Dmitri Mendeleev, "The Periodic Law of the Chemical Elements" Excerpted from <u>Liebigs Annalen</u>, 8th supplement (1871), pp. 133-239.¹

Up to the time of Laurent and Gerhardt the names molecule, atom, and equivalent were used without distinguishing between them. Similarly, at present the concept of simple substance is often confounded with the concept of an element, and yet the two have to be sharply separated in order to prevent confusion in chemical ideas. A simple body is something material, a metal or metalloid, endowed with physical properties and chemical reactivity. The thing that corresponds to the concept of the simple body is the molecule consisting of one atom (e.g., Hg, Cd, and probably many others) or of several atoms $(S_2, S_6, O_2, H_2, Cl_2, etc.)$. It can exist in isomeric and polymeric modifications and differs from a composite body only by the uniformity of its material parts. Elements, on the other hand, are those material parts of the simple and the composite bodies that cause their physical and chemical behavior. The thing that corresponds to the element is the atom.

The uncertainty in our ideas of valency is in part due to the facts that they have only recently been introduced into science and that they include the hypothesis concerning the combination of the elements through parts of their affinity. In my opinion, this uncertainty is furthermore caused by one-sided study of the forms of elementary combinations that disregards the connection with the other properties of the elements. The deficiencies in the theory of chemical composition that are produced by the presently accepted theory of valency will disappear when the atomic weights are used as the bases for studying the main properties of the elements; I shall prove that later on.

Since 1868, when the first part of my book *Outlines of Chemistry* appeared, I have endeavored to solve this task.

I designate as periodic law the mutual relationships of the properties of the elements to their atomic weights applicable to all elements; these relationships, to be developed further on, have the form of a periodic function.

The system of the elements has not only a purely pedagogical significance, as a means to facilitate learning various systematically arranged and mutually connected facts, but also a scientific one in showing new analogies and, thereby, new ways for studying the elements. All the systems known at present can be divided into two sharply separated categories.

To the first category (artificial systems) belong systems based upon a selected few characteristics of the elements; for example, the distribution of the elements according to their affinity, electrochemical and physical properties (division into metals and metalloids); their behavior toward oxygen and hydrogen, their valency, etc. In spite of their obvious deficiency, these systems are, nevertheless, worthy of notice because they have the merit of a certain accuracy and each one of these systems has contributed to the gradual elaboration of chemical concepts.

The systems of the second category (natural systems) arrange the elements into groups of analogues on the basis of many diverse and purely chemical characteristics.

The position of an element R in the system is defined by the row and the group to which R belongs, i.e., by the neighboring elements X and Y in the same row as well as by two elements from the same group with the next smaller (R') and of the next higher (R") atomic weight. The properties of R can be derived from the known properties of X, Y, R' and R".

Thus, the properties of all the elements are actually in intimate interdependence. I call the

relationship of R to X and Y, and to R' and R", "atomic analogy."

For example, consider an element with the following characteristics: its equivalent is = 38(a figure subject to a certain un avoidable error); it forms an oxide that cannot be oxidized further and is not strongly basic. The question is, what is its atomic weight or the formula for this oxide? If the formula R₂O were assumed, then R [atomic weight] = 38and the element would have to be placed in the first group; there, however, the position I already occupied by K = 39 and, by atomic analogy, it requires a strong, soluble base. If the oxide were assumed to be RO, the atomic weight would be 76, and this does not fit into the second group because Zn = 65, Sr = 87; all positions for elements of low atomic weight are taken in the same group. Now if the oxide were R₂O₃, the atomic weight would be 114 and the element R would belong in the third group, where indeed there is an open space between Cd = 112 and Sn = 118 for an element of the approximate atomic weight 114. In analogy with Al₂O₃ and Tl₂O₃ as well as with CdO and SnO₂, the oxide of this element must have weakly basic properties. Thus the element would have to be placed in the third group. For the formula RO₂, the atomic weight of R would be = 152; such an element cannot be accommodated in the fourth group because the open place there requires an element of atomic weight 162 and weakly acidic properties (as transition from PbO₂ to SnO₂). An element of atomic weight 152 could also be placed in the eighth group, but then it would form the transition between Pd and Pt and would have such striking properties that they could not have been overlooked; the element that does not have these properties does not have the atomic weight 152 nor a position in the eighth group. If the oxide were assumed to have the formula R_2O_5 , then R =190, which does not fit into the fifth group

where Ta = 182 and Bi = 208, and these are acidic as R_2O_5 oxides.

The formulas RO_3 and R_2O_7 do not correspond to our element either, so that the only possible atomic weight for it is 114, and its oxide is R_2O_3 . Such an element is indium.

Use of the Periodic Law for Determining the Properties of as Yet Undiscovered Elements

The periodic law offers the possibility of estimating the unknown properties of elements with known atomic analogues. The tables in which the periodic relationships of the elements are presented show that several expected elements are missing in the periods. Therefore, I shall describe the properties of some prospective elements and thus provide a new and perfectly clear proof that the periodic law is correct, even though the confirmation must be left to the future. The precalculated properties of unknown elements offer a possibility for their detection, since their reactions can be predicted.

In order not to introduce new names for unknown elements, I shall designate them by the next lower analogue in the even- or oddnumbered row of elements of the same group and attach a Sanskrit number (eka, dwi, tri, tschatur, etc.). Thus the elements from the first group are named eka-cesium Ec=175, dwicesium Dc = 220, etc. For example, if niobium were not known, it could be called ekavanadium. In these names, the analogies are clearly indicated; only for the elements of the fourth row they lack this advantage because they have to be derived from the second typical row, which is not completely analogous to the fourth. However, only one unknown element occurs in this row for the third group eka-boron, Eb. Since this follows upon K = 39, Ca = 40, and stands before Ti =48, V = 51, its atomic weight will be about Eb = 44; the oxide must be Eb_2O_3 with not very strongly pronounced (basic) properties; it should form the transition from CaO to TiO₂.

Since the volume of $CaCl_2 = 49$ and of TiCl_4 = 109, the volume of EbCl_3 should be about 78 and its specific gravity about 2.0.

The two elements missing in the fifth row (of the third and fourth group) should have much stronger characteristics. Their place is between Zn = 65 and As = 75, and they should be analogous to Al and Si; therefore one of them shall be named eka-aluminum and the other eka-silicon. As they belong to an oddnumbered row, they are expected to form volatile metal-organic and chlorine compounds, yet have more acidic properties than their analogues Eb and Ti from the fourth row. The metals should be easy to obtain by reduction with carbon or sodium. Their sulphur compounds will be insoluble in water, and Ea_2S_3 will be precipitated by ammonium sulphide, whereas EsS_2 will be soluble in it. The atomic weight of eka-aluminum will be

¹[Copied from Eduard Farber, Ed., *Milestones* of Modern Chemistry, Basic Books, New about Ea = 68, that of eka-silicon Es = 72. The specific gravities will be approximately Ea = 6.0, Es = 5.5, or the [atomic] volumes Ea = 11.5, Es = 13, because Zn = 9, As = 14, Se = 18.

To characterize an element, we need, at present, two data among others that are furnished by observation, experiment, and comparative arrangement; namely, the definite atomic weight and the definite valency. By bringing out the interdependence of these two characteristics, the periodic law furnishes the possibility of determining the one by the other—i.e., the valency by the atomic weight—and, therefore, when the theory of valency defines the chemical combinations, the periodic law defines them, too; but the latter goes a little further in defining also those oxygen combinations that have been left out in the theory of valency.

York, 1966, pp 31-35. Translation by Farber. –CJG]