A Puzzle with Many Pieces

Development of the Periodic Table

Dmitrii Ivanovich Mendeleev

Most everyone recognizes the periodic table of chemical elements. Found on science classroom walls and laboratories, in the back of science textbooks, and even sometimes even on t-shirts, beach towels and other everyday items, the periodic table has come to symbolize chemistry. For centuries humans have studied chemical substances, their properties, and how they react. However, the insight that resulted in early versions of the periodic table occurred in the last 150 years.

The development of the periodic table illustrates that patterns in nature are often not straightforward or obvious. In the early 1800s, chemists knew about the existence of elements, and often printed lists of the known elements alongside the most current measurements of their atomic weights. Chemists also knew that some elements had similar chemical properties. For example, chlorine, fluorine and bromine behaved similarly in chemical reactions, and sodium, potassium and lithium also had many similar properties. But no one had the insight that the chemical elements might be ordered in a way that could link their chemical and physical properties in a meaningful pattern.

Science teachers and curriculum materials often make statements such as "The data show…." or "The data tell us… ." This wrongly implies that the meaning of data are self-evident, interpretation is straightforward, and in turn communicates to students that science requires little creativity. As you read this story, pay attention to how humans have to creatively interpret data and develop patterns to account for that data.

A major reason for this was that in the early nineteenth century, no standardized system of atomic weights existed. Some chemists thought that oxygen had an atomic weight of 8; some thought it had an atomic weight of 16. Similar arguments existed over the weight of hydrogen, carbon, and most metals. These disagreements resulted in a great deal of confusion about the formulas for chemical compounds. In the 1840s, the French chemist Auguste Laurent, annoyed by the disorder in chemical classification, pointed out that over one-hundred published formulas for acetic acid (the compound we now know as CH_3COOH) existed. Because chemists did not agree on the atomic weights of the elements, the difficulty they experienced in creating an organizational scheme for chemical elements based on both their weight and their chemical properties is not surprising.

In 1860, 150 of the most prominent chemists in Europe gathered in the German city of Karlsruhe to discuss how they could make their atomic weights and chemical terminology more consistent. August Kekulé, a respected young German organic chemist, convened the Karlsruhe conference in order to resolve some of the issues in chemistry that he thought were creating confusion and holding back the development of new chemical ideas. Chemists from almost every European country traveled to Karlsruhe in order to discuss how they might standardize their systems of atomic weights.

Note that doing science well requires significant collaboration with others. This challenges the image of the scientist toiling alone in a laboratory. Science is not the solitary undertaking that many people think.

During the conference, an Italian chemist named Stanislao Cannizzaro brought up a long-forgotten idea developed by his fellow Italian Amedeo Avogadro in 1811. Avogadro had argued that equal volumes of gases at the same pressure and the same temperature would contain the same number of molecules. Cannizzaro argued that if chemists accepted Avogadro's argument as the basis of a new system of atomic weights, they would be able to standardize the weights of elements and calm the confusion that had arisen. Cannizzaro's suggestion met with widespread support.

1. Note that nearly a half-century passed before Avogadro's contribution was identified as a possible solution to the problem of atomic weight standardization. How does this demonstrate that (a) creative insight is crucial in science, and (b) that previous science ideas become useful in unanticipated ways?

The Karlsruhe conference was important for establishing a process to standardize atomic weights. But it was also important for another reason: one of the chemists in attendance was a twenty-six-year-old Russian named Dmitrii Mendeleev. Mendeleev was impressed with Cannizzaro's argument in favor of Avogadro's system, and when he returned to Russia in 1861, he was filled with excitement over the developments in chemistry he had seen at the conference.

Dmitrii Ivanovich Mendeleev was born in January 1834 in the Siberian town of Tobol'sk. Mendeleev's father, Ivan Pavlovich Mendeleev, was a teacher at the local gymnasium (what we would now call a high school). When Ivan went blind shortly after Dmitrii's birth, Dmitrii's mother Maria Dmitrievna Kornileva went to manage her family's glass factory in order to support her children (Dmitrii was the youngest of seventeen children, eight of whom survived to adulthood).

Maria was a clever woman who had great ambitions for her youngest son. After Mendeleev graduated from the local gymnasium in 1850, his mother traveled with him from Siberia to Moscow to try and enroll him at Moscow University. When he was not accepted, she took him to St. Petersburg University where he was also refused enrollment. Finally, with the help of a family friend, Mendeleev enrolled at St. Petersburg's Chief Pedagogical Institute, where his father had trained as a teacher.

