THE HISTORICAL DEVELOPMENT OF THE PERIODIC CLASSIFICATION OF THE CHEMICAL ELEMENTS

by

RONALD LEE PFISTER

B. S., Kansas State University, 1962

A MASTER'S REPORT

submitted in partial fulfillment of the

requirements for the degree

MASTER OF SCIENCE

Department of Physical Science

KANSAS STATE UNIVERSITY
Manhattan, Kansas

1964

Approved by:

W. G. Schrenk
Major Professor

TABLE OF CONTENTS

THE PROBLEM AND DEFINITION OF TERMS USED 1
- The Problem 1
  - Statement of the Problem 1
  - Importance of the Study. 1
- Definition of Terms Used. 2
  - Atomic Number. 2
  - Atomic Weight. 2
  - Element. 2
  - Periodic Classification. 2
  - Periodic Law 3

BRIEF REVIEW OF THE LITERATURE 3
- Books 3
- Other References. 4

BACKGROUND HISTORY 4
- Purpose 4
- Early Attempts at Classification. 4
  - Early "Elements" 4
  - Attempts by Aristotle. 6
  - Other Attempts 7

DOBEREINER'S TRIADS AND SUBSEQUENT INVESTIGATIONS. 8
- The Triad Theory of Dobereiner. 10
- Investigations by Others. .10
  - Dumas. 10
  - Pettenkofer. 10
  - Odling 11

THE TELLURIC HELIX OF DE CHANCOURTOIS. 11

Development of the Telluric Helix .11

Acceptance of the Helix 12

NEWLANDS' LAW OF THE OCTAVES 12

Newlands' Chemical Background 12

The Law of the Octaves. 13

Acceptance and Significance of Newlands' Work 15

THE CONTRIBUTIONS OF LOTHAR MEYER. .16

Chemical Background of Meyer. .16

Lothar Meyer's Arrangement of the Elements. 17

THE WORK OF MENDELEEV AND ITS CONSEQUENCES 19

Mendeleev's Scientific Background 19

Development of the Periodic Law .19

Significance of Mendeleev's Table 21

Atomic Weight Corrections. 21

Prediction of New Elements 22

Influence of the Periodic Law 23

SUBSEQUENT WORK ON PERIODIC CLASSIFICATION 24

Modification of Mendeleev's Table 24

Discovery of the Rare-Earth and Inert Gas Elements 24

Atomic Number as a Basis for Classification. 25

Completing the Gaps and the Transuranium Elements 27

Methods and Trends in Classification. 28

Methods of Representing the Elements 28

Forms of Periodic Tables 29

SUMMARY. 31

LITERATURE CITED 33

THE PROBLEM AND DEFINITION OF TERMS USED

In all branches of science a system of classification is of primary importance, but this is particularly true in the area of chemistry. It embodies many thousands of compounds and reactions, yet involving only a relatively few elements. The one-hundred-three elements show similarities and can therefore be arranged in a systematic pattern which comprises a basis for further analysis and study. Because chemistry is so complex, no completely satisfactory classification is feasible. However, the periodic table contains a basic foundation and outline of systemization. This system has a firm basis in the periodic law which grew out of a long sequence of investigations on atomic weights. It has served chemists as a valuable tool by unifying a vast amount of knowledge and has been the means of world-wide communication and of predicting discoveries of new elements.

The Problem

Statement of the Problem. It is the purpose of this study (1) to trace the historical development of the periodic system of classification of the chemical elements; (2) to show that the periodic table was the result of the accumulated efforts of a series of scientists from several countries; (3) to show the significance of the periodic table with respect to the discovery of new elements; and (4) to briefly show desirable attributes and trends of periodic classification.

Importance of the Study. In order to obtain a genuine appreciation of the concept of classification as displayed by the periodic table, it is necessary to trace its growth from the beginning and to have some knowledge of the circumstances existing in the field of chemistry at that period of history. When Mendeleev made his announcement of the periodic law, only sixty-three elements were known. In addition, the men who discovered that there was a periodic relation of the elements knew nothing of atomic structure, electrons, protons, or neutrons. All their knowledge was simply based upon chemical reactions. Although these chemists knew a relationship existed among the elements, they could not explain satisfactorily why it existed.

Definition of Terms Used

Atomic Number. Atomic number refers to the number of protons in the nucleus of an atom or to the number of electrons which surround the nucleus of a neutral atom.

Atomic Weight. The atomic weight refers to the relative weight of the atoms of the different elements based upon the arbitrarily assigned value of sixteen for oxygen. Hydrogen and carbon have also been used as a basis for determining the atomic weight of the elements.

Element. The word "element" comes from the Latin elementum. Origin of the Latin word is uncertain. One suggestion is that the Romans may have said that something was "as easy as L-M-N," just as we say "easy as A-B-C." At any rate, elementum came to mean something simple from which complex things were built.

Periodic Classification. Periodic classification refers to the arrangement of the chemical elements by increasing atomic numbers so that at certain intervals similar characteristics appear. Elements falling into these intervals are grouped together and are called families or groups. Each family of elements has a certain set of characteristics because of the structure of the atoms of the elements in the family. The most important characteristic is the arrangement of the electrons and the number in the outer energy shell.

Periodic Law. The periodic law states that the properties of the chemical elements are a function of the electron configuration of their atoms which vary with increasing atomic number in a periodic fashion. That is, if all the chemical elements arranged in order of increasing atomic numbers, at certain places in the group, like elements will fall together. Although slightly changed from the original, this law is credited to Mendeleev, the Russian scientist.

BRIEF REVIEW OF THE LITERATURE

Books

Much of the material concerning the history of the periodic classification of the elements was obtained from books. However, no attempt has been made to provide an exhaustive summary of the literature due to the great number of books which deal with the topic, either wholly or in part. Only those books of significance will be mentioned briefly.

