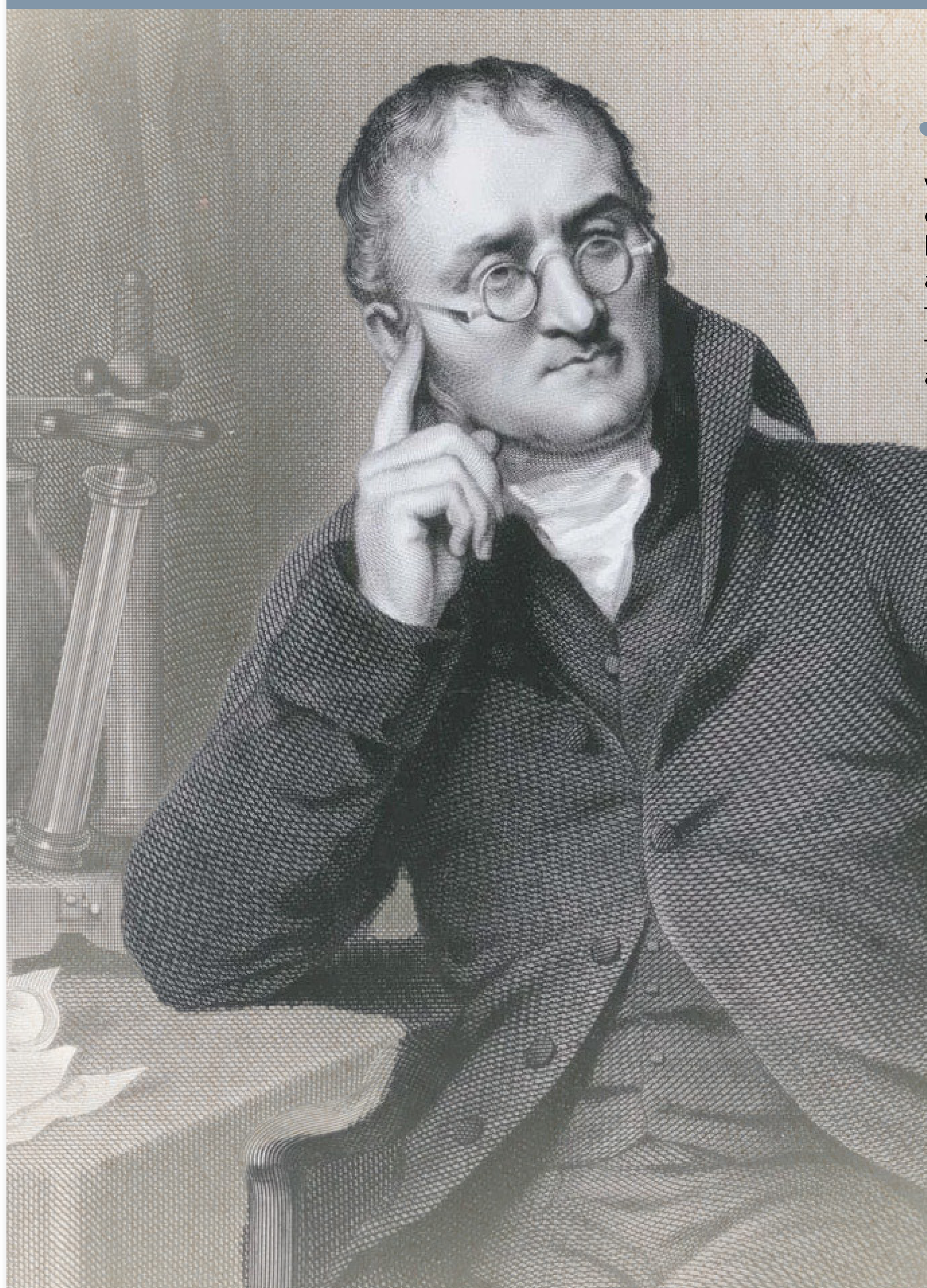
MODULE IV. 1750-1820

THE ELEMENTS

Early, ingenious ideas about the internal structure of crystals were mostly based on the close packing of particles. For example, the fact that quartz is often found with close geometric shapes was noted by Pliny the Elder (23–79) in his Natural History: “It is not easy to understand why it has six angles and six faces, especially as the angles do not always have the same appearance. As for the polish of the faces, it is such that no art can equal it.” In the last quarter of the 18th century, the French crystallographer René Just Haüy (1743-1822) proposed a revolutionary model