

The article below was prepared for a High School audience.

The Periodic Table of the Elements

Look on the walls of chemistry classrooms or laboratories in any country of the world and you will see a table of roughly 100 elements arranged to look something like a bed. (See Figure 1 at <http://www.dayah.com/periodic/>.) Boxes containing the letters H and He (the international symbols for hydrogen and helium) are stacked like bedposts on top of columns labeled as I and VIII respectively. Chemistry students quickly learn that the answers to many exam questions can be gleaned from the periodic table, once you know how to use it! The atomic number of each element tells how many protons are in the nucleus; the Roman numeral of the column is an indication of the valence or combining power of the element. Since lithium is in column I (under hydrogen) but beryllium is in column II, then we expect the formula of lithium chloride to be LiCl while beryllium chloride is BeCl₂. We also expect family resemblances between elements in the same column. For example, in column II a couple of squares under Be, we find Ca for calcium and right under it Sr for strontium. Knowing that calcium is an important component of bones, we aren't surprised to hear that its neighbor strontium is also found in the skeleton. This family relationship explains why during the period of atom bomb testing scientists were very concerned that a radioactive isotope of strontium (called Sr-90) might end up in milk just like calcium and be absorbed into the bones of growing children.

How did scientists come up with the idea for such a valuable table? How has it changed as we learn more about the world? And exactly why does it summarize so much useful chemical information? We will trace very early attempts to understand what chemical elements are and how they should be classified. Aristotle, Boyle and Lavoisier play important roles in this story, but the discoverer of the periodic system was Mendeleev. Ironically, he had no idea what the true basis of his table was! He thought the chemical characteristics of an element depended on its atomic weight. We now know that the key concept is atomic number. Yet following the reasoning processes of people like Mendeleev, even when their result is not exactly the right answer, will teach us a lot about how science progresses. (See also the article on scientific method.)

The Greek Theory of Four Elements

Modern science has its roots in the way Greek philosophers such as Aristotle (384-322 B.C.) thought about the natural world. Even earlier, ancient Babylonians had made careful astronomical observations and the Egyptians had developed elaborate metallurgical techniques for refining copper and making alloys of gold. What the Greeks added to this practical knowledge was an interest in asking about the underlying causes of things that happened in nature and in looking for fundamental principles. (See the article on Natural Philosophy.) The most familiar use of the word *element* was in the title of a geometry book. Euclid's *Elements* systematized everything that was known about the properties of triangles and circles by deriving theorems from five simple axioms.

Aristotle tried to find the fundamental elements of materials, such as solids, liquids and gases. He expressed his goal this way: "We are looking for the 'originative sources' of perceptible bodies." He wanted to understand the origins of their properties and how changes in their appearances take place. And he assumed that there would be only a few, simple "originative sources." Since we now know there are over a hundred chemical elements, it is no surprise that his system didn't work very well. But let's try to understand its appeal at the time.

Aristotle postulated that there were four elements: earth, air, fire and water. There were also two pairs of contrary qualities: hot vs. cold and wet vs. dry. Each element was associated with two of these fundamental qualities. (See Figure 2 at http://web.clas.ufl.edu/users/rhatch/pages/03-Sci-Rev/SCI-REV-Teaching/HIS-SCI-STUDY-GUIDE/0023_4ElementsAndHumorTheory.html.) So, for example, fire was associated with hotness and dryness. Its opposite, water, was cold and wet. Adding water to fire would temper its hot, dry qualities and the result would be something in between. Aristotle emphasized that these four elements were usually not encountered in pure form. For example, both metals and sand were "earths," but a ductile metal such as gold probably was a combination of the pure element earth with the pure element water. Blood was a liquid, an indication of the presence of water, but because of its role in sustaining life, it probably contained an unusual amount of elemental fire.

Today Aristotle's theory of four elements strikes us as terribly simplistic and fanciful, but it was very influential for centuries. (You can find references to

these four elements in popular contemporary cartoon shows such as Captain Planet or Avatar.) Nevertheless, his basic attempt to explain the multiplicity of chemical materials in terms of a limited number of active ingredients still guides research today. However, we cannot leave the Aristotelian account on such a positive note. For his theory also allowed for the possibility that one material could *transmute* into another. Consider the Aristotelian account of what today we would call the water cycle. When the sun shines on water, the cold, wet water is turned into hot, wet air or steam. If heat is removed, we once again get water. On a very cold, dry day (rarely encountered in the Mediterranean) the water might be transformed into ice, a material that has the coldness and dryness characteristic of earth. This idea of impressing qualities on matter formed the philosophical basis for the alchemical project of turning base metals, such as lead, into gold.