Mendeleev studied at the Chief Pedagogical Institute until 1855, where many distinguished professors encouraged his interest in chemistry. After finishing his degree, Mendeleev briefly taught secondary school in the Crimea (a remote peninsula south of what is now Ukraine). He was unhappy there, and in 1859 he accepted a government scholarship to travel to Germany and pursue his interest in chemistry.

In the nineteenth century, Germany was unquestionably the center of the chemical world. Mendeleev studied in the German city of Heidelberg, and became close friends with several other Russian students living and studying at the university. His studies in Heidelberg also gave him the opportunity to travel to nearby Karlsruhe when he heard of the important chemical conference being held there.

Mendeleev returned to St. Petersburg in 1861, where he began work on his first textbook, *Organic Chemistry.* In 1867 he was hired as a professor of chemistry at St. Petersburg University. One of Mendeleev's responsibilities was to teach a large introductory course in inorganic chemistry. To do so, he needed to choose a textbook. But Mendeleev was dissatisfied with the available texts. Chemistry was a rapidly advancing field. Most of the textbooks in Russian were translations of German textbooks, and by the time the translations were finished the original books were already out of date.

Mendeleev decided to write his own textbook in Russian, based on the latest chemical knowledge. He signed a contract with a Russian publisher promising a two-volume textbook entitled *Principles of Chemistry*. The first volume was largely designed to introduce students to proper laboratory practice and basic chemical theories. When Mendeleev sent Volume 1 to the publisher in January 1869, he realized he had a problem. At the time, there were 63 known elements. He had only discussed nine of them (hydrogen, carbon, nitrogen, oxygen, sodium, bromine, iodine, fluorine, and chlorine) in Volume 1. How could he possibly discuss all 54 remaining elements in Volume 2?

Mendeleev began considering how he could group the elements together to address them in the second volume of his textbook. He thought about elements that had similar reactive properties – for instance, sodium and potassium, and wrote the first two chapters on those elements which he completed by February 14th, a Friday. But Mendeleev was uncertain how to proceed from this point. He wanted to map out a strategy before he had to depart for Tver the following Monday to give a speech and spend three days inspecting farms there. But despite working feverishly on his problem the entire weekend with little sleep, Mendeleev had not come up with any sort of pattern that might link groups of elements having similar properties. That morning, over a cup of tea he turned his attention to mail that had recently arrived. On the back of one letter he eventually began listing several elements in the order of their atomic weights (This letter has been preserved and still shows a ring-mark from the bottom of a cup from which Mendeleev had been drinking tea.).

Note that Mendeleev persists in his idea that any systematic arrangement of the elements must be associated with atomic mass.

But this order didn't explain anything of importance. Mendel then began grouping elements with similar properties, but also noted their atomic weights. For instance, the halogens

F = 19   Cl = 35   Br = 80   I=127

The oxygen group of elements

O = 16   S = 32   Se = 79   Te = 128

And the nitrogen group of elements

N = 14   P = 41   As = 75   Sb = 122

Within each group, no relationship appeared to exist between the atomic weights. But the writing on the back of the letter shows that Mendeleev then arranged the three groups as follows:

F = 19	Cl = 35	Br = 80	I=127
O = 16	S = 32	Se = 79	Te = 128
N = 14	P = 41	As = 75	Sb = 122

2. Many people enjoy solving puzzles, yet think they would not enjoy a science career. Mendeleev is trying all sorts of ideas to make sense of the data. How is what Mendeleev doing like solving a puzzle? How does his work illustrate that doing science requires creativity and imagination?

