

MENDELEEV'S "PROBLEMS:" A MEANS TO ENGAGE STUDENTS AND TEACHERS IN THE HISTORY OF CHEMISTRY

Arthur Greenberg, Department of Chemistry, University of New Hampshire, Durham, NH 03824 USA, art.greenberg@unh.edu

Abstract

As others have also noted, one means of engaging students and educators with the history of chemistry is to examine the errors by great historical chemists in their contemporary context. After providing very brief biographical background as well as a brief description of the path to the periodic table, three of Mendeleev's "problems" associated with his periodic table are described: 1) the "discrepancy" between the atomic weights of tellurium and iodine, 2) Mendeleev's difficulties in his initial acceptance of helium and argon, and 3) his hypothesis of the "super-light" inert gas atoms comprising the celestial ether.

Introduction

It is a real challenge to interest students, and even most educators, in the history of chemistry despite the statement by Oliver Sacks, renowned neurologist and author of the chemical memoir *Uncle Tungsten*: "Chemistry has perhaps the most intricate, most fascinating, and certainly most romantic history of all the sciences" (1). One solution might be to "humanize" the science. Providing dramatic details of the life of a chemist can be helpful. Yet another approach is to "catch" an iconic chemist making errors, a point eloquently made two decades ago (2), and to "teach the nature of science through scientific errors" (3). From a modern perspective, it is all too easy to point out the errors and misconceptions

of even the most distinguished scientists, as theories and methodologies evolve. Value is only truly gained by understanding the contemporary context of these errors sometimes combined with some all-too-human foibles.

Dmitri Ivanovich Mendeleev is an iconic chemist (perhaps *the* iconic chemist). Indeed, the periodic table hangs in virtually every dedicated chemistry classroom and lecture hall, literally "the icon on the wall." Mendeleev has a very dramatic life story. His scientific "problems" reflect the absence of knowledge that awaited discoveries in future decades. But it is also clear that his magnificent development of the periodic law in 1869, initially handicapped somewhat his abilities to understand its occasional inconsistencies and extensions during his later years.

The details of Mendeleev's life will surprise most students (and many educators). The usual textbook photographs, dating from late in his life, suggest an almost biblical prophet. Indeed, his predicted discoveries of three new elements were prophetic. However, he also predicted the existence of elements never found (4) and classification of the lanthanides continued to confuse Mendeleev and others (5). As one might suspect, Mendeleev did not discover the periodic law in a dream (6). He was not a lone scientist, but active in industrial and governmental establishments. Perhaps the biggest surprise is that Mendeleev was never awarded the Nobel Prize in chemistry (7, 8).

The purpose of this brief article is to encourage the inclusion of history of chemistry in introductory courses. Its presentation is light and emphasizes three scientific problems: 1) Mendeleev's anticipated correction of the "reversal" of the atomic weights of iodine and tellurium, 2) Mendeleev's initial resistance to the discovery of the noble gases helium and argon, and 3) Mendeleev's hypothesis of atoms comprising the "universal ether."

A Very Brief Life of Mendeleev

Dmitri Ivanovich Mendeleev (February 8, 1834-February 2, 1907) (9) was born near Tobolsk in Siberia to Ivan Pavlovich Mendeleev (1783-1847) and Maria Dmitrievna Mendeleeva (née Kornilieva) (1793-1850) (10-13). He was the last of 14 children (9). To a comfortable family life came two disasters. Dmitri's father died in 1847 following years of illness and Maria was forced to work and resurrect the family glass factory in Tobolsk (13). The factory was destroyed by fire in 1848. Maria recognized Dmitri's intellectual gifts, sold her possessions and in 1849, with her youngest daughter Elizabeth also in tow, commenced a 2200-km journey to Moscow over the Ural Mountains. She failed in her attempt to enroll Dmitri in Moscow University and then traveled another 700 km to St. Petersburg (13). He was again denied entrance to the university but was admitted to the Chief Pedagogical Institute. The President of the Institute had been a fellow student of Dmitri's father. Fortunately, the Pedagogical Institute was located within the University of St. Petersburg and Dmitri had exposure to its scientists.

Exhaustion took its toll on Maria. She died in September 1850 from what is presumed to be tuberculosis just as sixteen-year-old Dmitri began his studies. Elizabeth also died a few months later. In a dedication to a paper published in 1887, Mendeleev wrote (13, 14):

This investigation is dedicated to the memory of a mother by her youngest offspring. Conducting a factory, she could educate him only by her own work. She instructed him by example, corrected with love, and in order to devote him to science she left Siberia with him, spending her last resources and strength. When dying, she said, "Refrain from illusions, insist on work, and not on words. Patiently search divine and scientific truth."

He graduated from the Pedagogical Institute in 1856 and received its gold medal. His undergraduate thesis was defended in spring 1855 and his Masters thesis defended in September 1856 (10-12). Following graduation, Mendeleev became very ill and spent time in the

milder climate in Crimea. He returned to St. Petersburg and was appointed a lecturer at the University. In 1859, the Russian government provided support for his study at Heidelberg University, which boasted famous chemists including Robert Bunsen (1811-1899) and Gustav Robert Kirchhoff (1824-1887). Bunsen and Kirchhoff would soon develop the spectroscope, the definitive detector of known and new chemical elements. Mendeleev declined the opportunity to work in Bunsen's laboratory, leading the great German scientist to resent the slight by the young Russian (15). In 1861, Mendeleev's textbook on organic chemistry won for him the prestigious Demidov Prize of the Petersburg Academy of Sciences. He married Feozva Nikitichna Leshcheva in 1862 and they had two children. Unhappily married from the start, he met Anna Ivanovna Popova in 1876, married her and divorced Lascheva in 1882. Anna and Dmitri had four children including twins. He became Doctor of Science in 1865 and was appointed Professor at the University of St. Petersburg in 1867. Teaching inorganic chemistry, Mendeleev began writing the textbook that would soon lead him to the periodic law.