Alchemical Active Principles

Our word *chemistry* comes from the Arabic word *al-khi-mia* which in turn comes from the Egyptian word *khem*. As the Roman Empire disintegrated there was less interest in learning. For example, the huge library in Alexandria that had been started by one of Aristotle's students was burnt on several occasions and was eventually destroyed. The Arab successors of Mohammed (d.632) soon occupied much of the Roman and Persian empires. The interest in natural philosophy then shifted east and became centered in Islamic cities such as Baghdad. Important Greek texts were translated into Syriac and Arabic. Egyptian texts had describe recipes for making alloys that looked like pure gold, but also alluded to the possibility of actually transmuting less valuable metals into gold. (See the article on Alchemy.) In their quest for what was sometimes called The Philosopher's Stone, Arab alchemists made many important chemical discoveries. They designed elaborate glassware and learned how to distill liquids. They synthesized the strong acids we call hydrochloric, sulfuric and nitric acids and used them to dissolve metals and react with soda, potash and lime.

These alchemists admired Aristotle and retained his idea of four elements. But the Aristotelian qualities of hot & cold, wet & dry seemed far removed from the properties of the new chemicals they were working with. So they postulated three additional fundamental principles: sulfur, salt and mercury. Like Aristotle's elements these were never encountered in pure form. "Philosophical sulfur" was not identical to the yellow powder used to fumigate unhealthy rooms, but it was responsible for the combustibility of

materials. “Salt” was the principle that underlay the reactivity of acids (when acids are neutralized they form ordinary salts) and “philosophical mercury” accounted for the malleability and shiny surfaces of metals.

Not surprisingly, ordinary mercury was a popular starting material in attempts to make gold. It is easy to laugh at stories of alchemists mixing up mercury, lead and some bright yellow material such as saffron, burying it in manure, and then warming the whole ensemble in an oven for weeks. Yet they could provide some plausible reasons for their recipes. It was widely believed that metals “grew” in mines. Often one would find nuggets of gold embedded in minerals containing copper. Perhaps copper or other metals were just immature forms of gold. If one could only speed up the growth process, maybe one could duplicate in the laboratory what nature did more slowly in the bowels of the earth. Manure appeared to be a likely catalyst. After all, little insects and maggots are formed in manure, so they believed. Therefore, it must have strong generative powers.

Muslim conquerors moved across North Africa and entered Spain in 711 A.D. The Arabs brought to Spain scientific writings in Arabic, both translated texts of the ancient Greeks and innovations of their Arab successors. Later, in the 12th and 13th centuries these writings were translated into Latin (often by Jewish scholars). The influx of these Greek texts (which had been preserved by the Arabs) along with Arabic contributions to natural philosophy accelerated the rebirth of learning in European universities. The German physician Paracelsus (1493-1541) was particularly taken with the three new alchemical principles and promoted them as part of the new doctrines that would outstrip the old dogmas of ancient Greece. Paracelsus, who was sometimes called “the Luther of physicians,” was quite a radical. He once burned copies of Aristotle’s and Galen’s books in a public bonfire at the University of Basel to show how dangerously outdated those theories were. Paracelsus introduced chemical medicines and recommended a mercury compound for the treatment of syphilis. (Luckily only small portions of this poison were prescribed!)

The Phlogiston Theory

Nearly two hundred years after Paracelsus, a German metallurgist and physician, Georg Ernst Stahl (1660-1734) modified the three-principle theory and used it to systematize a whole series of important reactions. He renamed the sulfurous principle “phlogiston” (from a Greek word for

burning) and claimed that it was forcibly expelled in all combustion reactions producing heat and light. To account for the fact that combustion won't occur unless there is lots of air around, Stahl claimed that the air was necessary to carry away the phlogiston! (See article on combustion.)

We now know that Stahl had it just backwards – when materials such as charcoal or sulfur burn, they are not decomposing. Instead, something from the air is added. The air is not acting as a passive receptacle for something that is given off; rather it is supplying oxygen, which combines with whatever is burning. The heat and light that is given off is energy produced by the oxidation reaction.

Yet Stahl was very successful in the way he used the phlogiston theory to systematize some important chemical reactions. He provides a good example of how scientists can make progress even when their starting assumptions are wrong. Stahl's first insight was to note the parallels between what happens when metals are heated in air and turned into a powder (a process he called "calcination") and ordinary combustion, such as when wood burns. Stahl noted that in both cases heat and light might be given off (perhaps you may have seen the sparks when iron filings are sprinkled into a flame) and that lots of air was required to keep the reaction going. (He would have said phlogiston was escaping while we know that oxygen is being combined, but we also recognize the parallel between the combustion of metals and nonmetals. Both are oxidation reactions.)