based on the periodic repetition of a submicroscopic polyhedron which is similar to the unit cell of modern structural crystallography. This model preceded the atomic theory of John Dalton (1766-1844) by more than thirty years and represented a first modern and general attempt to reasonably represent the atomic structure of the matter. Subsequently, Haüy’s structural model inspired Amedeo Avogadro (1776-1856) and André Amèpre (1775-1836) to draw fundamental theoretical consequences from the results published by Jean Louis Gay-Lussac (1778-1850) on the chemical combination of gases.

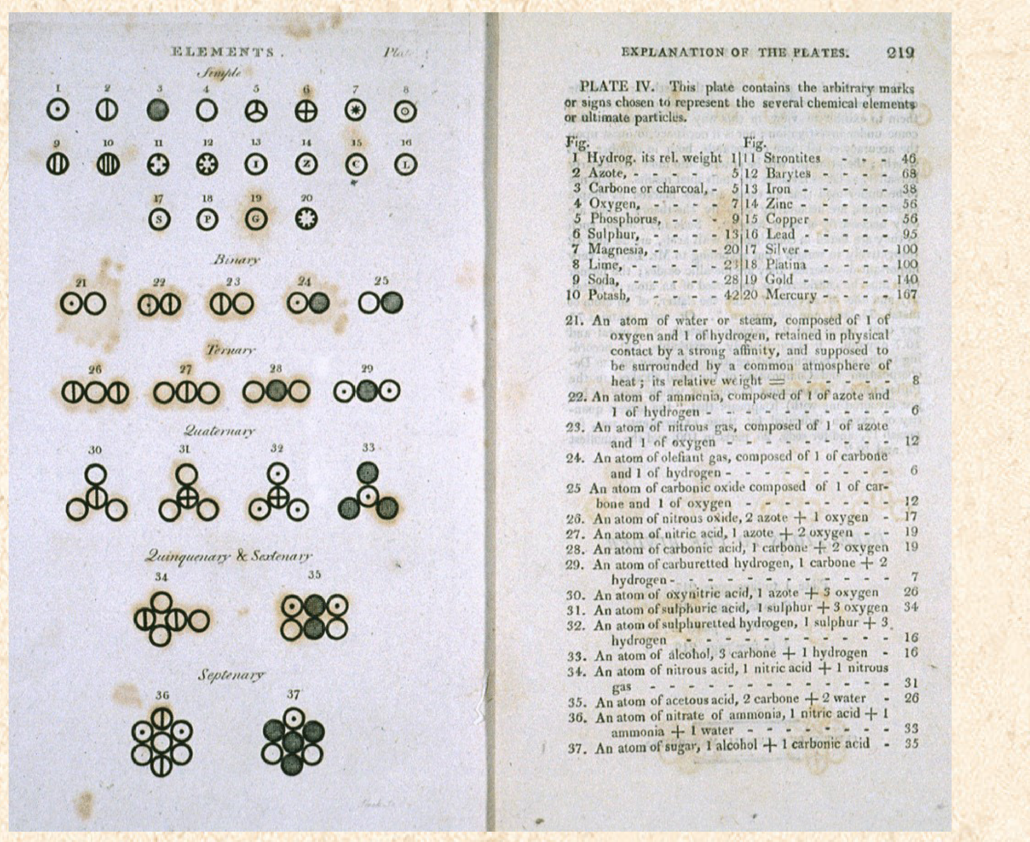


JOHN DALTON (1776-1844)