The Paths to the Periodic Law

It is not the purpose of this brief paper to treat the development of the periodic law in any depth. Rather, it is worthwhile for students and teachers to briefly consider some questions:

1. What were the early foundations leading to the periodic law?
2. What drew Mendeleev to atomic weights as a critical organizing principle?
3. Why is Mendeleev, among worthy competitors, considered the father of the periodic table?

One of the earliest efforts to systematize chemical substances was by the French physician, Étienne François Geoffroy (1685-1752), who published the first affinity table in 1718 (Figure 1) (16). Column 9 represents substances having affinities for sulfur (at the top) ranging from highest (iron, Fe) to lowest (gold, Au). Although the chemical observations of the period were not always consistent, the match with the activity series of metals (reduction potentials relative to hydrogen) is striking: Fe²⁺ (-0.44 V, most difficult in the Column 9 series to reduce to the metal; therefore, metal most easily oxidized); Cu²⁺ (+0.34 V); Pb²⁺ (-0.13 V); Ag⁺ (+0.80 V); Hg²⁺ (+0.85 V); Au³⁺ (+1.52 V; metallic gold: hardest to oxidize). Tin was known before 1600 (*e.g.*, see Column

TABLE DE M^R GEOFFROY en 1718.

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
(Acids)	(HCl)	☉	☉	☉	☉	☉	SM	♂ _(S)	♀	♂	♀	☉	♂	♂	☉ _(Water)
(Ni ₂ O ₃)	♂ _(Sn)	♂	♂	☉	☉	☉	☉	☉	☉	♂	♀	♂	♂	♂	☉ _(Alcohol)
(K ₂ CO ₃)	♂ _(Sb)	♀	☉	☉	☉	☉	☉	♂ _(Fe)	☉	♀	PC	♀	♂	♂	☉ _(Salt)
(Clay)	♀ _(Cu)	♂	☉	☉	☉	☉	☉	♀ _(Cu)	♂						
(Chalk)															
SM (Metals)	☉ _(Ag)	♀	☉		♂		♂	♂ _(Pb)	♀						
	♀ _(Hg)	☉	♂		♂			☉ _(Ag)	♂						
			♀					♂ _(Sb)	♂						
	☉ _(Au)		☉					♀ _(Hg)							
								☉ _(Au)							

Fig. 4.

☉_{c.} ☉_{m.} ☉_{c.} ☉_{m.}

Figure 1. A slightly modified version of Geoffroy's 1718 Table of Chemical Affinities (16). Photo courtesy of Richard P. Johnson.

2) although not listed in Column 9. Its reduction potential (Sn^{2+} , -0.13 V) makes it significantly easier to reduce than iron. Thus, tin and copper, the elements of bronze, were easier to smelt (reduce their sulfide ores) than iron. The Bronze Age began around 3000 B.C. while the Iron Age began around 1200 B.C. A serious definition of a chemical element by Antoine Lavoisier would still be some seventy years in the future and the concept of atomic weights by John Dalton (1766-1844), an additional twenty years (Table 1). It is easy to see from our modern perspective the problems in this table arising from experimental errors, assumptions that gases such as hydrogen, nitrogen and oxygen are monoatomic rather than diatomic, and that the "ultimate particles" of water and ammonia were simply HO and NH. Dalton continued to hold these views well beyond the wide acceptance of more correct stoichiometries (17).

Table 1. Partial list of John Dalton's first table of "Atomic" Weights ("of the relative weights of the ultimate particles of gaseous and other bodies," 1805) (18)

Hydrogen	1
Azot (Nitrogen)	4.2
Carbone	4.3
Ammonia ("HN")	5.2
Oxygen	5.5
Water ("HO")	6.5
Phosphorus	7.2
Gaseous Oxide of Carbon (CO)	9.8
Sulphur	14.4
Sulphurated hydrogen ("HS")	15.4
Carbonic Acid (CO ₂)	15.3
Carburetted hydrogen ("H ₂ C") from stag. water ^a	6.3

^a Carburetted hydrogen (CH₄) isolated from bubbles arising from swamps (stagnant water) and reported by Alessandro Volta (1745-1827) in 1777.

The next twenty-five years following Dalton's atomic theory were critical ones for placing it on a more solid foundation. The gas laws provided greater understanding of the actual combination ratios to form molecules (19). Gay-Lussac demonstrated that two volumes of hydrogen gas combine with one volume of oxygen gas to form water (19). In 1811, Amedeo Avogadro (1776-1856) published his major work, now referred to as Avogadro's Law: under the same conditions of temperature and pressure, equal numbers of ultimate particles occupy equal volumes (19). Avogadro's nomenclature was confusing to those who read the work of this somewhat obscure academician. Its full impact would only be appreciated a half century later and truly set the stage for the periodic table. In 1814, André Marie Ampère (1775-1836) independently concluded that equal numbers of particles occupy equal volumes (19). In 1819, chemist Pierre Louis

Dulong (1785-1838) and physicist Alexis Thérèse Petit (1791-1820) demonstrated that “atomic heat,” the product of specific heat (heat/mass) and atomic weight (mass/atom), was nearly constant for the 13 elements they reported (19).