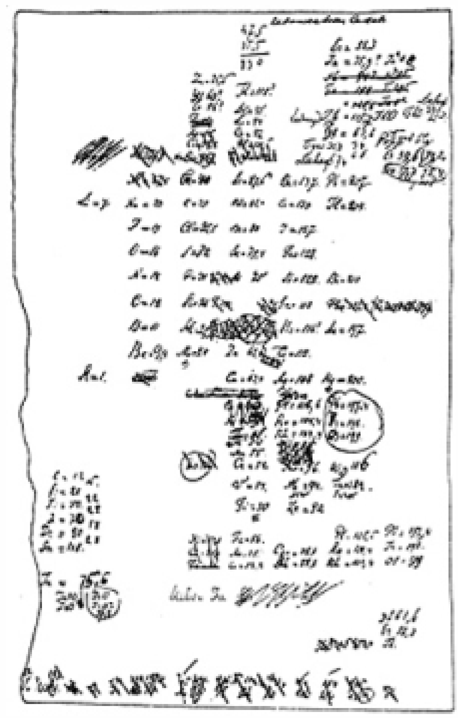

Figure 1. *Mendeleev's first periodic table. Oesper Collection, University of Cincinnati*

This task was not straightforward as it may seem. Mendeleev had to make judgments regarding similarities and differences between elements, and group them in a manner that made sense to him. He then noticed that with the exception of P and Te, each element descended by atomic weight. This didn't make any sense to Mendeleev, but he gambled that what was emerging to him was not simply coincidental. He continued trying to make sense of the pattern he had developed and later that afternoon, on 17 February 1869, Mendeleev first printed and circulated a table that he entitled "An Attempt at a System of Elements, Based on Their Atomic Weight and Chemical Affinity (Figure 1)."

Two weeks later Mendeleev published a paper titled "A Suggested System of the Elements" containing his periodic table (Figure 2). At first, Mendeleev thought his system of organizing the elements was a useful teaching tool. But as he thought about and investigated the chemical properties of various elements in the table, he became convinced that his system was, in fact, a law of nature. In 1870, Mendeleev defined the law of periodicity as "the periodic dependence in the change of properties of the elements on their atomic weight," and began writing articles in Russian and German arguing that his periodic system was both a useful pedagogical tool and an important new chemical law.

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	Rn=104,4	Ir=198.
			Ni=Co=59	Pl=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	I=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?		

Д. Менделѣевъ

Figure 2. *A Suggested System of Elements. Public Domain Image*

Prior to Mendeleev's announcement, others had also been working to make sense of the known elements. One notable success of Mendeleev's system is that it accounted for partial patterns suggested previously by other chemists such as Newland, Dobereiner and de Chancourtois. However, even Mendeleev acknowledged that several anomalies appeared in his organizational structure. In some cases, atomic weights did not fit the ascending order in his table, but Mendeleev simply questioned the veracity of the previously determined values. And where no known elements appeared to fit his organizational scheme, Mendeleev left gaps boldly predicting those elements did exist and would one day be isolated with properties fitting appropriately between the already known elements in his table. Interestingly, a German chemist, Julius Lothar Meyer, independently came to an arrangement of the elements similar to that of Mendeleev's. However, Meyer was far more tentative in his reply to critics, and did not put forward the same bold predictions for the anomalies as did Mendeleev.

3. Most people think that science ideas should be discarded if evidence appears to falsify it. Yet note Mendeleev's reaction to the anomalies. List several reasons explaining why abandoning an idea so easily is not always prudent.

Mendeleev's claim that his periodic system was a law of the natural world was met with significant skepticism. Critics kept pointing to the many holes Mendeleev had left in his Table. Mendeleev saw the same holes as a strength of his Periodic Law because he could make predictions with it. For instance, in 1871 Mendeleev predicted the existence of three previously unknown elements. He called these elements eka-boron, eka-aluminum, and eka-silicon. Eka-boron, he said, would be an element with an atomic weight of 44 with chemical properties like those of boron. Eka-aluminum would have an atomic weight of 68, and eka-silicon would have an atomic weight of 73.

In August 1875, a French chemist named Paul Émile Lecoq de Boisbaudran was analyzing a metal from a mine in the French Pyrenees, and noticed a line on its spectrum that did not correspond to any known element. Because each element has its own unique spectral signature, this was evidence for a previously unknown element. Lecoq de Boisbaudran called this new element "gallium." Lecoq de Boisbaudran was not aware of Mendeleev's prediction, but he himself had thought about ways of classifying elements and had also predicted the existence of an element with an approximate atomic weight of 68. However, the specific gravity of the new element departed significantly from that predicted by Mendeleev. Undeterred, Mendeleev wrote de Boisbaudran asking him to more rigorously repeat his specific gravity work. He agreed and this time came to the value predicted by Mendeleev. However, Mendeleev's prediction was more well known than the French chemist's, and when news of the discovery of gallium spread through the chemical world, Mendeleev announced that his prediction had been confirmed – gallium was the element he had called "eka-aluminum."