was an Englishman who formulated the law of partial pressures in 1801, according to which the pressure of a mixed gas is the sum of the pressures that each of its components would exert if occupying the same space. He also developed the law of the thermal expansion of gases. At the end of an 1803 paper on the absorption of gases by liquids, Dalton set out the first table of atomic weights. Dalton’s theory was based on the concept that each element consists of its own unique brand of indivisible atom; atoms of one element are all alike but they differ from atoms of other elements. Importantly, Dalton assigned atomic weights to the atoms of the 20 elements he knew of at the time. This was a revolutionary concept for the day, which would contribute to the development of the periodic table of the elements later in the 19th century. The concept, that atoms of different elements are distinguished by differences in their weights, opened up new fields of experimentation. Each aspect of Dalton’s theory has since been amended or refined, but its overall picture remains the basis of modern chemistry and physics.

BIRTH OF CRYSTALLOGRAPHY

From ancient times, it has been noted that certain minerals found in nature exhibit ordered structure. As we have seen, the characteristics of quartz were identified early. Calcite is another notable mineral in crystallography, first due to the spectacular variety of its natural crystal habits. It appears in caves as stalactites, stalagmites or abundant aggregates. In mines, it is often found with numerous angular shapes and is characterized by the shapes of its breaks (fractures). These fractures show similar shapes (i.e. rhombohedra), a constancy that contrasts with the amazing variety of crystals and concretions. Haüy’s interest in crystallography resulted, he later reported, from the accidental breaking of a piece of calcite. In examining the fragments he discovered that they cleaved along straight planes that met at constant angles. He broke more pieces of calcite and found that, regardless of the original shape, the broken fragments, were consistently rhombohedral. From subsequent experiments, he derived a thorough going theory of crystal structure.