Some credit William Prout (1785-1850) with the first numerical relationship between atomic weights (19). During 1815-1816 he compiled a table of densities of gaseous elements that were whole-number multiples of hydrogen. This suggested hydrogen as a sort of *primary material* constituting the mass of all other elements. As early as 1816-1817 Johann Wolfgang Döbereiner (1780-1849) observed that the atomic weight of strontium (accepted as 50 at the time), whose chemical properties were similar to calcium (27.5) and barium (72.5), was essentially the average of the other two (19). This *triad* might be considered as the first periodic relationship. During 1818-1819 Eilhardt Mitscherlich (1794-1863) related crystal structures and atomic composition (19). For example, phosphates and arsenates (*e.g.*, $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ and $\text{Na}_2\text{HAsO}_4 \cdot 12\text{H}_2\text{O}$) were found to be isomorphs, very similar crystal structures and analogous chemical compositions. Similar results were found for sulfates and selenates (*e.g.*, Na_2SO_4 and Na_2SeO_4). Today we recognize P and As in Group 15 (old VA) and S and Se in Group 16 (old VIA) of the modern periodic table. In 1818, Jöns Jakob Berzelius (1779-1848) published the most accurate known list of the atomic weights of 45 of the 49 elements known at the time (20). He extended this table with new discoveries in 1826 by which time there were 52 known elements. By 1829, other *triads* were recognized: lithium, sodium, potassium; sulfur, selenium, tellurium; manganese, chromium, iron. Döbereiner must have been elated that the atomic weight for the newly-discovered element bromine (1826), was the average of the atomic weights of chlorine and iodine. The isolation of fluorine was still some six decades away (but more on that later!). In 1826, Jean Baptiste André Dumas (1800-1884) developed a vapor density technique that established that gaseous elements, such as oxygen and chlorine, occur as diatomics, and that white phosphorus actually consists of P_4 molecules (19).

Efforts to systematize the elements continued during the 1840s and 1850s even with the uncertainties in atomic weights and uncertainties in stoichiometry. Thomas Graham (1805-1869) postulated eleven classes of elements based upon isomorphisms and chemical affinities (*e.g.*, **First Class:** oxygen, sulfur, selenium, tellurium; **Fifth Class:** chlorine, iodine, bromine, fluorine) (21) which influenced Mendeleev’s early thinking (22). In 1854, Josiah

P. Cooke (1827-1894), Erving Professor of Chemistry at Harvard, published a paper relating atomic weights and chemical properties and providing a classification of elements into six series according to crystallographic systems. Here is Professor Cooke describing the need to better organize the chemical elements (23):

In most elementary text-books on chemistry, the elements are grouped together with little regard to their analogies. Oxygen, hydrogen and nitrogen are usually placed first, and therefore together although there are hardly to be found three elements more dissimilar; again, phosphorus and sulphur, which are not chemically allied, are frequently placed consecutively, while arsenic, antimony, and bismuth in spite of their close analogies with phosphorus, are described in a different part of the book.

As well as to teach more effectively:

As chemistry is usually taught, the properties of the members of this series, nitrogen, phosphorus, arsenic and antimony, as well as the composition and properties of their compounds, make up a large body of isolated facts, which, though without any assistance for his memory, the student is expected to retain. Certainly, it cannot be wondered at, that he finds this a difficult task. The difficulty can, however, be removed if after he has been taught that nitrogen... (reacts) with three equivalents of hydrogen to form NH_3 , he is also told, that, if in these symbols of the nitrogen compounds he replaces N by P, As, or Sb, he will obtain symbols of similar compounds of phosphorus, arsenic or antimony.

The Impact of the Karlsruhe Conference of 1860

The uncertainties in the atomic weights of some elements and questions about stoichiometry prompted August Kekulé (1829-1896) to suggest the first major international meeting of European chemists, arguably the most important meeting in the history of chemistry (24). Kekulé and Charles-Adolph Wurtz (1817-1884) were the meeting organizers and Karl Weltzien (1813-1870), the host in the city of Karlsruhe, in September 1860. Among the 140 attending the meeting were chemists who would play major roles leading up to the periodic law: Jean Servais Stas (1813-1891, Belgium), Dumas (France), Julius Lothar Meyer (1830-1895, Germany), William Odling (1829-1921, England), Mendeleev (Russia) and Stanislao Cannizzaro (Italy). Cannizzaro’s 1858 pamphlet (25) and presentation in Karlsruhe clarified Avogadro’s half-century-old definition of atoms and molecules and

elements that fell on a line (14). John Alexander Reina Newlands (1837-1898) was an industrial chemist whose brief publications, in the *Chemical News*, beginning in 1863 were later collected into his 1884 book *On the Discovery of the Periodic Law and on Relations among Atomic Weights*. In 1864 he published an early version of his table of elements and commented that elements seven places apart frequently had similar properties (e.g., nitrogen (sixth) and phosphorus (thirteenth)). In 1865 he described this as a “Law of Octaves” similar to music (e.g., high C is the eighth note above middle C and twice the frequency) and he published a table of 62 elements highlighting chemical relationships. William Odling also published a table of elements in 1864, arranged in order of atomic weights and recognizing patterns in the atomic weights of elements having similar properties. Danish-born-and-educated Gustavus Hinrichs (1836-1923), published a helical table of the elements in 1867, while a faculty member at the University of Iowa (29). Probably the strongest claimant to some share of the credit for the periodic law was Julius Lothar Meyer. In 1868 he produced a table of elements meant to be included in a new edition of his textbook, but that table was never published. Intriguingly, his table not only left a gap in the carbon family between silicon and tin, it estimated an atomic weight (73) for the missing element that interpolated them. Meyer finally published his revised table of elements in 1870, very similar to Mendeleev’s 1869 table although not claiming originality (14).