The works of Asimov (1), Leicester and Klickstein (6), and Farber (3), were particularly important in providing background history information. Valuable information on the men who contributed to modern periodic law were found in books by Weeks (20), Harrow (4), and Asimov (1). A reference used concerning the periodic properties of the elements was the book by Sanderson (16). Also, the work of Moeller (8) provided a good general reference, as well as presenting modern trends in periodic classification. In addition, several other books supplemented the above references; however, only certain chapters or pages applied to periodic classification (5, 9, 10, 11, 14, 17).

Other References

There have been many articles written in magazines, journals, and other publications concerning periodic classification. In this report, only those sources were used that helped to bring one closer to the actual contribution (2, 7, 13, 15). Each of these sources pertain to the original works of Dobereiner, Mendeleev, Newlands, and Rutherford, respectively.

Various forms of periodic tables were discussed in the Encyclopedia Britannica (19). In this article, the advantages and disadvantages of different forms of periodic classification were presented. In particular, the long and short forms of periodic classification were compared.

BACKGROUND HISTORY

Purpose

Since the beginning of time, man has constantly tried to understand the nature of the world about him and classify his knowledge into more easily interpreted forms. The purpose of this section is to show how early thinkers attempted to find an order of the things about them just as scientists similarly later attempted to find an order to the chemical elements which comprise the entire universe.

Early Attempts at Classification

Early "Elements." The Greek thinkers, beginning with Thales of Miletus about 600 B. C. were primarily interested in explaining the working of the whole cosmos around them (6). Thales, after long thought, decided that the element out of which all the universe was built was water. In the first place, there was a great deal of water on the earth. Secondly, when water evaporated it apparently became air. Air also seemed to turn back to water in the form of rain. Finally, rain falling on the ground might eventually harden, he thought, and thus become soil and rock (1).

His own pupil, Anaximander, thought that water could not possibly be the building block of the universe, because its properties were too specific. Anaximander could not describe the fundamental element, but he gave it the name "apeiron." He maintained that the universe had been put together from a limitless supply of apeiron. Some day, if and when the universe was destroyed, everything would turn into apeiron again.

Anaximenes, a younger philosopher of Miletus, nominated air, instead of water, as the element of the universe. Since everything was surrounded by air, he reasoned that the earth and the oceans were formed by the congealing or condensation of air. Still others, like the Greek philosopher Heraclitus, insisted that the ultimate element was fire. The most important and universal feature of the universe, he felt, was change. Day followed night and night, day. One season gave way to another. The face of the earth was continually altered by rivers and earthquakes. Even man was ephemeral--he was born, grew up, and finally died. All this changeability was epitomized best of all by fire. This "substance," continually changing its form, blazing up and dying down, represented the essence of the universe, in Heraclitus' opinion. So he concluded that the universe must be made of fire in various manifestations (1).

Thus, out of these ideas, earth, water, and air stood for solid, liquid, and gas. To these was added fire, the principle of heat, or motion, the element of which the heavenly bodies were composed. Therefore, any solid body was an earth and any liquid was a water. Moreover, water, a liquid, could be converted to gas by boiling, or to earth, a solid, by freezing. Thus the elements were mutually interconvertible. These basic ideas were modified in different ways by various philosophers, but all the concepts were finally brought together by Aristotle (384-323 B. C.) in a synthesis to which his established position in later centuries gave an authority that was not shaken for many years (6).

Attempts by Aristotle. Aristotle assumed a prime matter of which everything was composed. This matter, however, was entirely without form and had no distinctive properties until form was impressed on it. Everything material was produced by the interaction of matter and form. By changing the form, new substances were produced. This theory was made concrete by the further idea of the opposing qualities: heat, cold, moisture, and dryness. Those qualities could be combined in any way, so long as the direct contraries did not unite.

In this way, four elements resulted. The ideal earth consisted of cold and dryness, water of cold and moisture, air of heat moisture, and fire of heat and dryness. The actual substances earth, water, air, and fire approached these on composition, but the balance was slightly disturbed by an excess of one quality over another. Thus everything could theoretically be transformed into anything else, especially since the four elements could combine into homoeormeria, or compound atoms, of which all material objects actually consisted. Substances were classified in terms of their predominant element, which gave to them their chief properties. Thus a substance which could be melted was called a water, since it partook of the nature of water. Like water, however, it could be congealed by replacing the quality of moisture with that of dryness, while cold remained; thus it was changed to an earth. Metals were therefore waters, and their oxides were earths (6).

Aristotle decided that the stars in the heavens must belong to a completely different category. Unlike the changeable matter on the earth, they seemed unchanging and eternal. So Aristotle invented a fifth element which he thought of as composing all of the universe outside the earth. He called it "aether;" later philosophers named it "quintessence," Latin for "fifth substance." Since the fifth element was supposed to be perfect, we still use "quintessence" in English to mean the purest form of anything (1). The ideas of Aristotle formed the basis for scientific thought in succeeding centuries.

Other Attempts. However, it was evident that there were certain other substances which gave a new concept to the meaning of the word "element." Gold, silver, copper, iron, tin, lead, mercury, carbon, and sulfur were elements known to the ancients. In addition, arsenic, antimony, bismuth, and zinc were discovered by the alchemists before 1700 (1, 9). As the list of newly discovered elements grew, the old ideas of earth, water, air, and fire among others as being elements gradually disappeared.

As attention became increasingly focused upon the elements, many men attempted to find some relationship among them. Although it is conceivable that early investigators may have attempted to classify known elements shortly after their discovery and give them recognition as fundamental substances, all modern effort may be traced directly or indirectly to the atomic theory proposed by John Dalton. Dalton's theory did not propose any system of arranging the elements, but it did provoke thought and speculation as to whether atoms of the various elements, although apparently different in properties, might be composed of the same fundamental substance and whether the marked similarities among certain elements might be traceable to their atoms (8).

Search for rules was greatly stimulated by William Prout's hypothesis in 1815 that all atoms were built of primordial atoms which he tried to identify with the hydrogen atom (3). Fundamental as was Prout's hypothesis, it was discredited by experimentally observed deviations of atomic weights from whole numbers, and in 1860 the precise atomic weight determinations of Stas lead to its complete abandonment (8).