This was convincing evidence of Mendeleev's claim that his periodic law could make scientific predictions, but many chemists wondered whether eka-aluminum had simply been a lucky guess. What about the other two elements Mendeleev had predicted? In 1879, a Swedish chemist named L.F. Nilson isolated a rare earth metal that did not correspond to any known element. Nilson named this new element "scandium." Scandium's atomic weight was measured to be 45, and it had many of the chemical properties Mendeleev had predicted for eka-boron. It was less basic than yttrium, its salts were colorless, and its oxide had the formula Sc_2O_3. Nilson also did not know of Mendeleev's prediction, but another Swedish chemist named Per Cleve did. Cleve wrote an excited letter to Mendeleev announcing that Nilson had discovered eka-boron, further evidence in support of Mendeleev's periodic law.

Mendeleev's third predicted element, eka-silicon, was not discovered for another seven years. In February 1886, the German chemist Clemens Winkler, a professor at the Mining Academy in Freiburg, announced that he had discovered a new mineral in the German mines. He called this element "germanium," and it had an atomic weight of 73. Remarkably, like Nilson and Lecoq de Boisbaudran, Winkler also did not know about Mendeleev's prediction; it was another German chemist, V.F. Richter, who wrote to Winkler about the connection with the Russian chemist's periodic system. Winkler was astonished that another chemist had predicted germanium's existence, and enthusiastically agreed that Mendeleev had indeed developed a scientific law capable of making striking predictions about the chemical elements. Increasingly, scientists began to accept Mendeleev's law, that many of the physical and chemical properties of the elements tend to recur in a systematic manner with increasing atomic weight. By 1886, the status of the periodic table, and Mendeleev's own status as its discoverer, seemed stable. But in the 1890's, there were many further developments in the understanding of the theory explaining the periodic table – many of which Mendeleev opposed.

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As you read the story of the development of the period table, note that scientific laws and theories are different forms of knowledge. Both make assertions about the natural world, and one never becomes the other. Scientific laws, like Mendeleev's Periodic Law, state invariable relationships in nature. Scientific theories explain those relationships.

In 1894, the Scottish chemist William Ramsay announced the discovery of a new element, "argon." According to Ramsay, argon was a gas with an atomic weight of 40, placing it between chlorine and potassium. Argon was also inert – it did not react with other elements. Mendeleev was less than enthusiastic about Ramsay's "argon." He had not predicted the existence of an element between chlorine and potassium. Ramsay's argument that argon was inert was also deeply troubling. To Mendeleev, who had based his periodic system around the careful study of the way elements reacted with one another, the idea of an inert element that did not react with anything seemed impossible. He suggested that argon must be a compound of some sort, perhaps N_3.

In 1895, Ramsay discovered another inert gas, helium, with an atomic weight of 4. Eventually, as Mendeleev studied the density and spectra of Ramsay's new gases, he came to believe that Ramsay had been right – argon could not possibly be N_3. By 1903, in the seventh edition of the *Principles,* Mendeleev was praising Ramsay's work as some of the most important recent chemical research, and had created a new place on his periodic table for the "argon group" of inert gases.

Mendeleev was able to make room in his system for Ramsay's noble gases. However, he was never able to come to terms with another major discovery of the 1890s:

radioactivity. In 1896, the French physicist Henri Becquerel discovered that uranium (one of the elements on Mendeleev's table) could spontaneously emit energy. Two years later, Pierre and Marie Curie discovered two more elements, radium and polonium, both of which were extremely rare, and both of which were also radioactive. The French physicists argued that radioactivity was the result of elements disintegrating.

Mendeleev thought the idea of an element disintegrating was patently absurd. Elements, in his view, were unchanging and indestructible. The idea that one element could turn into a different element sounded more like medieval alchemy than modern science. A visit to the Curies' laboratory in 1902 did little to change his mind. He wrote to a friend that he was not about to abandon his views on elements just because of radium:

> Tell me, please, are there a lot of radium salts in the whole earth? A couple of grams! And on such shaky foundations they want to destroy all our usual conceptions of the nature of substance!

