Series	3rd Series	4th Series	5th Series
XXII.	Na 23	Cu 64	Ag 108	—	—	—
XXIII.	vol. I. 132	vol. I. 538	vol. II. 398	vol. II. 415	—	—
XXIV.	Mg 24	Zn 65	Cd 112	—	—	—
XXV.	vol. I. 690	vol. II. 39	vol. II. 47	—	—	—
XXVI.	Al 27	Ga 70	In 114	—	—	—
XXVII.	vol. II. 70	vol. II. 90	vol. II. 91	—	—	—
XXVIII.	Si 28	Ge 72	Sn 119	—	—	—
XXIX.	vol. II. 99	vol. II. 124	vol. II. 125	—	—	—
XXX.	P 31	As 75	Sb 120	—	—	—
XXXI.	vol. II. 149	vol. II. 179	vol. II. 166	—	—	—
XXXII.	S 32	Se 79	Te 125	—	—	—
XXXIII.	vol. II. 200	vol. II. 270	vol. II. 270	—	—	—
XXXIV.	Cl 35.5	Br 80	I 127	—	—	—
XXXV.	vol. I. 459	vol. I. 484	vol. I. 498	—	—	—

Note.—Two lines under the elements indicate those which are very widely distributed in nature; one line indicates those which, although not so frequently met with, are of general use in the arts and manufactures.

There are gaps in Mendeléev's table, some that he recognized as corresponding to hitherto undiscovered elements, and others to radioactive elements, many of which are artificial and short-lived. But his table represents one of the great advances in the understanding and systematization of chemistry, and it is an essential tool in teaching chemistry.

■ D. Mendeléev, *The Principles of Chemistry*, 3rd English trans. (London, 1905), 1: xvi.

Mendeléeev and the Periodic Table: A Russian Revolution

By the 1860s, chemists had a set of atomic weights that were self-consistent, based on accurate analyses, and generally accepted. There were no more disagreements about whether the atomic weight of oxygen was 8 or 16. All agreed that it was 16. The kinds of regularities that had attracted Döbereiner's attention earlier in the century now began to strike other chemists. John Newlands (1837–98) in England arranged elements according to their equivalent weights and numbered them sequentially, hydrogen 1, lithium 2, and so on. He found that the eighth element after any given one "is a kind of repetition of the first, like the eighth note of an octave in music."^{*} Thus chlorine (number 15) is the eighth element after fluorine (number 7), and both are members of the halogen group; sodium (number 9) is the eighth element after lithium (number 2), and both are alkali metals, and so on. Because of Newlands's reference to music, this numerical regularity coinciding with analogies in properties is known as *Newlands's law of octaves*.

During the 1860s, other chemists throughout Europe numbered the elements and arranged them in tables, wrote them on a line wrapped around a cylinder, plotted them on graphs, and pursued a dozen ingenious ways of displaying regularities in atomic weights or equivalent weights. Their aim was to show how such regularities brought out groupings or analogies in chemical properties. The most important and the most influential of these attempts to construct the perfect table to display the elements was by a Russian, Dmitri Mendeléeev, who was born in Siberia in 1834 and died in St. Petersburg in 1907.

Mendeléeev was trained as a teacher. He had published a textbook on organic chemistry in 1861. While writing it, he had been struck by one of the characteristics of Gerhardt's homologous series: within a series, physical properties and molecular weights are related, for example, the density of paraffins increases with their molecular weights. In 1868, while engaged in writing a textbook for his students, he looked for a way of classifying the elements and wondered whether something analogous to the homologous series relationship might work for elements. He became convinced that the mass of an atom and the properties of an element had to be related. By this date, around sixty elements were known, more than double the number in Lavoisier's day. Mendeléeev had been to the Karlsruhe conference, and he was able to benefit from the resulting consistency in determining atomic weights. He began to write down each element on its own card, together with its atomic weight (he rejected Prout's hypothesis), its properties, and analogous elements. Then he

^{*}Quoted in J. R. Partington, *A History of Chemistry* (London: Macmillan, 1964), 4: 887.

looked for the best arrangement of the cards, the arrangement that would most fully bring out analogies in properties and relate them to atomic weights. He concluded that the properties of the elements were in periodic dependence upon their atomic weights. By periodic he meant regular and recurring. This was the origin of the periodic table of the elements, which has evolved and grown since Mendeléeev's time, but which still appears in every classroom where chemistry is taught. And of course the periodic table is based on Mendeléeev's periodic law: "The properties of the elements, as well as the forms and properties of their compounds, are in periodic dependence or (expressing ourselves algebraically) form a periodic function of the atomic weights of the elements."^{*}

Mendeléeev's periodic table worked remarkably well, and he revised and improved it. Elements were ranked in increasing order of their atomic weights; the rows were arranged in columns that, read horizontally, brought out groupings of analogous elements. Alkali metals, alkaline earth metals, halogens, and other groups of elements slotted beautifully into the table. Where necessary, Mendeléeev left blanks, so as to keep known elements in positions that corresponded to their chemical properties. Then, with remarkable confidence, he predicted that those blanks would later be filled by hitherto undiscovered elements, and he went on to predict the atomic weights and the chemical natures of the "missing" elements. There was a blank after zinc, in the same group as boron and aluminum. Mendeléeev predicted that this blank would be filled by an element with properties similar to those of aluminum and having an atomic weight of 68 and specific gravity of 6.0. In 1875 the missing element was discovered, called gallium, with atomic weight 69.9 and specific gravity 5.96. Other elements that he predicted and that were equally close to his predictions include scandium and germanium. The periodic table not only brought out groupings and regularities among the elements, which made and makes it a valuable teaching tool, but it also encouraged chemists to look for missing elements. In many cases, they found them.

There were problems, for example, with pairs of atomic weights that were out of order for the representation of periodic properties. In Mendeléeev's first periodic table, iodine (atomic weight 127) clearly belonged with the other halogens, following fluorine, chlorine, and bromine. Tellurium (atomic weight 128) belonged at the end of the sequence oxygen, sulfur, and selenium. Using atomic weight as the guide, tellurium would have come after iodine in the table, which would have meant that both elements were in the wrong groups,

^{*}D. Mendeléeev, *The Principles of Chemistry*, 4 vols. (New York: Collier, n.d.), 3: 17.

considered in the light of chemical and physical properties. So Mendeléeu reversed the order of atomic weights and suggested that the weight for tellurium was wrong; it should have been less, not more, than that of iodine. He was right to be guided by the analogy of properties, and he put both elements in what we know to be the right place on the table. He was wrong in seeking to correct the atomic weight for tellurium, since it turned out to have been accurate. But without twentieth-century knowledge of atomic structure and isotopes, he had to resolve conflicting evidence, and he chose to be guided by chemical and physical analogies. In so doing, he made the decision that any good chemist would have made—the periodic table was too good to ruin.