Nevertheless, the groundwork had been provided for Dobereiner to propose his triads and thus to become the first person to report an attempt at classification of the elements (2, 4, 8).

DOBEREINER'S TRIADS AND SUBSEQUENT INVESTIGATIONS

The Triad Theory of Dobereiner

The use of the spectroscope aided greatly in revealing hidden elements such as the alkali metals. However, each new discovery was an unexpected event. Before the periodic law had been discovered by Lothar Meyer and Mendeleev in 1869, there was no way of predicting what elements lay undiscovered nor of foretelling their physical and chemical properties. One of the important steps leading up to this great generalization was the discovery by Professor Johann Wolfgang Dobereiner of his triads.

Dobereiner was born in December, 1780, the son of a coachman at Hof, near Beyreuth. He developed a great ability for original research in chemistry although he had only a meager educational background. In 1820, he became professor extraordinary of chemistry at Jena (20).

Dobereiner first expressed his ideas as early as 1817. In that year he noticed that within a group of elements closely related to each other in chemical properties, atomic weights are either nearly the same or else the atomic weight of the middle element is approximately the arithmetic mean of those of the other two (8). This stirring observation attracted much attention, for it seemed to show a numerical law governing chemical behavior. The first published explanation of his system of triads appeared in the paper, "An Attempt to Group Elementary Substances According to Their Analogies," in 1829 (2,6).

Using the atomic weights established by Berzelius, Dobereiner noticed the mean of chlorine (35.470) and iodine (126.47) was 80.97 for bromine. This number was larger than the atomic weight found by Berzelius for bromine (78.383); however, Dobereiner hoped that the difference would vanish after repeated atomic weight determinations of the three elements (6).

Three more elements which Dobereiner noticed were sulfur, selenium, and tellurium. He felt these elements could be compared since the specific gravity of selenium turned out to be the arithmetic mean of the specific gravities of sulfur and tellurium and all three substances combined with hydrogen to form characteristic hydrogen acids. Using atomic weights determined by Berzelius, the atomic weight of selenium was 79.263 which compared favorably with 80.741 determined by Dobereiner.

One interesting series of analogous metals which Dobereiner investigated are those which occur in platinum ores. Among these are platinum, palladium, rhodium, iridium, osmium, and ruthenium. At the time, the existence of ruthenium was still in doubt. The above elements fall into two groups according to their specific gravities and atomic weights. In the first group were platinum, iridium, and osmium, while in the second group palladium, rhodium, and ruthenium were placed. Dobereiner was able to compare these elements because the specific gravities of the various elements indicated a trend.

Since the specific gravity and atomic weight of lead were fairly near the arithmetical mean of the specific gravities and atomic weights of silver and mercury, Dobereiner placed these metals into a triad group. Whether tin and cadmium, antimony and bismuth, gold and tungsten, or tungsten and tantalum belonged together, Dobereiner did not venture to decide due to a lack of other analogies (6).

The fact that the arithmetical mean of the atomic weights of oxygen (16.026) and carbon (12.256) expressed the atomic weight of nitrogen (14.138) was not considered by Dobereiner because no analogies among these substances could be found.

Two other triads were found by Dobereiner: Ca, Sr, Ba; and Li, Na, K (10).

Investigations by Others

Dumas. J. B. Dumas applied the theory of triads to other groups of elements such as phosphorus, arsenic, and antimony (3).

Pettenkofer. In 1850, Pettenkofer suggested that among chemically similar elements successive differences in atomic weights amount to either some constant or to a multiple of some constant. Thus in the series oxygen (16), sulfur (32), selenium (80), and tellurium (128), the difference between the first two is 16 and between any other two is 48, or 3 x 16 (8).

Odling. In 1857, William Odling arranged the known elements into thirteen groups on the basis of similarities in chemical and physical properties, the members of each group being listed in order of atomic weights. Odling's arrangement resembles present-day grouping in qualitative analysis, since elements forming compounds of similar solubilities were placed together. However, his arrangement showed no relationships between atomic weights and chemical characteristics (8).

THE TELLURIC HELIX OF DE CHANCOURTOIS

Development of the Telluric Helix

By about 1860 the list of elements had grown to over 60. It was still just a list. With the exception of Dobereiner, no one had seen any kind of rhyme or reason in the collection.

Alexandre E. Beguyer de Chancourtois, a professor of geology in the School of Mines in Paris, made in 1862 a "telluric screw," or helix, on a vertical cylinder on which he placed the symbols of the elements at heights proportional to their atomic weights. He plotted the atomic weights as ordinates on the generatrix of a cylinder the circumference of which, since the atomic weight of oxygen is 16, he divided into sixteen equal parts (20). He traced on the surface of the cylinder a helix making a 45° angle with the axis. The spiral therefore crossed a given generatrix at distances from the base which were a multiple of 16. Thus lithium, sodium, and potassium with atomic weights of 7, 23, and 39, respectively, fell on one perpendicular, whereas oxygen, sulfur, selenium, and tellurium fell on another (20).

He observed the close similarity existing between elements on the same vertical line. De Chancourtois commented on this periodic recurrence of properties by stating that "the properties of substances are the properties of numbers" (16). The interesting thing about his playful arrangement was that Dobereiner's triads fell into line in a related order. For instance, the triad of calcium, strontium, and barium, were in one vertical line, with strontium just under calcium and barium under strontium. The same was true of the triad chlorine, bromine, and iodine and also the triad sulfur, selenium, and tellurium (1).

Acceptance of the Helix

De Chancourtois presented to the French Academy a diagram and a model of his "telluric screw." Unfortunately, his heavy, obscure literary style, his use of terms more familiar to geologists than to chemists, and the failure of anyone to publish a reproduction of his diagram contributed to a lack of appreciation of his contribution (20).