Mendeleev also rejected the theory, gaining strength among many chemists and physicists, that atoms might be composed of smaller particles. In 1897 the English physicist J.J. Thomson proposed that cathode rays were made up of "corpuscles" that were 1000x smaller than a hydrogen atom. Thomson argued that these "corpuscles" (which soon became known as electrons) were the building blocks that composed all atoms. This was yet another theory that seemed to go against everything Mendeleev knew about chemistry, elements, and mass.

Mendeleev argued passionately against the new theories of radioactivity and subatomic particles. He was still an extremely famous scientist, especially in Russia, but he increasingly found himself in the minority. Mendeleev died in 1906, still denying radioactivity and subatomic particles.

Despite Mendeleev's thinking that radioactivity and subatomic theory undermined his entire system of chemistry, the new theories did not result in the abandonment of his periodic system of the elements. Instead, the periodic system evolved after his death to incorporate the new theory and an important correction was made to Mendeleev's Periodic Law. That is, the systematic recurrence of physical and chemical properties is associated with increasing atomic number (i.e. the number of protons in the nucleus), not atomic weight. In 1911, the Dutch scientist Anton van den Broek used the new subatomic theories to re-order the periodic table according to the atomic numbers of the elements, rather than by atomic weight. In 1914, the English chemist Henry Moseley was able to further demonstrate that each element in the periodic table had a characteristic atomic number, and was able to show that several "new elements" were in fact compounds. Moseley identified seven gaps in the new atomic number periodic table elements 43, 61, 72, 75, 85, 87, and 91, all of which would be discovered by 1945. (Moseley did not live to see these discoveries; he died in World War I at the age of 26.)

Ernest Rutherford's discovery of the proton in 1919, and James Chadwick's discovery of the neutron in 1932, deepened scientists' understanding of the structure of the atom and why the chemical properties of the elements fall into a periodic pattern. Niels Bohr's work on the structure of the atom further illuminated why elements in the same column have similar chemical properties: they have the same number of electrons in their outer electron shell. Mendeleev would no doubt be quite surprised to sit in an introductory chemistry class today and hear that his periodic system of the elements can be explained by studying the subatomic particles that he insisted did not exist!

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Again, note how scientific laws and theories are different, yet related kinds of assertions about the natural world. Also note that Mendeleev's Period Law had to be corrected when chemical theory put forward the existence of protons that more accurately explained chemical periodicity. These chemical theories are now well-established, yet remain theories. All scientific theories, no matter how well established, remain theories.

Mendeleev's periodic table (Figure 2) doesn't look much like the modern periodic table (Figure 3), but it uses a similar format. The elements are grouped in order of increasing atomic weight (we use atomic number now) in a way where elements with common properties appear together, in the same columns. You'll see this type of chart in textbooks and schools all over the world, but it's not the only way to group the elements. There are circular tables (Figure 4), helical tables (Figure 5), three-dimensional tables, and many more. The *Chemogenesis Web Book** offers a sampling of different types of periodic tables. Note that the tables are still *periodic*. The elements are categorized according to trends in their properties. These illustrate that while the several different ways have been developed to represent the relationship among elements, the modified core of Mendeleev's period law still pervades all of them.

4. Many people wrongly think experiments and a step-by-step scientific method are the only routes to good scientific knowledge. How does Mendeleev's work and important contribution show this not to be the case?