Initially, the organizing relationship between elements was valence (e.g., Na_2O , CaO), so recently formalized by Edward Frankland (1825-1899) as well as Kekulé (30). But almost immediately it appeared quite reasonable to Mendeleev to build the periodic table according to increased atomic weight in combination with similarities in chemical and physical properties. At first glance it works quite well. But there were subtle inconsistencies that defied simple explanation. As reasonable as it appeared, almost a half-century later strict arrangement in accord with atomic weights was shown to be the incorrect approach. So why did Mendeleev settle on atomic weights for his ordinal arrangement of elements? Here Eric Scerri offers what he terms the “core philosophical idea of the periodic system” (30). He writes that Mendeleev differentiated *simple substances* and *elements*. Scerri employs an example to make his point. As we all enjoy teaching our students, the violently reactive, poisonous metal sodium combines with the violently reactive, poisonous gas chlorine to form table salt. Does sodium remain sodium, chlorine remain chlorine and the two somehow display

affinity and combine in salt? Metallic sodium and gaseous chlorine are, according to Mendeleev, the familiar *simple substances* that exist prior to their combination. An *element* is, however, a more abstract thing and exists in some form in the compound. Thus, sodium is no longer a highly reactive, toxic metal and chlorine no longer a highly reactive toxic gas when combined in table salt. The chemical properties of these two simple substances are not invariant but change drastically in compounds. In contrast, all experimental data support the view that from element to compound to new compound, atomic weights remain invariant. Therefore, using this invariant, intrinsic property to order and classify the elements appears to have been a most sensible approach. Figure 3 is an image of Mendeleev’s the periodic table printed in the first edition of *Osnovy Khimii* (31). P. A. Druzhinin makes the compelling case for this being the first printed version (32).

ОПЫТЪ СИСТЕМЫ ЭЛЕМЕНТОВЪ,
ОСНОВАННОЙ НА ИХЪ АТОМНОМЪ ВѢСѢ И ХИМИЧЕСКОМЪ СХОДСТВѢ.

		Ti=50	Zr=90	?=180.
		V=51	Nb=94	Ta=182.
		Cr=52	Mo=96	W=186.
		Mn=55	Rh=104,4	Pt=197,4
		Fe=56	Ru=104,4	Ir=198.
		Ni=Co=59	Pt=106,6	Os=199.
H=1		Cu=63,4	Ag=108	Hg=200.
Be=9,4	Mg=24	Zn=65,2	Cd=112	
B=11	Al=27,4	?=68	Ur=116	Au=197?
C=12	Si=28	?=70	Su=118	
N=14	P=31	As=75	Sb=122	Bi=210?
O=16	S=32	Se=79,4	Te=128?	
F=19	Cl=35,5	Br=80	I=127	
Li=7	Na=23	K=39	Rb=85,4	Cs=133
		Ca=40	Sr=87,6	Ba=137
		?=45	Ce=92	Pb=207.
		?Er=56	La=94	
		?Yt=60	Di=95	
		?In=75,6	Th=118?	

Figure 3. Mendeleev’s first printed periodic table from 1869 *Osnovy Khimii* (Principles of Chemistry) (31) (from the collection of Gregory S. Girolami and Vera V. Mainz).

Mendeleev's Successful Predictions of New Elements

The unique triumph of Mendeleev's periodic law was his daring prediction of three unknown elements corresponding to gaps in the table: *ekaboron*, *eka-aluminum* and *ekasilicon* including the prediction of their physical and chemical properties (*eka* = "one" in Sanskrit implying one beyond). Partington comments: "The publications of Lothar Meyer in 1870 and Mendeléeff in 1871 attracted very little interest" (14). This changed abruptly when Paul Émile Lecoq de Boisbaudran (1838-1912), working in the laboratory of Wurtz in Paris, discovered *eka-aluminum* (gallium) via spectroscopy in 1875 (33). In 1879, the Royal Society awarded Lecoq de Boisbaudran the Davy Medal (named for the great early nineteenth century chemist Humphry Davy, 1778-1829) for this ground-breaking discovery. Lars-Fredrik Nilson (1840-1899), working in Uppsala Sweden, reported *ekaboron* (scandium) in 1879 (34). In 1882, the Royal Society presented the Davy Medal jointly the Mendeleev and Meyer ("For the discovery of the periodic relations of the atomic weights"). In the preface to his aforementioned 1884 book, Newlands states (35):

Having been the first to publish the existence of the periodic law more than nineteen years ago, I feel, under existing circumstances, compelled to assert my priority in this matter.

Among his claims, Newlands mentions his "Prediction of the atomic weight of missing elements, such as the missing element of the carbon group = 73, since termed *eka-silicium* by M. Mendelejeff" (35). Clemens Alexander Winkler (1838-1904), in Freiberg Germany, reported *ekasilicon* (germanium) in 1886 (36). Its atomic weight is 73. In 1887, Newlands received the Davy medal from his fellow countrymen ("For his discovery of the periodic law of the chemical elements").