NEWLANDS' LAW OF THE OCTAVES

Newlands' Chemical Background

Another important advance in the classification of the elements was made by John Alexander Reina Newlands, just two years after the "telluric screw" of de Chancourtois. Newlands was born in Southwark, England, in 1837 and was educated privately by his father, a minister of the Established

Church of Scotland. When he was nineteen years old he entered the Royal College of Chemistry to study under Hofmann. His sympathy for Italy, the land of his maternal ancestors, led him to volunteer in 1860 for military service under Garibaldi. When Italian freedom had been won he returned to London to practice for a time as an analytical chemist. He then taught at the Grammar School of St. Saviour's, Southwark, at the School of Medicine for Women, and at the City of London College. For many years he was the chief chemist in a large sugar refinery at Victoria Docks, and with his brother, Mr. B. E. R. Newlands, he later published a treatise on sugar (20).

In 1864, he arranged the elements in the order of increasing atomic weights and noticed that after each interval of eight elements, similar physical and chemical properties reappeared.

The Law of the Octaves

To gain a better understanding of Newlands' arrangement of the elements, the first three columns of his table will be discussed. In the first column, he placed hydrogen, lithium, beryllium, boron, carbon, nitrogen, and oxygen. In the second column fluorine, sodium, magnesium, aluminum, silicon, phosphorous, and sulfur were placed while the third column consisted of chlorine, potassium, calcium, chromium, titanium, manganese, and iron. Although fluorine had not been officially isolated, Newlands placed it in his table because its existence was strongly suspected. He should have placed vanadium in the third column, after titanium, but he had the wrong atomic weight for the element and hence placed it much farther down the list.

Upon examining Newlands' arrangement of the elements, some trends readily became apparent. For example, in the first column came hydrogen, a fairly active gas; lithium, an active solid; beryllium, a less active solid; boron, a still less active solid; carbon, an even less active solid; nitrogen, an inactive gas; and finally, oxygen, an active gas (1).

In the second column was fluorine, an active gas; sodium, an active solid; magnesium, a less active solid; aluminum, a still less active solid; and silicon, an even less active solid.

Newlands felt that he had made a definite advancement. The second column repeated the pattern of the first. For example, fluorine showed several chemical similarities to hydrogen and sodium proved to be very similar to lithium. Likewise, magnesium, aluminum, and silicon showed chemical similarities to beryllium, boron, and carbon, respectively.

The third column also showed similar trends and comparisons to the first two columns. Newlands was certain he had something. His table explained Dobereiner's triads very nicely. For example, chlorine headed the third column, bromine headed the fifth, and iodine headed the seventh column. Also, calcium, strontium, and barium were all in the third position in their respective columns. To these, Newlands added beryllium and magnesium. Moreover, sulfur, selenium, and tellurium, a third triad, were all at the bottom of the columns (1).

Newlands' table then revealed not triads, but quintets and even larger families of similar elements. All one had to do to find families was to read horizontally across the various columns. Although Dobereiner had been on the right track, he had simply not gone far enough.

Because the arrangement of the elements in the table reminded Newlands of the musical scale, he called his discovery the "law of the octaves."

Just as music had its octaves, so his table of elements had octave intervals, with seven elements in each group corresponding to the seven notes do, re, me, fa, sol, la, te (1).

Acceptance and Significance of Newlands' Work

From this "law of octaves," Newlands gained nothing but public ridicule from the English Chemical Society. The importance of atomic weights was so little realized that he was once asked if he could not get the same result by arranging the elements according to the initials of their names (13).

The learned editor of the English Chemical Society's journal refused to publish Newlands' paper, despite the fact that it was one of the most important contributions to the development of the periodic law. The time was not quite ripe for acceptance of such novel ideas. Twenty-three years later, the Royal Society awarded Newlands their highest honor, the Davy Medal, for his work. Fortunately, he was still alive, or he might have died without enjoying the satisfaction that was his due (16).

In a biographical sketch in Nature, W. A. Tilden stated that this tardy recognition, which came five years after the same honor had been conferred on Mendeleev and Lothar Meyer, did not do Newlands full justice (4).

However, Newlands' table did have some bad flaws. Some of the elements obviously didn't fit into the places he had assigned to them. For instance, iron, the last element in the third column, was completely different in every way from oxygen and sulfur, the last elements in the first and second columns. Iron didn't even form the same kind of compounds (1).

All of the elements at the top of Newlands' eight columns did not fit perfectly either. Although hydrogen, fluorine, chlorine, bromine, and iodine could be placed in the same family, cobalt, nickel, palladium, platinum, and iridium certainly did not belong with these. For example, fluorine is extremely reactive and a gas while iridium is the least reactive of the above elements and a solid.

In addition, it was necessary to double up some elements in the same positions in order to maintain the periodic likenesses. Cobalt was doubled with nickel and platinum with iridium. Some elements had to be placed out of the order of atomic weight. Hence, chromium was placed ahead of titanium, although Newlands knew that titanium had a greater atomic weight. This was necessary because chromium seemed more like aluminum than like silicon.

Newlands basically had the right idea but had made the mistake of counting off by sevens for all his columns. This threw his entire table hopelessly askew (1). But some of the inconsistencies were due to the discovery of elements unknown in Newlands' time and inaccuracies in his atomic weight data (8).

At any rate, the final evolution of the periodic classification soon occurred as a result of apparently independent efforts of Dimitri Mendeleev and Lothar Meyer in 1869.

THE CONTRIBUTIONS OF LOTHAR MEYER

Chemical Background of Meyer

In 1869, just six years after Newlands attempted a periodic classification of the elements, a German chemist named Julius Lothar Meyer apparently discovered the trouble.

After receiving his degree of doctor of medicine from Wruzburg University in 1854, Meyer knew that he was more interested in research than in the practice of medicine. Therefore, he went to Heidelberg to study under Bunsen and Kirchhoff, where the latter soon aroused in him an intense interest in applied mathematics. Meyer made his name well known throughout the scientific world with his book Modern Theorien der Chemie, published in 1858, which contained his first incomplete periodic table (20).

Lothar Meyer's Arrangement of the Elements

Meyer took a different approach to arranging the elements. Instead of trying to fit them into a hard-and-fast arrangement, as de Chancourtois and Newlands had done, he let the properties of the elements dictate the arrangement. Meyer concentrated on the particular property of weight. He noticed the odd fact that the weight of a given volume of each of the elements was not consistent with its relative atomic weight. Taken for instance, cesium and barium. In bulk, barium was found to be nearly twice as heavy as cesium. Yet both elements had similar atomic weights.