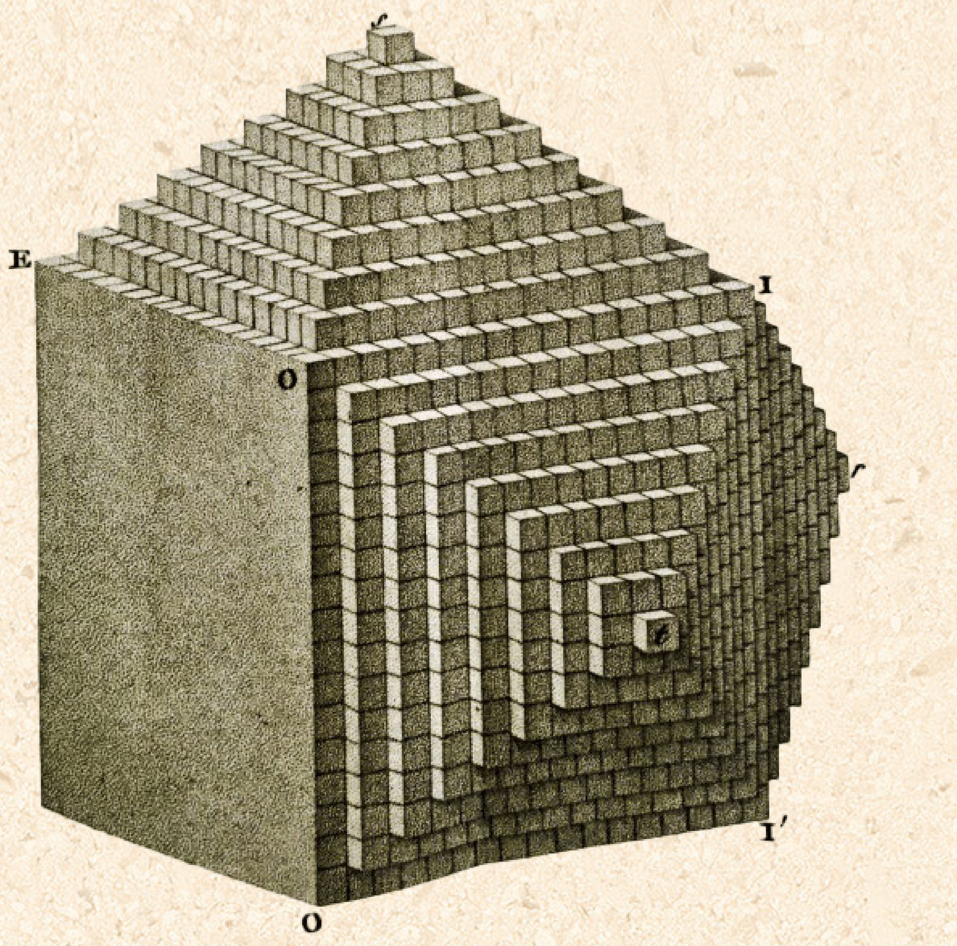
DALTON’S ATOMIC THEORY

- All matter is made of atoms. Dalton hypothesized that the law of conservation of mass and the law of definite proportions could be explained using the idea of atoms. He proposed that all matter is made of tiny indivisible particles called atoms, which he imagined as “solid, massy, hard, impenetrable, movable particle(s).” It is important to note that since Dalton did not have the necessary instruments to see or otherwise experiment on individual atoms, he did not have any insight into whether they might have internal structure. We might visualize Dalton’s atom as a piece in a molecular modeling kit, where different elements are spheres of different sizes and colors. While this is a handy model for some applications, we now know that atoms are far from being solid spheres.

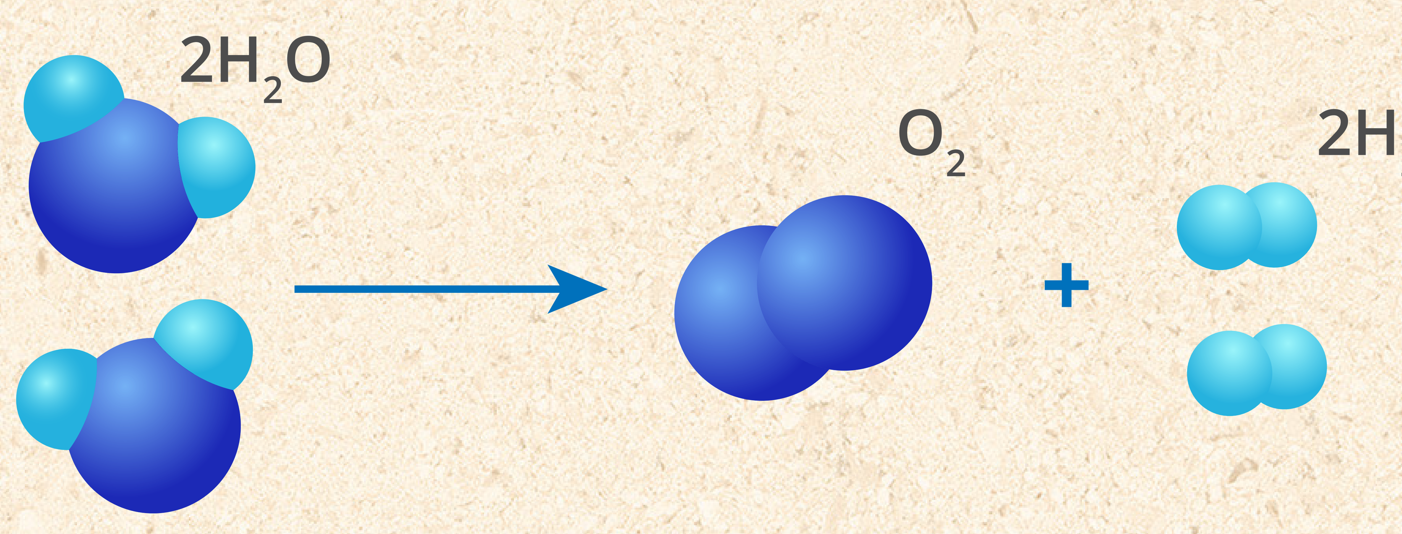
- All atoms of a given element are identical in mass and properties. Dalton proposed that every single atom of an element, such as gold, is the same as every other atom of that element. He also noted that the atoms of one element differ from the atoms of all other elements. Today, we still know this to be mostly true. A sodium atom is different than a carbon atom. Elements may share some similar boiling points, melting points, and electronegativities, but no two elements have the same exact set of properties.