Then Stahl used his system to describe what happened when metallic ores were reduced to metals. He noted that copper miners often mixed the minerals they took from the ground with charcoal and heated them up while stirring the molten results with a green stick. Stahl reasoned that the metallic ores had lost their phlogiston. They were powdery just like the metal calxes that were the products of calcination. To turn them into shiny metals, one needed to add phlogiston. But he was convinced that charcoal was a rich source of phlogiston because it burned so well. So unbeknownst to them, the miners were transferring phlogiston from the charcoal into the metal ore and thus producing metals. Since the miners thought of the charcoal as only a fuel, not as an ingredient in a chemical reaction, they sometimes didn't add enough charcoal to reduce all of the metal present in the ore. So Stahl explained to them the necessity of doing so.

Stahl spoke of the reactions above as analyses and syntheses. In calcination, a metal was analyzed (separated) into a metallic powder and phlogiston. What the miners were doing was synthesizing the metal by combining the metallic ore with phlogiston that came from the charcoal. One of Stahl's students proposed the axiom that every analysis should be followed by a synthesis if one wanted to prove that one understood the composition of a material. Stahl certainly felt that he had proved that metals were compounds, not elements. Lavoisier was soon to use the same methods of analysis and synthesis to prove him wrong!

Lavoisier's Scientific Criterion for Chemical Elements

Aristotle thought of elements as "originative principles." Nearly two thousand years later the Irish chemist Robert Boyle defined elements as "... certain primitive and simple, or perfectly unmingled bodies; which not being made of any other bodies, or of one another, are the ingredients of which all those called perfectly mixt bodies are immediately compounded, and into which they are ultimately resolved." (The Sceptical Chymist, 1661) But how were chemists to determine exactly what these primitive and simple materials were? Aristotle had proposed four elements, earth, air, fire and water; the alchemists added salt, sulfur and mercury. Yet none of these so-called elements could be put in a bottle or experimented with. Remember that the alchemists' third element was "philosophical mercury," not the quicksilver that was used in barometers.

It was the French chemist and public servant Antoine Lavoisier who finally provided a workable definition of chemical element in 1789. Since it was impossible to reach agreement about the invisible constituents of bodies, Lavoisier proposed that

"...we apply the term *elements*, or *principles of bodies*, to express our idea of the last point which analysis is capable of reaching, we must admit, as elements, all the substances into which we are capable, by any means, to reduce bodies by decomposition." (*The Elements of Chemistry*)

Lavoisier recognized that the list of elements might change as chemists figured out how to further decompose complex materials. Thus he tentatively included lime and magnesia on his list, but noted that they might not be simple substances. (We now know they were oxides of calcium and

magnesium.) Yet an additional step was required before chemists could unambiguously agree on a list of elements. Stahl was dead by the time Lavoisier proposed his definition, but if he had been alive, he would have argued that metals were not elements! On his account metals contained phlogiston which was then freed upon heating. So phlogistonists considered a metal calx to be a simpler substance than a metal.

Lavoisier provided a direct way to show that metals were elements. He weighed the sample of metal, heated it in air and then weighed the powdery product. Since the calx was heavier, something must have been added in calcination. Through more elaborate experiments Lavoisier isolated the gas from the atmosphere that was absorbed during both calcination and combustion and called it oxygen.

Chemists rapidly accepted Lavoisier's new definition of element and adopted the helpful strategy of keeping track of the weights of products and ingredients. At the time Lavoisier published his *Traité élémentaire de chimie* (the English translation was called *The Elements of Chemistry*), there were 33 elements on his list, including the common metals, sulfur, arsenic, phosphorus, oxygen and nitrogen. Soon hydrogen and chlorine were discovered by means of electrolysis and by the time Mendeleev began his textbook, there were over 60 known elements, each with a set of distinctive chemical properties.

Assigning Atomic Weights

Throughout history many natural philosophers and chemists have speculated about the existence of atoms. Aristotle and much later Descartes thought that a vacuum would be physically impossible so they both rejected the Democritean theory of atoms in a void. (See article on atomic theory.) However, virtually everyone was willing to entertain the idea that matter might be composed of tiny corpuscles that would move closer together when gases were compressed. Yet as was the case with elements before Lavoisier, it seemed impossible to find out anything specific about these invisible particles. It was John Dalton, an English meteorologist and schoolteacher, who came up with the crucial inferences that made modern atomic theory viable.