To Meyer, this meant only one thing. In their bulk agglomerations barium atoms must have been packed together twice as closely as cesium atoms. To put it another way, the "atomic volume" of barium was only half that of cesium (1).

Meyer went through the whole list of known elements, plotting atomic volume against atomic weight. The result showed a graph which took the form of a series of waves. For example, Meyer found that the atomic volumes of the elements following lithium declined. Thus, the graph curve declined for beryllium and boron. However, the atomic volumes for other elements, such as carbon, nitrogen, and oxygen, began to rise and finally reached another maximum with sodium. After that, the atomic volumes began to fall again and then rise until they reached a higher peak at potassium. The atomic volumes rose and fell like a set of waves. The peaks in his graph consisted of lithium, sodium, potassium, rubidium, and cesium. These are all alkali metals and form a true, consistent pattern of closely related elements. Various other positions on the waves corresponded to groups of closely related elements. In other words, when Meyer classified the elements according to atomic volume in relation to atomic weight, they fell into families (1).

The graph constructed by Meyer showed where Newlands had gone wrong. The waves got longer as he went down the list of elements according to increasing atomic weight. For example, in the second and third sections of his graph, the atomic weight increased by increments of sixteen units. But in the fourth and fifth sections, the atomic weight increments were much larger since they consisted of about forty-six units each. If Newlands had made his later columns twice as long as his first two, many of his difficulties would have been solved.

Meyer then prepared other curves which showed that fusibility, volatility, malleability, brittleness, and electrochemical behavior are also periodic properties. The volatile and easily fusible elements lie on the ascending portions of the curves, whereas the refractory elements are on the descending portions or at the minima (1).

From this information, Lothar Meyer extended his periodic table to fifty-six elements, arranged in groups and subgroups. It was not until

1870 that the first graph by Meyer was published. History might have made him a very famous man, but he was just a little too late. In 1869, a Russian chemist, Dmitri Mendeleev, published a table which was to become the best classification of the elements of that time (16).

THE WORK OF MENDELEEV AND ITS CONSEQUENCES

Mendeleev's Scientific Background

Dmitri Ivanovich Mendeleev was born in Tobolsk in western Siberia on February 8, 1834. As a child, he excelled in mathematics, physics, and history, but he never liked Latin. His first science teacher was his brother-in-law, Basargin, a well-educated Russian who had been exiled for attempting to start a revolution. Dmitri completed the gymnasium course at the age of sixteen years. When Mendeleev graduated from the Pedagogical Institute, he received a gold medal for excellence in scholarship. Between 1859 and 1861 he worked with Regnault in Paris and with Bunsen in Heidelberg. Upon returning to Petrograd in 1861, he was granted his doctorate and was appointed professor of chemistry at the Technological Institute. Eight years later he became the professor of general chemistry at the University of Petrograd (20).

Development of the Periodic Law

In the late 1860's Mendeleev, like so many chemists before him, tackled the problem of finding some sort of order in the list of elements. Meyer in Germany was working on the problem from the point of view of atomic volumes. Mendeleev, unaware of Meyer's work, approached the matter from a different angle. His starting point was the valences of the elements.

For many years it had been known that each element had a certain combining power. The hydrogen atom, for instance, could not take on more than one other atom at a time. It never combined with two atoms of oxygen, say, to form HO_2. In 1862, an English chemist named Edward Frankland coined the term "valence" to denote combining power.

Mendeleev focused his attention upon the valences of the elements. He listed the elements in order of molecular weight and wrote down the valence beside each element. From this he observed that the valences of the elements moved up and down in waves. Later in his list, matters weren't quite so simple, but the valence continued to move up and down although the waves were longer, just as Meyer discovered in his graph of atomic volumes (1). What Mendeleev saw was that the valence and other properties were related to atomic weight. In this vision he was not alone, for a few of his contemporaries reached the same conclusion independently. However, Mendeleev was the first to apply it to all the known elements (6).

On the basis of the cycles, or "periods," revealed by the valences, Mendeleev composed a "periodic table" of the elements. In March, 1869, he presented to the Russian Chemical Society his immortal paper, "On the Relation of the Properties to the Atomic Weights of the Elements" (16). In this paper Mendeleev introduced his periodic law. One way of stating the law is: "If the elements are listed in the (approximate) order of their atomic weights, elements with similar properties recur at definite intervals" (6).

All of the known 63 elements were now arranged for the first time in the order of their atomic weights, whereupon they were seen to be periodic in that they fell into successive lines of a table in which similar elements came in the same vertical column. There were gaps and discrepancies, but closer study justified Mendeleev's classification.

Significance of Mendeleev's Table

Atomic Weight Corrections. The immediate results of Mendeleev's statements wore astounding. To begin with, a number of the elements did not fit in with his scheme. But Mendeleev announced that the fault lay with incorrect atomic weights which had been assigned to these elements. He proved right in all such cases. For example, the then accepted atomic weight for gold was 196.2. Therefore, it should have been placed before such elements as platinum, iridium and osmium with atomic weights of 196.7, 196.8, and 198.6, respectively. But Mendeleev insisted upon putting gold after these elements, claiming that their atomic weights, and not his table, needed revision. A revision of the atomic weights gave osmium a weight of 190.9, iridium a weight of 193.1, platinum a weight of 195.2, and gold a weight of 197.2, which was exactly the order in which Mendeleev had originally placed them (4).

Mendeleev placed tellurium ahead of iodine in his table in spite of its higher atomic weight, because the switch put these elements in the proper rows with their chemical cousins. In addition, he made other shifts which shocked chemists even more. Beryllium was supposed to have an atomic weight of about 14, but Mendeleev knew there was no vacancy for an element of that weight in his table. He placed beryllium in row IIa alongside magnesium, which it resembled. This meant that beryllium should have an atomic weight of about 9. Sure enough, it was eventually established to be 9.013. Similarly, he said that the chemists were wrong in their atomic weights for indium and uranium, too, and the weights he gave these two elements were later proved correct.