Before moving on, let us spend a moment on the topic of "simultaneous discoveries" in chemistry. Perhaps the classic is the discovery of oxygen. It is popularly credited to Englishman Joseph Priestley (1733-1804) who made his discovery in 1774 and published first in 1775 (37). However, the discovery of "fire air" was made first in Uppsala, Sweden by Carl Wilhelm Scheele (1742-1786) somewhere between 1770 and 1773, but publication was delayed until 1777 (38). Priestley was unaware of Scheele's discovery (38). Both Priestley, who named the newly-discovered gas "dephlogisticated air," and Scheele were proponents of the phlogiston theory that would soon be totally discredited by Lavoisier. Since

the purpose of the present article is to stimulate interest in incorporating history of chemistry into the introductory course, let us "give a plug" to the play *Oxygen*, authored by the distinguished chemists Carl Djerassi and Roald Hoffmann, authors of novels, plays and poetry (39). They imagine the first "retro-Nobel Prize" and a dramatic debate among a modern committee about the appropriate awardee(s) (Lavoisier, Priestley or Scheele or some combination). It is instructive and fun for students (and teachers) to perform the play in full or even in part in class. Perhaps an even more striking case of simultaneous discoveries is the near-simultaneous publications in 1874 of the tetrahedral carbon by Jacobus Henricus van't Hoff (1852-1911) and Joseph Achille Le Bel (1847-1930) who knew each other while working in close proximity in Wurtz's Paris laboratory. Their papers took very different approaches reaching similar conclusions and were developed totally independently (40). In the case of the periodic table, the Karlsruhe conference stimulated the contributions to the periodic law that almost immediately followed. For van't Hoff and Le Bel, one can argue that the advancement of structural organic chemistry during the prior two decades set the stage for the next logical steps climbed virtually simultaneously by two young chemists. Let us also note Jeffrey Seeman's discussion, including a very thorough taxonomy, of "Multiple Simultaneous Independent Errors" in contrast to "Multiple Simultaneous Independent Discoveries" (41). He provides the example of two research groups independently publishing the same incorrect structure for the newly-discovered organometallic molecule ferrocene. Indeed, Scheele's and Priestley's adherence to phlogiston theory to explain combustion, even as they each discovered oxygen, is another example.

On June 4, 1889, Mendeleev delivered the Faraday Lecture before Fellows of the Chemical Society in the Theatre of the Royal Institution (42). He lauds the contributions by Cannizzaro at Karlsruhe that clarified the difference between atomic and equivalent weights and dismisses some details of Newlands' periodic table, noting for example, that some of Newlands' octaves had ten elements with two elements occupying the same space (e.g., Co and Ni). Mendeleev admits to not knowing the physical origin of atomic weights but dismisses Prout's revival of the ancient Greek concept of a *prima materia*, noting that while some had assigned the 0.0005875 mm line in the sun's corona to a new element ("helium"), others equated it to the primary material. Mendeleev also rejects "helium" since it was not observed outside the sun's flares; he considered it an artifact of high temperature and pressure on the spectrum of a solar element,

perhaps hydrogen. Proudly referring to the discoveries of gallium, scandium and most recently germanium, Mendeleev declared (42):

When, in 1871, I described to the Russian Chemical Society the properties, clearly defined by the periodic law, which such elements ought to possess, I never hoped that I should live to mention their discovery to the Chemical Society of Great Britain as a confirmation of the exactitude and the generality of the periodic law.

He then went on to predict the existence and, in considerable detail, the physical and chemical properties of “dvi-tellurium” (*dvi* = two in Sanskrit). The element in question was ultimately radioactive polonium, discovered by Marie and Pierre Curie in 1898 (43). (Radioactivity was unknown in 1889.)

Solutions to Mendeleev’s Confusion on “Inverted” Atomic Weights: Isotopes and Atomic Numbers

Among the small discrepancies that still existed among atomic weights even after the superb experimental work by Stas, the anomaly between tellurium and iodine depicted in Table 2 was particularly vexing to Mendeleev. He clearly recognized the appropriate placement of iodine below bromine and tellurium below selenium despite the significant reversal in atomic weights. Mendeleev was confident that future experimental analyses would place these elements in their proper order of atomic weights.

Prout’s rule, simple and attractive as it was, led to considerable confusion once it was more closely examined. In Berzelius’ 1826 table, the atomic weight of chlorine was listed at 35.4 (hydrogen = 1). Thomas Thomson (1773-1852), a respected chemist, published a table of atomic weights in 1825, which were, conveniently, whole number multiples of hydrogen including chlorine which he rounded up to 36. To this, Berzelius wrote (19):

Much of the experimental part, even of the fundamental experiments, appears to have been made at the writing desk; and the greatest civility which his contemporaries can show its author, is to forget that it was ever published.

Working with Josiah Cooke at Harvard, his student Theodore William Richards (1868-1928) was able to very carefully check and slightly modify Stas’s atomic weights. Cooke and Richards demonstrated that the accurate atomic weight ratio of oxygen to hydrogen was 15.95, not 16.00 (44). Richards would join the Harvard faculty, later determining that cobalt is indeed heavier

than nickel (45, 46) despite the seeming anomaly (Table 2).

Today we recognize that one major problem for Mendeleev was the absence of knowledge of isotopes during his lifetime (see Table 2). During 1906 and 1907, the year Mendeleev died, a number of researchers investigated the elements produced by radioactive decay (47). In 1913, Frederick Soddy (1877-1956), one of the principal researchers in this newly-emergent field of radiochemistry, defined isotopes as examples of the same element differing only in atomic weight (47). Soddy would win the 1921 Nobel Prize. Richards, continuing his careful redetermination of atomic weights discovered that naturally-occurring lead and lead derived from radioactive decay were isotopes (47). He won the Nobel Prize in Chemistry in 1914, the first American so honored. In 1919, Francis William Aston (1877-1945), with his early mass spectrometer (1922 Nobel Prize in chemistry), an instrument that separates positive ions based upon mass/charge differences, discovered two isotopes of neon: the first identification of non-radioactive isotopes (47). The underlying difference between isotopes was the neutron which would await James Chadwick’s (1891-1974) discovery in 1932 (48) (1935 Nobel Prize in Physics).

Table 2. Problems in placing elements in strict order of atomic weight (modern atomic weights listed based upon ^{12}C).