In a book called *A New System of Chemical Philosophy* (1808), Dalton noted that it was now well established that when elements combined to make a

new compound, they almost always did so in the same proportion by weight. (Alloys were the exception.) So it seemed reasonable to assume that the compound always contains the same ratio of atoms. Dalton put it this way: “Therefore we may conclude that *the ultimate particles of all homogeneous bodies are perfectly alike in weight, figure, &c.* In other words, every particle of water is like every other particle of water; every particle of hydrogen is like every other particle of hydrogen, &c.” If we knew the formula for a compound, then we could easily calculate the relative weights of the atoms. But how could one determine the formula?

To solve this problem Dalton took the bold step of postulating rules for making conjectures about the formulae for compounds:

“The following general rules may be adopted as guides in all our investigations respecting chemical synthesis.

1st. When only one combination of two bodies can be obtained, it must be presumed to be a *binary* one, unless some other cause appear to the contrary.

2d. When two combinations are observed, they must be presumed to be a *binary* and a *ternary*.”

For example, if carbon and oxygen form only one compound, one should assume the compound contains only two atoms. Hence its formula should be CO. So if a certain sample of carbon monoxide (to use our name for it) consists of 3 grams of carbon combined with 4 grams of oxygen, we presume the ratio of their atomic weights is 3 to 4. However, if carbon and oxygen form two different compounds (which is actually the case), then one of the combinations is CO, while the other consists of three atoms. Hence its formula should be either CO₂ or C₂O and if it analyzes into 3 grams of carbon for every 8 grams of oxygen, then we know the correct formula is carbon dioxide (to use our name for it).

The example above illustrates the way Dalton reasoned, but it makes the job of coming up with a comprehensive, consistent system of relative atomic weights look much easier than it actually was. First of all, the experimental data on combining weights were not very accurate. Secondly, Dalton got off on the wrong foot because since only one compound of hydrogen and oxygen was known at the time, his rules led him to assign water the formula HO instead of H₂O. So when he set the atomic weight of hydrogen as 1, oxygen came out to be half of its correct value! It was nearly 50 years later at a conference in Karlsruhe, Germany in 1860 that the Italian chemist

Canizarro finally presented a method for determining atomic weights that all chemists found acceptable. In attendance at that conference was a young Russian chemist who had come to Germany to study. His name was Dimitri Ivanovich Mendeleev. (Don't be confused by the various ways his name is transliterated into English.)

Mendeleev's Periodic Table and Periodic Law

Mendeleev was born in a small Siberian town 1300 miles from Moscow in 1834. After his father died he and his mother hitchhiked to the capitol city so he could go to the University of Moscow. Unable to get him a scholarship, they traveled another 400 miles east to St. Petersburg. Soon after graduating first in his class Mendeleev went for postgraduate studies at Heidelberg University in Germany. At that time Germany was home to many famous chemists while Russia was a bit of a backwater. When Mendeleev returned to Russia to take up an academic position at the University of St. Petersburg one of the first things he did was to write a 500-page organic chemistry textbook for his students to use. It was a huge success (financially as well as intellectually) and so he set out to write another textbook that would cover the chemistry of all the elements.

He began the manuscript with a chapter for each element that discussed its chemical properties. But it soon became apparent that he couldn't devote an entire chapter to each of the 60-odd elements known at the time. Furthermore he needed some rational way to order the discussions. At the Karlsruhe Conference Mendeleev had become convinced that a key property of an element was its atomic weight. So he made a note card for each element and started arranging them on his desk in order of atomic weight. Then he made the array of cards two-dimensional by grouping together elements that had similar chemical properties. (See figure 3 for the first published version of his table.) (Legend has it that Mendeleev liked to play the card game Solitaire in which cards end up in rows organized by both suit and numerical order and that this experience helped him make his discovery.)

Tabelle I.

Typische Elemente											
H = 1	Li = 7	Na = 23	K = 39	Rb = 85	Cs = 133	—	—	—	—	—	—
	Be = 9,4	Mg = 24	Ca = 40	Sr = 87	Ba = 137	—	—	—	—	—	—
	B = 11	Al = 27,3	—	?Yt = 88?	?Di = 138?	Er = 178?	—	—	—	—	—
	C = 12	Si = 28	Ti = 48?	Zr = 90	Co = 140?	?La = 180?	Th = 231	—	—	—	—
	N = 14	P = 31	V = 51	Nb = 94	—	Ta = 182	—	—	—	—	—
	O = 16	S = 32	Cr = 52	Mo = 96	—	W = 184	U = 240	—	—	—	—
	F = 19	Cl = 35,5	Mn = 55	—	—	—	—	—	—	—	—
			Fe = 56	Ru = 104	—	Os = 195?	—	—	—	—	—
			Co = 59	Rh = 104	—	Ir = 197	—	—	—	—	—
			Ni = 59	Pd = 106	—	Pt = 198?	—	—	—	—	—
			Cu = 63	Ag = 108	—	Au = 199?	—	—	—	—	—
			Zn = 65	Cd = 112	—	Hg = 200	—	—	—	—	—
			—	In = 113	—	Tl = 204	—	—	—	—	—
			—	Sn = 118	—	Pb = 207	—	—	—	—	—
			As = 75	Sb = 122	—	Bi = 208	—	—	—	—	—
			S = 32	Se = 78	Ta = 125?	—	—	—	—	—	—
			Br = 80	—	J = 127	—	—	—	—	—	—

Der chemischen Elemente.