Prediction of New Elements. But Mendeleev's most daring prediction concerned certain missing elements. To make his periodic table work, he had to leave several holes in it. There was a gap between zinc and arsenic large enough for two elements. He then proceeded to call these elements "eka-aluminum" and "eka-silicon" as well as predict their properties. Mendeleev's table had a third vacancy in the fourth period next to yttrium in row IIIa. He was sure that an element was missing there also, and that its properties should be like those of yttrium and lanthanum. This element was called "eka-boron" by Mendeleev (1).

At first chemists refused to take Mendeleev's predictions seriously. Many foolish things had been done in the name of chemistry, but no one had ever attempted to make up elements out of pure imagination. People had deduced elements from the death of mice, from colors of minerals, and from mere lines in a spectrum. But Mendeleev described, down to the smallest details, elements which had never given any tangible sign of their existence.

However, one by one, the missing elements predicted by Mendeleev began to show up. A young French chemist named Paul Emile Lecoq de Boisbaudran was working with the spectroscope and noticed some strange spectral lines. After careful isolation and analysis, the new element showed nearly the identical properties predicted by Mendeleev for his eka-aluminum. The new element was called gallium. Four years later, in 1878, Per Teodor Cleve, a Swedish chemist, noticed that a newly discovered element, scandium, behaved just as Mendeleev had predicted eka-boron would have. Further analysis showed Mendeleev's description of the element to be almost exact in every detail. Mendeleev's final triumph came in 1886 when a German chemist, Clemens Alexander Winkler, discovered a new element in a mineral from a silver mine which he called germanium. He also noticed that the properties of germanium were nearly identical with eka-silicon, thus filling a third gap in Mendeleev's table.

The accuracy which Mendeleev displayed in predicting properties of unknown elements was amazing. For example, Mendeleev predicted the atomic weight of germanium would be 72; it was found to be 72.5. He predicted the density would be 5.5; it was determined to be 5.469. Mendeleev predicted the density of the oxide would be 4.7 and the density of the chloride would be 1.9. They were found to have densities of 4.703 and 1.887, respectively. The predicted value for the boiling point of the ethide was 160°C, which was exactly the same as the experimentally determined value (1). There was little doubt that Mendeleev knew what he was doing.

Influence of the Periodic Law

The great work of Lothar Meyer and Dmitri Mendeleev brought them the coveted Davy Medal in 1882. The triumph of Mendeleev's periodic table also brought recognition and vindication to Newlands, and even to Beguyer de Chancourtois. In 1887, Newlands was awarded the Davy Medal and in 1891, a French scientific journal belatedly printed the diagram of de Chancourtois' "telluric screw" (16).

Like many other great scientific discoveries, the periodic law was discovered entirely empirically and long before its fundamental basis was understood. The discoverers, and those who contributed to its early development, knew nothing about electrons, protons, or neutrons, nothing about atomic number, nothing about atomic structure. Yet this did not prevent immediate usefulness of the periodic table both as a basis for seeking unknown elements and as a framework for the organization for the ever increasing multitude of chemical facts. The periodic law and periodic tables contributed immeasurably to the development of chemistry for over half a century before enough had been learned about atomic structure to establish the law on a sound, fundamental basis.

SUBSEQUENT WORK ON PERIODIC CLASSIFICATION

Modification of Mendeleev's Table

Discovery of the Rare-Earth and Inert Gas Elements. After the discovery of gallium, scandium, and germanium, there were three holes left in Mendeleev's table—one in the fifth period and two in the sixth. Nobody doubted that these would eventually be filled by new discoveries. However, there were several known elements for which no room could be found in the table.

The difficulty started with the three rare-earth elements cerium, erbium, and terbium. Mendeleev's table had no proper place for them. These three elements might have been overlooked, but the list of rare-earth elements began to multiply like weeds. De Boisbaudran discovered samarium and dysprosium. Cleve discovered and named holmium. A Swiss chemist, Jean-Charles Galissard de Marignac discovered two new elements which he called ytterbium and gadolinium. Praseodymium and neodymium were soon discovered by Carl Auer von Welsbach, an Austrian chemist (1).

Logically, these elements belonged in row IIIa with the other known rare-earth elements. All the rare-earth elements were very much alike; all had a valence of three and all seemed to go together. To make the table workable, twelve elements had to be placed in the space occupied by lanthanum.

At the end of the nineteenth century, another stunning surprise upset the chemists. Robert John Strutt found that nitrogen from the air weighed slightly more than samples of nitrogen from nitrogen-containing minerals. William Ramsay, a Scottish chemist, worked on the problem and finally discovered it was due to a completely inert new element which he called argon. Its atomic weight, 39.944, was between potassium and calcium, but there was no vacancy between them. This time the solution was easy. Mendeleev had simply left out a whole row. Confirmation of this followed shortly upon the discovery of the other inert gases. For his discovery of the "noble" gases, Ramsay received the Nobel Prize in chemistry in 1904 (1).

Most of the other elements discovered around the turn of the century, such as polonium, radium, actinium, radon, europium, and lutetium, fitted beautifully into the periodic table. Radon was an inert gas; radium, an alkaline-earth element; polonium, a relative of tellurium; and actinium, a relative of lanthanum. There was a place for each of them. Furthermore, they helped to fill out the sixth and seventh periods where there was plenty of room for new elements.

<u>Atomic Number as a Basis for Classification</u>. Another problem arose when chemists began to look into the products of radioactive decay. They

found three different series of products named the "uranium series," the "thorium series," and the "actinum series," for the starting element in each case. Very quickly, chemists identified more than 40 new "elements" among these products. The isotope theory at once accounted for the 40-odd species of elements discovered between uranium and lead. They were, in fact, isotopes of just a few elements. The theory also showed for the first time why the atomic weights of most of the elements were not whole numbers. The reason was simply that the elements found in nature were mixtures of isotopes. Many stable elements were also shown to be composed of isotopes after the invention of the mass spectrograph, developed by the English physicist Francis William Aston.