- Compounds are combinations of two or more different types of atoms. In the third part of Dalton’s atomic theory, he proposed that compounds are combinations of two or more different types of atoms. An example of such a compound is table salt. Table salt is a combination of two separate elements with unique physical and chemical properties. The first, sodium, is a highly reactive metal. The second, chlorine, is a toxic gas. When they react, the atoms combine in a 1:1 ratio to form white crystals of NaCl, which we can sprinkle on our food. Since atoms are indivisible, they will always combine in simple, whole-number ratios. Therefore, it would not make sense to write a formula such as Na0.5Cl0.5 because you can’t have half of an atom!

- A chemical reaction is a rearrangement of atoms. In the fourth and final part of Dalton’s atomic theory, he suggested that chemical reactions don’t destroy or create atoms. They merely rearrange the atoms. Using our salt example again, when sodium combines with chlorine to make salt, both the sodium and chlorine atoms still exist. They simply rearrange to form a new compound.



HAÜY’S MODEL OF A CUBIC CRYSTAL SHOWING THE PERIODIC TRANSLATION OF A BASIC CUBIC BUILDING BLOCK (INTEGRANT MOLECULE) AND HOW DIFFERENT CRYSTALLOGRAPHIC FORMS CAN BE OBTAINED SUBTRACTING INTEGRANT MOLECULES FROM AN ORIGINAL CUBE.



ORDERING THE ELEMENTS

In the early 19th century, German scientists began to formulate the earliest attempts to classify the elements. In 1829, German physicist Johann Wolfgang Döbereiner found that he could form some of the elements into groups of three, with the members of each group having related properties. He termed these groups triads. Chlorine, bromine, and iodine formed a triad; as did calcium, strontium, and barium; lithium, sodium, and potassium; and sulfur, selenium, and tellurium. German chemist Lothar Meyer also noted the sequences of similar chemical and physical properties repeated at periodic intervals. According to him, if the atomic weights were plotted as ordinates (i.e., vertically) and the atomic volumes as abscissae (i.e., horizontally) — the curve obtained a series of maximums and minimums — the most electropositive elements would appear at the peaks of the curve in the order of their weights. In 1864, a book of his was published; it contained an early version of the periodic table containing 28 elements, and classified elements into six families by their valence — for the first time, elements had been grouped according to their valence.

THE PERIODIC TABLE OF THE ELEMENTS

Dmitri Mendeleev was a Russian chemist and inventor. He is best known for formulating the periodic law and creating a version of the periodic table of elements. On February 17, 1869, Mendeleev began arranging the elements and comparing them by their atomic weights. He began with a few elements, and over the course of the day his system grew until it encompassed most of the known elements. After finding a consistent arrangement, his printed table appeared the next month in the journal of the Russian Chemical Society, before which he made a presentation on March 6, 1869, stating:

- The elements, if arranged according to their atomic weight, exhibit an apparent periodicity of properties.

- Elements that are similar regarding their chemical properties either have similar atomic weights (e.g., Pt, Ir, Os) or have their atomic weights increasing regularly (e.g., K, Rb, Cs).

- The arrangement of the elements in groups in the order of their atomic weights corresponds to their so-called valencies, as well as, to some extent, their distinctive chemical properties; this is apparent among other series in that of Li, Be, B, C, N, O, and F.