© Science Museum / Science & Society Picture Library
Viewed by Guest on 6/17/2006

Ueber die Beziehungen der Eigenschaften zu den Atomgewichten der Elemente. Von D. Mendelejeff. — Ordnet man Elemente nach zunehmenden Atomgewichten in verticale Reihen so, dass die Horizontalreihen analoge Elemente enthalten, wieder nach zunehmendem Atomgewicht geordnet, so erhält man folgende Zusammenstellung, aus der sich einige allgemeinere Folgerungen ableiten lassen.

			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	Pd = 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	Sn = 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	J = 127	
Li = 7	Na = 23	K = 39	Rb = 85,4	Cs = 133	Tl = 204
		Ca = 40	Sr = 87,6	Ba = 137	Pb = 207
		? = 45	Ce = 92		
		?Er = 56	La = 94		
		?Yt = 60	Di = 95		
		?In = 75,6	Th = 118?		

1. Die nach der Größe des Atomgewichts geordneten Elemente zeigen eine stufenweise Abänderung in den Eigenschaften.
2. Chemisch-analoge Elemente haben entweder übereinstimmende Atomgewichte (Pt, Ir, Os), oder letztere nehmen gleichviel zu (K, Rb, Cs).
3. Das Anordnen nach den Atomgewichten entspricht der *Werthigkeit* der Elemente und bis zu einem gewissen Grade der Verschiedenheit im chemischen Verhalten, z. B. Li, Be, B, C, N, O, F.
4. Die in der Natur verbreitetsten Elemente haben *kleine* Atomgewichte

Figure 3: Mendeleev's Periodic Table Was First Published in German in 1869
 copied from
<http://www.chemsoc.org/networks/learnnet/periodictable/post16/develop/mendeleev.htm>

If we use this version, please delete the German prose before and after the table itself.

Others before Mendeleev had noticed that some of the elements could be grouped together into families. A German chemist Doebereiner (o umlaut) had even pointed out that in triads such as lithium(7), sodium(23), potassium(39), the atomic weight of the middle member was about halfway in between the atomic weights of the extremes. And an English chemist John Newlands had proposed a "law of octaves" because when arranged by

atomic weight, the chemical properties of elements repeated themselves in periods of eight just like the notes on a scale. But no one paid much attention to his pattern, in part because it broke down when one got to elements of higher atomic weight.

Mendeleev was convinced that there was what he called a “Periodic Law” that governed the properties of elements. In Newton’s Laws mass played a central role (see the article on mechanics) and so he felt that the weights of atoms somehow caused their chemical properties. He believed it was not a coincidence that there were periodic similarities in the chemical properties of elements. (We now know that it indeed is not a coincidence -- each row on the Periodic Table corresponds to the filling of a shell of electrons but at Mendeleev’s time no one knew anything about the internal structure of atoms.) Mendeleev was so convinced that a Law of Nature underlay his table that he made several bold predictions based on the table.

First he predicted the existence of three new elements based on gaps in his table. Note in Figure 3 there are question marks at atomic weights 45, 68, 70 and 180. Mendeleev was convinced that there should be two new elements between zinc and arsenic because the properties of arsenic showed that it should be in the phosphorus family. Furthermore the jump in atomic weight was unusually large. Using the known properties of the neighbors of the missing elements, Mendeleev predicted not only their atomic weights, but also the values of their densities and melting points. When the element gallium was discovered a few years later its actual properties were extremely close to Mendeleev’s forecast. (See Figure 4) When the discoveries of the other two gap elements followed in short order, chemists all over the world were convinced that the Periodic Table reflected a deep truth about the world.