The isotope discoveries reduced the importance of atomic weight. This property was not the decisive one in identifying the elements. A British physicist, Henry Gwyn-Jeffreys Moseley, made a systematic study of the elements with X-rays as a probe. As he went down the list of elements, Moseley found that the wavelength of the characteristic X-rays became progressively shorter as the atomic weight increased. He decided that the wavelength reflected the size of the electrons' orbits around the nucleus of the atom. Probably the electrons were responsible for the emissions of X-rays. He reasoned that the closer the electrons were to the nucleus, the smaller would be their orbit; and the tighter their orbit, the shorter the wavelength of the X-rays emitted (1).

Since the wavelength decreased with the weight of the atom, Moseley reasoned that the electrons should be closer in the heavier atoms. Thus Moseley believed that an increase in the nucleus' positive charge was necessary to attract the negatively charged electrons. In other words, the nuclear charge must be increased from element to element through the periodic table. Moseley felt the most reasonable way to account for this was to suppose that each element had one more unit of positive charge than the one before.

The atomic number at once proved to be much more useful than the atomic weight for organizing the table of elements. For instance, in terms of atomic weight there was a substantial gap between hydrogen and helium. It left room for an element with an atomic weight between them. But their respective atomic numbers of 1 and 2 definitely ruled out the possibility of any element occurring between them. On the other hand, a missing atomic number in the list definitely meant a missing element. In short, the use of atomic numbers pinpointed all the missing elements and also made it plain when an element was not missing.

The atomic number system also solved the mystery of the few elements that had to be placed in the wrong order of atomic weight in the periodic table. For example, Mendeleev had to place tellurium ahead of iodine, although its atomic weight was greater. The atomic numbers of these elements are 52 and 53, respectively. So on the basis of nuclear charge, Mendeleev had been right. The reason tellurium has a higher atomic weight is that its isotopes load the element on the heavy side.

It is unfortunate that Moseley did not live to see how beautifully his discovery of the atomic number worked out. In 1915, he was killed by a bullet in the battle of Gallipoli at the age of 27 (1).

Completing the Gaps and the Transuranium Elements

By 1925, the search for the elements had uncovered 88, of which 81 were stable and seven radioactive. Only four were still believed missing; these were numbers 43, 61, 85, and 87. In 1931, missing element number 43 was discovered using artificial transmutation by bombarding molybdenum, element number 42, with protons. The element was named technetium. Elements 61, 85, and 87 followed soon thereafter, apparently completing the table of elements (1).

There followed, however, the identification of a new series of transuranium elements increasing the number of known elements further. Fermi created the first, element number 93, although he could not identify it. The others were produced soon by using the principle of artificial transmutation. Only three years ago, in 1961, the last element called lawrencium, number 103, was created at the University of California in an atom smasher. Lawrencium lasted about sixteen seconds and for elements 104, 105, 106, and 107, the lifetimes will get progressively shorter and the identification will get progressively more difficult. Nevertheless, each of these elements will fit into the periodic table without any trouble due to the use of atomic number rather than atomic weight as the basis for classification (18).

From the work of Moseley and others, the periodic law might indeed be restated: "The physical and chemical properties of the elements are a function of the electronic configurations of their atoms which vary with increasing atomic number in a periodic manner" (16).

Methods and Trends in Classification

Methods of Representing the Elements. Ever since the successful reception of Mendeleev's table, chemists the world over have been interested in developing superior ways of representing the periodic law. Scores of different representations have been proposed: two-dimensional, three-dimensional, rectangular, triangular, circular, helical, or cylindrical. The complexity of chemistry is so great that probably no single form of periodic table can ever be devised to organize chemistry in a manner completely satisfactory to everyone (16).

The major objection offered to the Mendeleev tabulation centers in the inability of that arrangement to reflect the electronic configurations of the atoms of the elements. This is important for several reasons. Inconsistencies in oxidations state predictions, dissimilarities between subgroups within a given group in general, marked differences in the properties of elements placed in the same group, incompleteness in the separation of metals from non-metals, and inconsistencies in the grouping of materials giving colorless and diamagnetic ions as opposed to those giving colored and paramagnetic ions all depend upon the absence of exact electronic configuration relationships. The ideal periodic arrangement, therefore, should be based upon electronic configurations.

Due to the above factors, most modern tables break all groups down into subgroups or families, except for the inert gas group. The families have ordinarily been designated as "A" or "B", although a certain lack of consistency in the designation of A and B families characterizes all except those elements in Groups I and II (8).

Forms of Periodic Tables. Two major forms of the periodic tables are the short form and the long form. The short form commonly has seven periods and nine groups. All groups except the inert gas group have the "A" and "B" family elements together. The disadvantage of the short form is that it confuses the user by placing in the same group such dissimilar elements as the halogens and manganese and its congeners. Thus, the chemical properties and electronic configurations of the elements within a group are not the same. The long form contains all of the elements in seven horizontal periods of varying lengths with the rare-earth metals cerium, 58, to lutecium, 71, and the uranium metals, thorium, 90, to lawrencium, 103, indicated separately below (19).

The long form is derived from the original Mendeleev form by merely extending each of the long periods and breaking the short periods to accommodate the transition series in the long periods. The long form relates the position of an element to the electronic arrangement in its atoms. It also reflects the similarities, differences, and trends in chemical properties more clearly than the short form. In short, it provides a clearer means of correlating the mass of information which has accumulated about the elements and their compounds.

Despite its advantages, the long form is not free from defect. The exact distribution of electrons among all the orbitals is not indicated. There is no specific position for hydrogen. It is placed with both the alkali metals and the halogens, which reflects both its ability to lose an electron or gain an electron. Also, the elements of the inner transition type are not placed where they are completely satisfactory. The elements lanthanum and actinium are given places as analogs of scandium and yttrium in the sixth and seventh periods (8).

As mentioned previously, there have been many unsuccessful attempts to devise a completely satisfactory periodic table. No attempt has been made to discuss comprehensively the wide variety of periodic tables which have been described. The attempt has been only to present some of the mechanics and bases of periodic classification and to indicate its general utility.