ELEMENTS SEEMINGLY OUT OF ORDER:

15 (VA)	16 (VIA)	17 (VIIA)
As	Se	Br
74.92	78.97	79.90
Sb	Te	I
121.76	127.60	126.90

9 (VIII)	10 (VIII)
Co	Ni
58.93	58.69

Returning to the seeming anomaly between iodine and tellurium, while the isotope ^{127}I comprises virtually 100% of the naturally-occurring element, there are six significant naturally-occurring tellurium isotopes with the heaviest, ^{130}Te , comprising 34.1%. Cobalt is virtually 100% ^{59}Co , while the lightest isotope, ^{58}Ni , is the most abundant (68.1%) of nickel’s five major isotopes.

Henry G. J. Moseley (1887-1915) studied the series of certain X-rays (termed K_{α}) emitted from different

metallic anticathodes (48). He observed a near-perfect linear relationship when plotting the square root of their frequencies versus simple ordinal numbers (1, 2, 3, ...). These *atomic numbers* determine the true order of elements in the periodic table. Thus, the final clarification of Mendeleev's worries about inconsistencies in order occurred not long after his death. Moseley, who volunteered to fight in the First World War, was killed at the age of 28 in the disastrous Battle of Gallipoli (48).

Mendeleev's Helium and Argon Problem

Mendeleev's skepticism about the discovery of helium was noted earlier. Observed close to the doublet of sodium D-lines (49), the new solar emission reported by Joseph Norman Lockyer (1836-1920) was designated D₃. Lockyer and Frankland unsuccessfully attempted to reproduce the line by putting known elements under extreme conditions. Although these investigators did not formally attribute the line to a new element, such an explanation circulated widely among chemists and astronomers (50). The name "helium" (after the Greek *helios* = sun) is attributable to Lockyer (51). Part of Mendeleev's problem with helium was that he could not envision a place for this lone element in his periodic table. But the other part was that there were no earthly samples that could be checked for the D₃ line spectroscopically or analyzed for physical and chemical properties.

Precise measurement of atomic mass occupied many scientists during the second half of the nineteenth century and into the early twentieth century. John William Strutt (1842-1919, Lord Raleigh), a physicist, demonstrated even greater precision than Cooke and Richards with an O/H atomic weight ratio of 15.869 (44). He then set his sights on nitrogen, the most abundant element in the earth's atmosphere and encountered a conundrum. The density of atmospheric nitrogen was 0.535 percent greater than that of nitrogen obtained from pure chemical compounds. He communicated with chemist William Ramsay (1852-1916) who carefully ran atmospheric air through a series of chemical traps, removing CO₂ and H₂O using soda lime and Fe₂O₃, followed by red hot copper to remove O₂ and finally bright red hot magnesium to remove N₂. The remaining unreacted gas accounted for nearly 1% of the atmosphere, with a density twenty times that of H₂. Particularly unsettling, the ratio of specific heats at constant pressure to constant volume (C_p/C_v) was consistent with a monoatomic gas, the only precedent being mercury vapor. Rayleigh and Ramsay announced their findings in August 1894, published their discovery in the *Philosophical Transactions of the Royal*

Society in 1895 and their Hodgkin's Prize-winning paper was published by the Smithsonian Institution in 1896 (52). This paper even acknowledged Henry Cavendish (1731-1810) who, in 1785, isolated a totally unreactive bubble comprising 1/120 of his original air sample. Over a century after Cavendish, the gas was named "Argon" (Greek = "inactive") (53). Rayleigh received the 1904 Nobel Prize in Physics and Ramsay the 1904 Nobel Prize in Chemistry.

Mendeleev was very discomfited by this discovery. There was apparently no place in the periodic table for argon. Assuming it really was monoatomic, its atomic weight might somehow squeeze it between potassium (39) and calcium (40) with chemistry totally unlike these metallic elements. Very skeptical about the discovery, Mendeleev postulated that argon was very possibly N₃ (molecular weight 42). Although the oxygen allotrope ozone (O₃) was known, it was far more reactive than the common atmospheric gas. It would seem something of a stretch to assume that a putative nitrogen allotrope (N₃) would be even less reactive than N₂ and that the atomic weight of a totally unreactive gas could be in error by some five percent.

As early as 1888, mineralogist William F. Hillebrand (1853-1925) of the U.S. Geological Survey discovered that minerals containing uranium, such as cleveite, included tiny quantities of an unreactive gas. In January 1895 the British mineralogist Henry Miers wrote to Ramsay about Hillebrand's work, and Ramsay purchased some cleveite intending to analyze what gas might be trapped within. In March 1895, Ramsay and William Crookes (1832-1919) demonstrated that its emission spectrum (D₃ line) corresponded to the solar element and thus, helium was indeed an earthly element (54). In 1904, the cleveite mystery was solved when Ramsay and Soddy established that α -particles emitted from radium were, effectively, helium.

Not long after the discoveries of argon and helium, Ramsay applied newly-discovered techniques for liquifying air and in 1898, with his graduate student Morris William Travers (1872-1961), detected and characterized neon (Ne), krypton (Kr) and xenon (Xe). Here is Travers writing about the first detection of neon (55):

We each picked up one of the little direct-vision spectroscopes which lay on the bench. But this time we had no need to use the prism to decide whether or not we were dealing with a new gas. The blaze of crimson light from the tube told its own story, and it was a sight to dwell upon and never forget.