Figure 4: Comparison of Predicted and Experimental Values for Mendeleev’s First Missing Element

	<i>Eka-aluminum (Ea)</i>	<i>Gallium (Ga)</i>
Atomic weight	68	69
Density	6.0	5.96
Melting point	low	30 degrees C
Oxide	Ea ₂ O ₃	Ga ₂ O ₃

Mendeleev also used his Table to predict that some of the current experimental values for atomic weight were incorrect. Note in Figure 3 that he has a question mark by the atomic weight 128 assigned to tellurium (Te). If he had arranged the elements in that row strictly according to increasing atomic weight, iodine (I) with atomic weight 127 would have come before tellurium (128). But Mendeleev knew that because of its chemical properties iodine belonged in the same horizontal row with fluorine, chlorine and bromine while tellurium was more like its neighbor to the left, selenium. So he placed these elements where they belonged, based on their chemistry, and challenged chemists to redo their experimental determinations of the values of atomic weights! In many cases Mendeleev's guess that the atomic weight values were a little off was correct. But the so-called reversed pair of tellurium and iodine remained an anomaly. (Look up today's values for the atomic weights of tellurium and iodine in figure 1, remembering that we now put families such as fluorine, chlorine, bromine and iodine in vertical columns while Mendeleev put them in horizontal rows.)

Chemists continued to find new elements. Some of them filled gaps in Mendeleev's table but others didn't seem to fit at all. Helium was first discovered through spectrographic analysis of sunlight and later isolated from uranium ore. (We now know that uranium emits alpha particles, which are helium nuclei.) At first Mendeleev didn't think there was a place for it in his table but when other inert gases such as argon and neon were found in the atmosphere he simply inserted a whole new family into the table. Because these gases do not form compounds he assigned them a zero valence and they actually formed a useful buffer between the highly reactive alkali metals such as lithium and sodium and the halogen gases such as fluorine and chlorine. But Mendeleev was never able to figure out what to do with the so-called rare earth metals (now called lanthanides). According to their atomic weights these metals should all come immediately after barium. But the problem was that all fourteen of these elements have the same valence (+3) and very similar chemical properties! This totally violated the principle of periodicity on which his table was based. Mendeleev eventually concluded that the rare earths "broke" the Periodic Law. When we look at the modern periodic table (see Figure 1 at <http://www.dayah.com/periodic/>) we see that both the lanthanides and actinides are displayed sort of like a postscript below the table even though according to atomic number they should appear above! Mendeleev's contemporaries had no idea of how the rare earths could be fitted into the pattern represented

by the Periodic Table. We now know that the theory of quantum numbers predicts their existence and they do fit smoothly into the underlying theory of the elements that is based on atomic number.

By the end of the 19th century the very conception of chemical element that had been developed by Boyle, Lavoisier and Dalton and which underlay Mendeleev's wonderful system was to undergo profound changes. Through the discovery of radioactivity, scientists learned that atoms were not the smallest pieces of matter. And the discovery of isotopes proved that not all the atoms of a given element were alike! Yet despite these revolutionary changes, the basic shape of the Periodic Table remained intact. Let us see how this was possible.

From Atomic Weight to Atomic Number

Mendeleev received early reports about cathode rays, X-rays, and radioactivity a few years before his death in 1907 (see article on radioactivity). However, he was not very receptive to them, in part perhaps because all the talk about glowing fluorescent screens caused by invisible rays reminded him of the claims spiritualists of his time made about occult phenomena. (Mendeleev had led a scientific investigation of the claims by Russian mediums that they could communicate with the dead and uncovered some of their methods of deception.) But very soon there was conclusive evidence that atoms consisted of positive particles and negative electrons. Ernest Rutherford, a scientist from New Zealand who came to Cambridge, England after doing research in Montreal, showed in 1911 that the positive particles were concentrated in a nucleus. (See article on nuclear physics) And in 1913 his British student Frederick Soddy found that not all atoms of a pure element were identical. For example, although a material then called mesothorium because it was found in thorium ores, had an atomic weight of 228, its chemical properties were identical to those of radium whose atomic weight was 226! (We now know that thorium undergoes radioactive decay to produce radium.) Soddy called atoms that were chemically identical but which had differing atomic weights *isotopes*. Using the mass spectrograph (see article on spectroscopy), scientists were able to separate all sorts of elements into their constituent isotopes.

These new discoveries caused chemists to revise their definition of chemical element. Boyle had said that elements were the simplest substances out of which all materials were made, but it was now clear that the fundamental

building blocks were subatomic particles such as protons and electrons. Lavoisier had defined elements as the last products of analysis, but scientists could now divide samples of what had been thought to be homogeneous materials into isotopes. For example, in 1920 Francis Aston reported that gaseous neon consisted of Ne-20 and Ne-22 while chlorine consisted mostly of Cl-35 and Cl-37 with traces of Cl-36 and Cl-38. John Dalton would have been shocked to learn that it was just not true that all atoms of an element had the same atomic weight! And if the identity of elements did not depend on their atomic weight, then order by atomic weight could hardly provide the foundation for Mendeleev's Periodic Table.