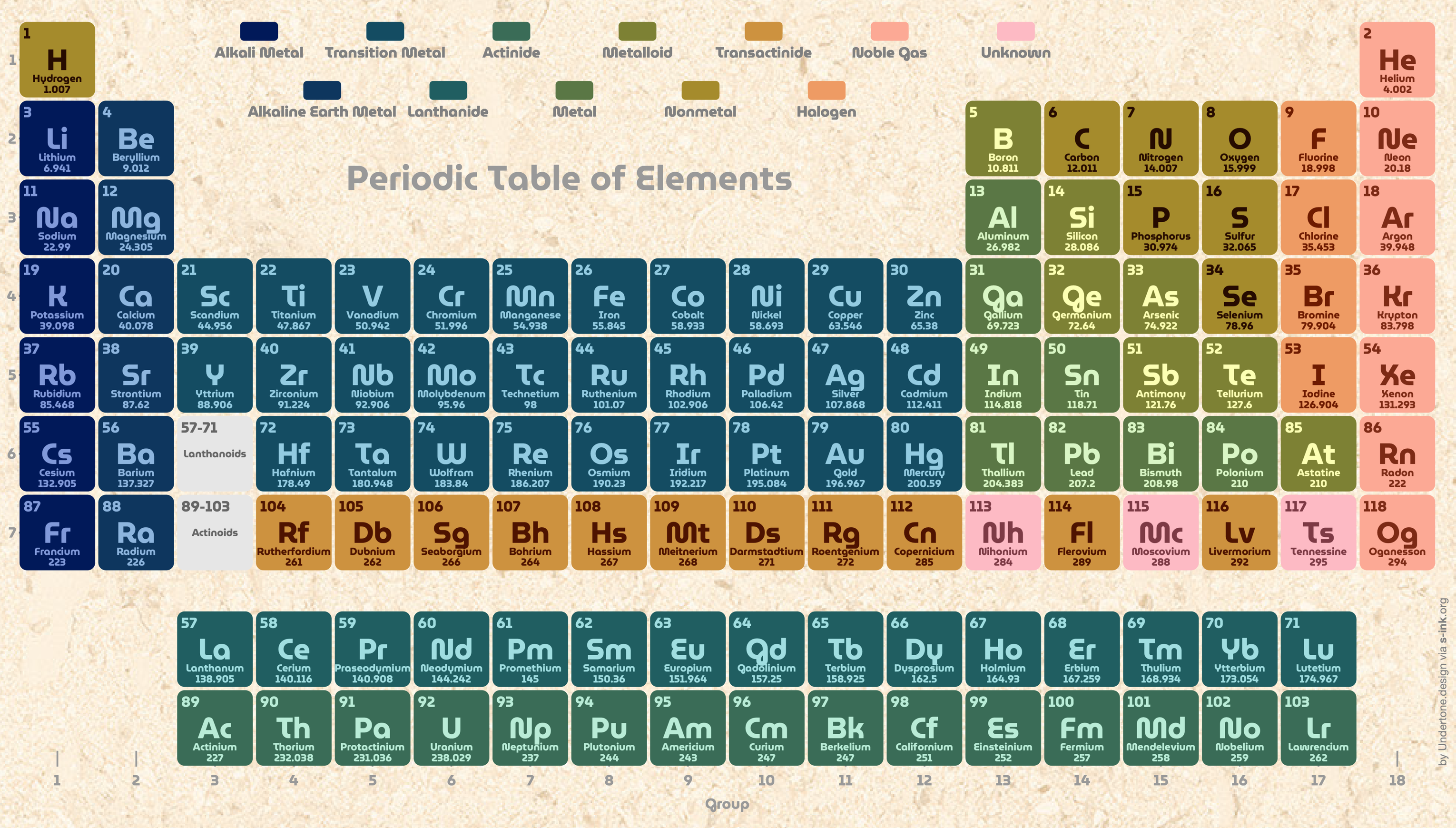
- The elements that are the most widely diffused have small atomic weights.

- The magnitude of the atomic weight determines the character of the element, just as the magnitude of the molecule determines the character of a compound body.

- We must expect the discovery of many yet-unknown elements – for example, two elements, analogous to aluminium and silicon, whose atomic weights would be between 65 and 75.

- The atomic weight of an element may sometimes be amended by a knowledge of those of its contiguous elements. Thus the atomic weight of tellurium must lie between 123 and 126, and cannot be 128. (Tellurium’s atomic weight is 127.6, and Mendeleev was incorrect in his assumption that atomic weight must increase with position within a period.)

- Certain characteristic properties of elements can be foretold from their atomic weights. The modern periodic table of 118 elements is shown on the right.



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