*http://www.meta-synthesis.com/webbook/35_pt/pt.html

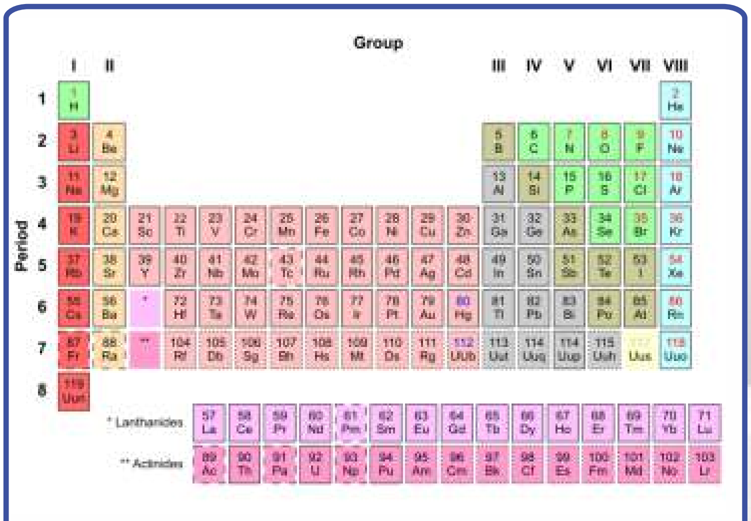

Figure 3. *Modern Periodic Table*

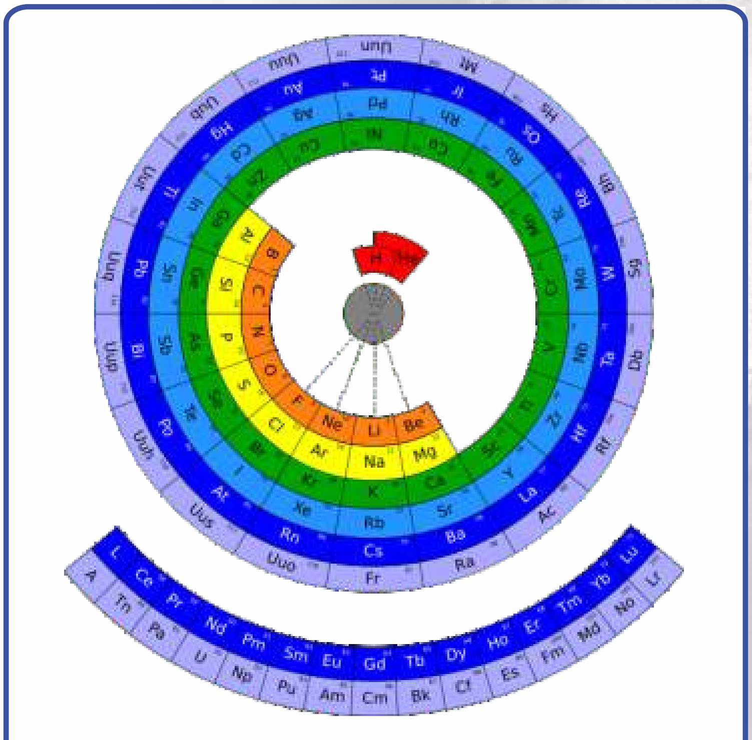

Figure 4. *Circular Periodic Table*

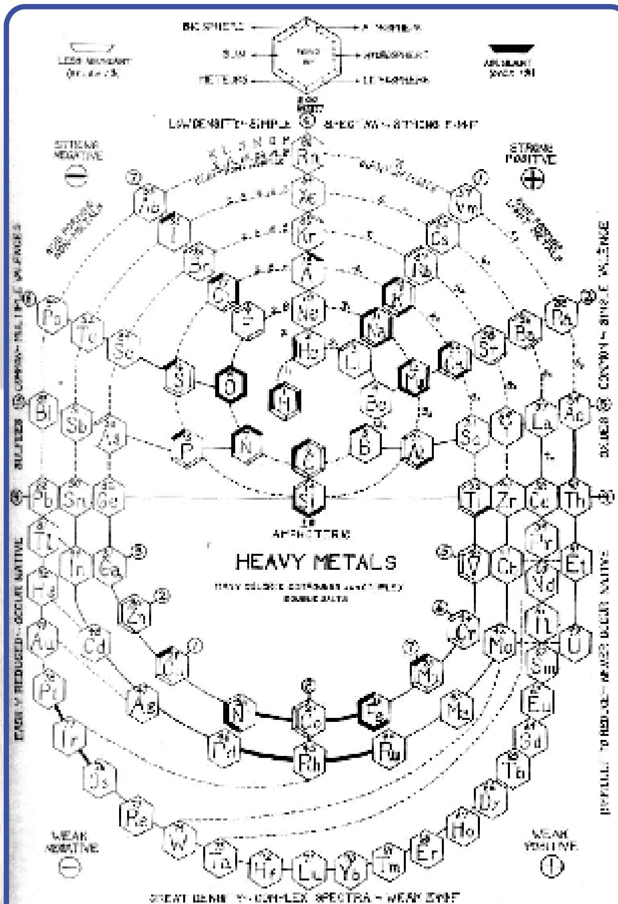

Figure 5. *Helical Periodic Table*

A Puzzle With Many Pieces: Development of the Periodic Table written by Melinda Baldwin, Michael P. Clough, and Thomas Greenbowe

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