The solution, which may seem obvious today, is to define chemical elements in terms of their atomic *number*. Chemical properties depend on the positive charge on the nucleus and the corresponding number of electrons outside the nucleus. Atoms of the same atomic number have different atomic weights if they have different number of neutrons in their nuclei. Mendeleev's Periodic Table worked as well as it did because there is a very close correspondence between order by atomic weight and order by atomic number. Sometimes the order is not the same (remember the reversed order of tellurium and iodine) but because nuclei that have many more neutrons than protons are unstable, Mendeleev's idea of ordering elements by weight turned out to be a very close approximation of the true ordering principle, namely atomic number.

Not all chemists immediately accepted the new definition of element –some argued that each isotope should be considered to be a separate element . After all, a Uranium-235 atom is much more highly radioactive than a U-238 atom. (The controversial centrifuges that Iran was accused of building were designed to extract U-235 from naturally occurring uranium ores, which are mostly U-238.) There are also chemically significant differences between ordinary hydrogen H-1 and deuterium H-2. In fact deuterium oxide (so-called heavy water) is poisonous to animals. On this proposal atomic weight would have remained the defining property. The chemical community wisely decided to identify elements by atomic number. Can you imagine what a mess the Periodic Table would be if each individual isotope got its own box! Yet even with all this new information about atoms one major puzzling feature of the Periodic Table remained: its periodicity. Why should there be a repetition of chemical properties after every 8 or in some cases 18 elements? Why was it that the numerically ordered string of elements should wrap around so that if sodium (Na) is placed under lithium, where it

obviously belongs, then chlorine automatically takes its place under fluorine? Why were some periods longer than others? And what about those pesky rare earths where the valence remained +3 even as the atomic number kept increasing? The answers were provided in the 1920s by the new and very mysterious quantum theory.

Quantum Numbers and the Periodic Table

Each element when heated gives off light with a characteristic spectrum. (If you sprinkle ordinary table salt into a blue flame you will see the characteristic reddish orange color of sodium.) When the emitted light is analyzed with a spectroscope (see article on spectroscopy), one finds that the spectrum contains sharp lines. It was because the light from the sun contained lines that did not correspond to any element known on earth that spectroscopists knew there was a new element on the sun and they named it helium from the Greek word *helos*, which means sun. But why should light of only certain specific wavelengths be emitted? This and many other considerations led physicists such as Niels Bohr to the conclusion that the electrons that surrounded the nucleus occupied orbits at certain discrete distances from the nucleus. When an individual atom absorbed energy, say from a flame, an electron in one of those shells jumped up to a new orbit that was farther away from the nucleus. It would eventually fall down and in doing so it would produce light of a single wavelength determined by the energy difference between the two orbits. In the case of a very simple atom such as hydrogen, Bohr was even able to calculate from his theory what the spectrum of excited hydrogen should be. (See article on quantum mechanics.)

According to quantum theory, the orbits available to any electron in an atom are described by integers called quantum numbers. In an unexcited atom (one that is not being bombarded by an outside energy source), the electrons gravitate to the orbits of lowest energy. But only two electrons can occupy a given orbit. If we look again at the Periodic Table and apply the principles of quantum mechanics, it turns out that there can only be two elements in the first row because there is only space for two electrons in the first shell. However, quantum mechanics tells us that there can be eight electrons in the second shell because it contains four available orbits and we indeed find eight elements in the second row of the Periodic Table. Lithium (atomic number 3) has two inner electrons and one electron in its outer shell. In chemical reactions it may lose that electron and become a Li^{+1} ion. Fluorine

(atomic number 9) has two inner electrons and seven outer electrons. Because a full outer shell is an especially stable arrangement (that is why the rare gases are inert), in reactions fluorine atoms often gain an electron and become negative F^{-1} ions.

As we move to higher numbers of shells, describing the number of orbitals and their relative energies becomes more complicated but the existence of horizontal families of elements like the lanthanides and actinides is predicted from the theory. All of the lanthanides have three electrons in their outermost shell (hence the valence of +3) but they differ in the number of electrons in the shell just beneath. Hence as the atomic number increases there is little variation in the properties of the outside electrons, which are those that typically enter into chemical bonding. (See article on Molecular theory.)

At last scientists have a comprehensive understanding of why the elements exhibit the relationships that Mendeleev discovered by shuffling note cards and arranging them into a table. His classification system was not in the least arbitrary. It reflects perfectly the underlying quantum structure of chemical atoms. However, the quest for a deep understanding of the simplest materials of which our world is composed has not ceased. We now want to know how many fundamental particles there are and whether all those recently discovered quarks and mesons can somehow be organized into a rational system. None of the attempts so far are satisfactory, but the search for a beautiful, comprehensive periodic classification of fundamental particles continues.