SUMMARY

Through the centuries, the concept of classification of matter has changed from pure speculation and abstraction to a concrete level using the application of physical laws. Inquisitive minds have brought the vague ideas of early philosophers and scholars into the realm of reality. The ideas of Aristotle concerning the "qualities" were soon replaced with theories based upon mathematical calculations and measurements. As the laws of physics were discovered, the concept of periodic classification was brought into full focus.

As new ideas were introduced, they became fused with or superimposed on the old. Introduction of atomic numbers as the basis for periodic classification substantiated the earlier use of atomic weight and offered further evidence that some ordered relationship existed among the elements.

Today, the periodic table is one of the most useful and valuable tools of science. It is a testimony to the many scientists who experimented in atomic weights and constantly sought new discoveries. Periodic classification, as illustrated in the periodic table, shows the order based on natural laws that exists in the universe. Recognition of the orderliness in science has helped man advance his civilization.

The periodic table has been called the bible of the elements because it established certain relationships. By looking at the position of an element on the periodic table, the structure and properties can be predicted in a general way.

Although there have been many attempts to perfect the periodic table, there are still several inadequacies present. The element hydrogen and the elements of the rare-earth and the actinide series have no definite position on the table. In addition, there is no way to indicate multiple valences for an element. There are also inconsistencies in the classification shown on the periodic table and the arrangement suggested by the electromotive series and some of the analytical schemes (11). These inadequacies serve as a challenge to modern scientists to find a satisfactory revision.

All over the world today, scientists are constantly trying to find the secrets of the universe. In so doing, they are being guided by the efforts of the pioneers in chemistry and physics who helped formulate the periodic table.

LITERATURE CITED

(1) Asimov, Isaac.
The search for the elements. New York: Basic Books, 1962. 300 p.

(2) Dobereiner, J. S.
An attempt to group elementary substances according to their analogies. Poggendorf's Annalen, 15:301-307, 1829.

(3) Farber, Eduard.
The evolution of chemistry. New York: Ronald Press, 1952. 349 p.

(4) Harrow, Benjamin.
Eminent chemists of our time. New York: D. Van Nostrand, 1927. 471 p.

(5) Krauskopf, Konrad.
Fundamentals of physical science. New York: McGraw-Hill, 1959. 636 p.

(6) Leicester, Henry M. and H. S. Klickstein.
Source book in chemistry. New York: McGraw-Hill, 1952. 554 p.

(7) Mendeleev, Dmitri.
Faraday memorial lecture. Chem. News, July 13, 1879, 40:159.

(8) Moeller, Therald.
Inorganic chemistry. New York: John Wiley and Sons, 1961. 966 p.

(9) Moore, F. J.
History of chemistry. New York: McGraw-Hill, 1931. 292 p.

(10) Muir, M. Pattison.
History of chemistry theories and laws. New York: John Wiley and Sons, 1907. 570 p.

(11) Nebergall, W. H. and F. C. Schmidt.
General chemistry. Boston: D. C. Heath, 1959. 688 p.

(12) Newlands, John A. R.
On the discovery of the periodic law. London: E. and E. N. Spon, 1883. 60 p.

(13) ———.
Relation among the elements. Chem. News, August 20, 1864, 10:60; March 16, 1866, 13:130.

(14) Partington, J. R.
A short history of chemistry. New York: Macmillan, 1957. 415 p.

(15) Rutherford, E.
Henry Gwyn Jeffrys Moseley, Nature 96:33-34. 1915.

(16) Sanderson, R. T.
Chemical periodicity. New York: Reinhold, 1960. 330 p.

(17) Seaborg, Glenn T.
Man-made transuranium elements. Englewood Cliffs, N. J.: Prentice-Hall, 1963. 108 p.

(18) The elements: four more to go? Newsweek, November 20, 1961, 58(21):92.

(19) The periodic law. Encyclopedia Britannica. 25th ed. 17:517-521.

(20) Weeks, Mary Elvira.
Discovery of the elements. Easton, Penn.: Journ. of Chem. Ed. Pub., 1956. 898 p.

THE HISTORICAL DEVELOPMENT OF THE PERIODIC CLASSIFICATION OF THE CHEMICAL ELEMENTS

by

RONALD LEE PFISTER

B. S., Kansas State University, 1962

AN ABSTRACT OF A MASTER'S REPORT

submitted in partial fulfillment of the

requirements for the degree

MASTER OF SCIENCE

Department of Physical Science

KANSAS STATE UNIVERSITY
Manhattan, Kansas

1964

The purpose of this study is to show that the periodic classification of the chemical elements was developed as the result of the efforts of scientists from several countries using information from atomic weight investigations. In addition, this study attempts to show the significance of the periodic table with respect to the discovery of new elements plus some desirable attributes and modern trends of periodic classification. This study has been an attempt to further an appreciation of periodic classification by telling the story of its development.

Because the development of periodic classification parallels the chronological history of civilization, this study was begun with a consideration of the ideas held by the early Greeks, alchemists, and chemists of the eighteenth and nineteenth centuries. The works of several leading chemical historians were used for this purpose. In addition, several primary sources were referred to in finding specific information about chemists who contributed to the founding of the periodic law.

Accounts are given of the discoveries of new elements which were predicted by Mendeleev. In addition, the work of Moseley and others after the periodic law was known are presented.

Throughout this study, the technical details of the various experiments are not indicated. It is concerned only with the various theories and discoveries as related to the general concept of periodic classification.

It was found in this study that the periodic classification of the elements can not be credited to any one individual. The shift from atomic weights to atomic numbers as a basis for a periodic system of classification has occurred. Although the usefulness of the periodic table for

finding new elements is essentially past, its usefulness for confining a wealth of information about the properties of the elements is ever present.

Many different forms of periodic tables have been constructed to try to meet the demands for a particular situation. However, probably no one individual periodic arrangement of the elements is suitable for everyone.

As scientists try to find the many secrets of the universe today, they are constantly being guided by the chemists and physicists who helped formulate the periodic law.