Series	Zero Group	Group I	Group II	Group III	Group IV	Group V	Group VI	Group VII	Group VIII			
0	<i>x</i>											
1	<i>y</i>	Hydrogen H=1.008										
2	Helium He=4.0	Lithium Li=7.03	Beryllium Be=9.1	Boron B=11.0	Carbon C=12.0	Nitrogen N=14.04	Oxygen O=16.00	Fluorine F=19.0				
3	Neon Ne=19.9	Sodium Na=23.05	Magnesium Mg=24.1	Aluminium Al=27.0	Silicon Si=28.4	Phosphorus P=31.0	Sulphur S=32.06	Chlorine Cl=35.45				
4	Argon Ar=38	Potassium K=39.1	Calcium Ca=40.1	Scandium Sc=44.1	Titanium Ti=48.1	Vanadium V=51.4	Chromium Cr=52.1	Manganese Mn=55.0	Iron Fe=55.9	Cobalt Co=59	Nickel Ni=59	(Cu)
5		Copper Cu=63.6	Zinc Zn=65.4	Gallium Ga=70.0	Germanium Ge=72.3	Arsenic As=75.0	Selenium Se=79	Bromine Br=79.95				
6	Krypton Kr=81.8	Rubidium Rb=85.4	Strontium Sr=87.6	Yttrium Y=89.0	Zirconium Zr=90.6	Niobium Nb=94.0	Molybdenum Mo=96.0		Ruthenium Ru=101.7	Rhodium Rh=103.0	Palladium Pd=106.5 (Ag)	
7		Silver Ag=107.9	Cadmium Cd=112.4	Indium In=114.0	Tin Sn=119.0	Antimony Sb=120.0	Tellurium Te=127	Iodine I=127				
8	Xenon Xe=128	Cæsium Cs=132.9	Barium Ba=137.4	Lanthanum La=139	Cerium Ce=140							(—)
9												
10				Ytterbium Yb=173		Tantalum Ta=183	Tungsten W=184		Osmium Os=191	Iridium Ir=193	Platinum Pt=194.9 (Au)	
11		Gold Au=197.2	Mercury Hg=200.0	Thallium Tl=204.1	Lead Pb=206.9	Bismuth Bi=208						
12			Radium Rd=224		Thorium Th=232		Uranium U=239					

Figure 4. Mendeleev's hypothesis of element "x" comprising the "celestial ether" (56). Photograph courtesy of Richard P. Johnson.

Clearly, a new chemical family, a group of inert gases, existed and did indeed fit at the end of the periodic table. But which end: left or right? The right-hand side would place the group next to other non-metals (the halogens, Group VII) including two gases. Placement on the left-hand side would have them neighboring the alkali metals, but also hydrogen (Group I). Since the new gases were zero-valent, placing them in Group Zero to the left of Group I would appear to make some sense although this led to other problems.

Is The Celestial Ether Composed of Inert Gas Element "x" (Atomic Weight 0.00000096 or less)?

The wave nature of light was fully established in the nineteenth century. Just as air is required to carry sound waves, could an all-surrounding "fabric," an invisible "celestial ether" be required to carry light waves? Since the earth presumably moves through this stationary ether, the velocity of light should vary when measured in different directions. Physicist Albert Abraham Michelson (1852-1931) began an investigation in Germany in 1880-81 and, working in the United States, with chemist Edward W. Morley (1838-1923). In 1887,

they discovered that the velocity of light is independent of direction, a crucial indicator that there is no "celestial ether." Michelson received the 1907 Nobel Prize in physics. Nevertheless, Mendeleev remained a believer and in 1902 published a pamphlet in Russian [1904 English translation, *An Attempt Towards A Chemical Conception of the Ether* (56)]. By this time, fully accepting the inert gases (Group Zero), he conceived of unimaginably light inert gas atoms capable of fully penetrating matter (57). Instead of the interpolating logic of Döbereiner, nearly ninety years earlier, Mendeleev used extrapolation on Group Zero. Since Helium could be classified in Period 2 Group Zero (Figure 4), there should be an element ("y"), the putative "coronium" (58, 59), in Period 1 Group Zero. Its atomic weight extrapolated to 0.4 (hydrogen = 1.0), clearly too massive for atoms of the celestial ether. So, Mendeleev invoked element "x," in Period Zero Group Zero, as the element comprising the celestial ether. He estimated its atomic mass as 0.00000096 or much lighter (hydrogen = 1).

Here is Mendeleev explaining his hypothesis of atoms lighter than hydrogen with reference to his original (1869) periodic table (56):

... although I had a vague notion that hydrogen might be preceded by some elements of less atomic weights,

I dared not put forward such a proposal, because it was purely conjectural, and I feared to injure the first impression of the periodic law by its introduction.

How does one come to grips with a theory that one might even consider “crank science”? Mendeleev was so strongly wedded to his periodic table, validated by his amazing predictions of new elements, that he may have misled himself into “cramming” ether theory into his periodic law (60). One can imagine an analogy here. Books depicting dinosaurs in the late nineteenth century included pictures like those in Figure 5. What were the origins of these strange images? Fossils are not discovered neatly arranged in skeletons. Rather, once discovered and typically incomplete, they were assembled during the nineteenth century according to contemporary knowledge and experience. The largest land-roaming carnivores were bears. So why not assemble megalosaurus to look like a bear? In the case of the vegetarian iguanodon, also assume a four-legged beast. Today we know that both these dinosaurs were bipedal and mostly vertical. Just as these constructions involved “cramming” fossil bones into pre-conceived skeletal configurations, so too did Mendeleev fall into the trap of “cramming” ether theory into the periodic law.