Timeline

322 B.C.: Aristotle dies. His theory of four elements, namely earth, air, fire, and water, is widely disseminated throughout Greek society.

391 A.D.: A traditional date assigned to the destruction of the Library of Alexandria, a huge repository of Greek scholarly works. Historians now think it was damaged on several different occasions.

9th-10thc: Alchemy flourishes in Baghdad. Three alchemical elements are added to Aristotle's four-element theory.

1541: Death of Paracelsus who publicly burnt the books of ancient authorities, such as Aristotle and Galen and promoted the alchemical theory of three elements: sulfur, salt and mercury.

1661: Robert Boyle publishes *The Sceptical Chemist*, a book that criticizes previous approaches to chemistry.

1734: Death of Stahl, who developed the phlogiston theory of combustion. It remains popular throughout much of the century.

1789: Lavoisier's *Traité élémentaire de chimie* defines element as the last product of analysis and presents a table of approximately 30 substances that qualify as elements under his definition.

1808: Dalton's *A New System of Chemical Philosophy* presents rules for determining atomic weight, the property he considers to be the fundamental characteristic of elements.

1869: Mendeleev's two-volume work *The Principles of Chemistry* shows the usefulness of the Periodic Table.

1875 - 86: The three "missing elements" are discovered and have properties very close to Mendeleev's predictions.

1913: The discovery of isotopes leads to a new definition of chemical element, one based on atomic number instead of atomic weight.

1920s: Quantum theory explains the properties of elements in terms of electron shells.

End timeline

Glossary

Alchemy: The study of the reactions of chemicals in pre-modern times. It was often, but not always, directed by the goal of making gold.

Analysis: The process of separating out the constituents of a complex chemical substance.

Atomic number: The number of protons in an atom of a chemical element. Neutral atoms have the same number of electrons.

Atomic weight: A measure of the average weight of the protons and neutrons in the atoms of a chemical element.

Calcination: An old term used to describe the process of heating metals and other materials in air.

Generative elements or principles: These were the basic, active ingredients from which everything was thought to originate.

Isotopes: Atoms with the same atomic number but differing atomic weights. Their nuclei have identical numbers of protons but differ in the number of neutrons.

Periodic Law: Mendeleev thought there to be a law of nature that would explain why there were regular repetitions of chemical properties when elements were arranged in order of atomic weight.

Philosophical elements or principles: The underlying essential constituents of bodies that could not be directly perceived.

Quantum number: A variable in quantum mechanics that specifies the state of electrons in an atom.

Synthesis: The process of combining simpler chemicals to make a more complex compound.

Transmutation: A transformation of the essential properties of a chemical element. Alchemists hoped to transmute base metals such as lead into gold. In modern science nuclear reactions can change one element into another by fission or fusion.

Valence: The combining capacity of an atom. The valence of hydrogen is one; that of oxygen is two. Hence, a molecule of water consists of two hydrogen atoms bonded to one atom of oxygen.

End glossary

Further reading

Books

Ball, Philip. *The Ingredients: A Guided Tour of the Elements*. Oxford and New York: Oxford University Press, 2002.

Ball, Philip. *The Elements: A Very Short Introduction*. Oxford and New York: Oxford University Press, 2004.

Boyle, Robert. *The Sceptical Chymist*, 1661.

Brock, William H. *The Norton History of Chemistry*. New York and London. W.W.Norton & Co., 1992.

Dalton, John. *A New System of chemical Philosophy*, 1808.

Gordin, Michael D. *A Well-Ordered Thing: Dmitrii Mendeleev and the Shadow of the Periodic Table*. New York: Basic Books, 2004.

Lavoisier, Antoine. *Elements of Chemistry*. This English translation appeared 1790.

Mendeleev, Dimitri. *Principles of Chemistry*. The first English translation appeared in 1891.

Morris, Richard. *The Last Sorcerers: The Path from Alchemy to the Periodic Table*. Washington, D.C.: Joseph Henry Press, 2003.

Strathern, Paul. *Mendeleev's Dream: The Quest for the Elements*. New York: St. Martin's Press, 2001.

Web Sites

“Chemical Achievers: The Human Face of the Chemical Sciences.”

Chemical Heritage Foundation.

<http://www.chemheritage.org/classroom/chemach/index.html> (accessed on June 8, 2006).

“History of the Periodic Table.” *Royal Society of Chemistry*.

<http://www.chemsoc.org/networks/learnnet/periodictable/pre16/develop/mendeleev.htm> (accessed on June 8, 2006).

“History of the Periodic Table of the Elements.” *AUS-e-TUTE*.

<http://www.usetute.com.au/pthistor.html> (accessed on June 8, 2006).

-- Noretta Koertge