No Nobel Prize for Mendeleev: Strange Goings-On in Sweden

It does come as a disappointment and indeed almost a shock to learn that Mendeleev did not win a Nobel Prize. The details (61) are not pretty. When Nobel prizes were first awarded in 1901, they were intended to recognize recent research. However, the 1905 Nobel Prize in chemistry was awarded to Adolph von Baeyer

(1835-1917) in recognition of his work on dyes and other contributions to organic chemistry significantly accomplished in the 1860s. Invoking a rule that allowed recognition of older advances achieving importance in recent times cleared the way for Baeyer and opened the door in 1906 for Mendeleev. Although the periodic law was almost forty years old, more recent discoveries, including the predicted elements and comfortable fit of the noble gases into the periodic table, satisfied these criteria. In 1905, Mendeleev and Ferdinand Frédéric Henri Moissan (1852-1907), who isolated fluorine developed the electric furnace, were the most significant competitors to Baeyer. In 1906, despite more previous nominations and votes for Moissan, the five-person chemistry Nobel committee voted four-to-one in favor of Mendeleev. However, the dissenting vote, Peter Klason, Royal Institute of Technology in Stockholm, argued strenuously against this choice. One line of argument, incredibly enough, was that the periodic table was already in use worldwide-effectively “old news.” The argument was also made that the periodic law could not have been developed without Cannizzaro’s clarifications of Avogadro’s law. Therefore, a Nobel awarded to Mendeleev must be shared with Cannizzaro. However, since Cannizzaro had not been nominated earlier in 1906 for the prize, he was ineligible for the award that year. The Swedish Academy, which would normally “rubber stamp” the recommendation of the chemistry committee, added four distinguished chemists to the committee, hoping for clear consensus. The augmented committee proceeded to vote five to four in favor of Moissan who duly received the 1906 Nobel Prize. There was another major obstacle between Mendeleev and the Nobel Prize: Svante Arrhenius (1859-1927, 1903 Nobel Prize in chemistry). Mendeleev had been critical of the ionic theory of Arrhenius and this

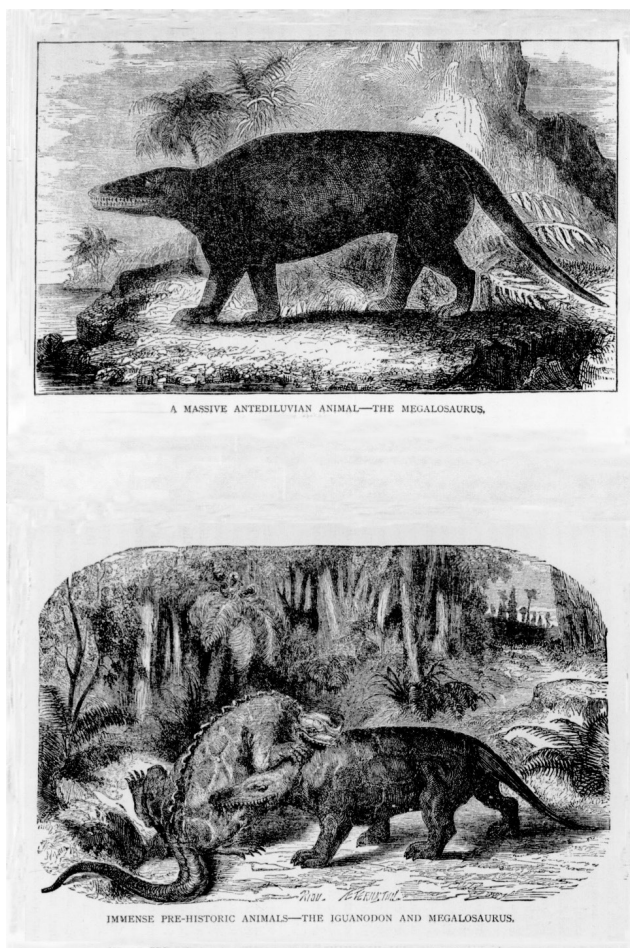


Figure 5. Nineteenth century depictions of dinosaurs formed by “cramming” fossil remains into pre-conceived models of large land animals (60).

earned him a degree of antipathy from the great Swedish scientist (8). In early 1907, Mendeleev died. Nobel prizes are not awarded posthumously. As the authors note (61), October 27, 1906, when the committee voted for Moissan "...is not one of its more glorious days." How ironic that Moissan died in 1907, having just been awarded the 1906 Nobel Prize, while Mendeleev died in 1907 having just missed the 1906 Nobel Prize. There is some poetic justice in that among the names cited earlier, most closely associated with the development of the periodic table, there is only the eponymous element, Mendeleevium (Md, $Z = 101$), and it precedes Nobelium (No, $Z = 102$).

Conclusions

There is enough content in introductory chemistry courses to discourage adding history of chemistry. However, teaching how science is "done," beyond the formulaic "scientific method," is really critical, especially at a time when the process itself is under populist pressure. It is important to teach young scientists that doing science is not the same as learning settled science. In the former, the right answers are not known (or at least not yet known). Scientists at the forefront of new knowledge often propose explanations that are later seen to be incorrect or inadequate. As inspiring as is the history of discovery that led to the science taught in textbooks (such as the periodic table), it is also important for students to see that not all of the work of even the most successful scientists stands the test of time. Mendeleev is hardly alone among scientists of the past about whom this point can be made; he is just one of the most likely to be mentioned in an introductory textbook.

Moreover, there is much to be said for "hands-on" learning. Performing the brief "masque" by the Lavoisiers in the play *Oxygen* (39) is one opportunity. The meeting between Werner Heisenberg and Niels Bohr, concerning the atomic bomb, in the play *Copenhagen* offers another opportunity explore the roles of scientists as human beings (62). And there was surely enough drama at the Karlsruhe conference to stimulate academic research and student performance.

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About the Author

Arthur Greenberg was born in Brooklyn, New York and received his Ph.D. in chemistry from Princeton University (1971). He retired in May 2021 following twenty-one years at the University of New Hampshire as Dean of Engineering and Physical Sciences (2000-2005) and Professor of Chemistry (2000-2021).

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