

each form of flask to be marked. This may always be readily accomplished by placing a temporary mark on any flask and then determining the capacity to this mark. With this and the interior diameter of the neck of the flask known we may compute where the mark should be placed to give the correct capacity. When this point has been determined a permanent mark may be made with the device by adjusting the cutter to travel across this point.

The use of this method of marking flasks is restricted on account of the pressure exerted by the mercury on the walls of the flasks, which is sometimes sufficient to cause them to break. This does not occur often with 100 cc. flasks, but it is doubtful whether ordinary flasks of greater capacity than 500 cc. would sustain the pressure with safety.

THE CYCLICAL LAW OF THE ELEMENTS.¹

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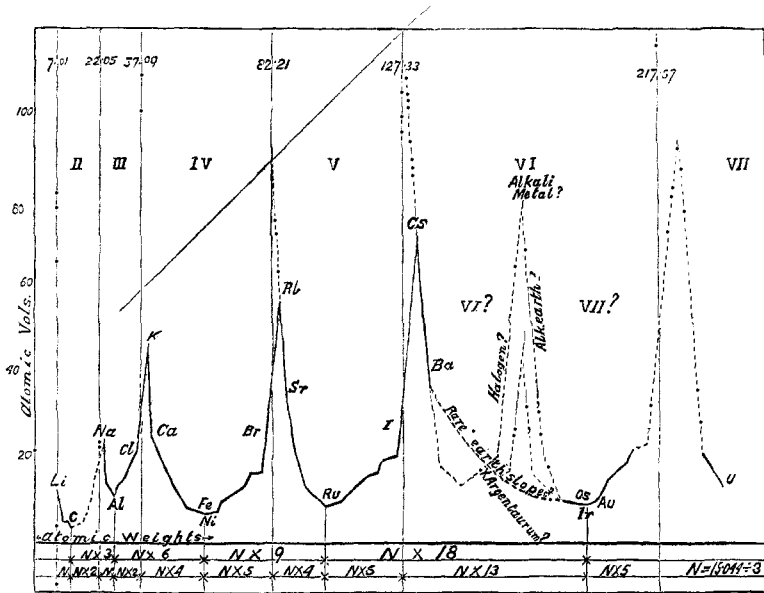
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WHEN the elements are arranged in a line in the order of their atomic weights, it is apparent that there is from lithium to fluorine an orderly transition from the intensely positive alkali-metal type to the intensely negative halogen type, and then a sudden reappearance of the positive type in sodium, after which there is a second orderly transition to the negative type (chlorine), and then another change to positivity (potassium). Up to this point, therefore, two complete cyclical changes have been established, the first cycle from lithium to sodium—in all its essential details—being analogous with the second from sodium to potassium. If then we proceed with the lineal arrangement, it is clear that we must first of all look for transitions and for reappearances of the alkali-metal type; in other words, for the continued development of the cyclical arrangement. And since analogous but modified transitions actually recur, and halogens followed by alkali metals reappear, it is evident that the law of progression is actually cyclical. The first and fundamental feature of atomic progression is a progression in cycles.² The lithium-sodium cycle is a cycle involving the seven elements, lithium, beryllium, boron, carbon, nitrogen, oxygen, and fluorine,

¹ Reprinted from *Chemical News*, April 7, 1898.

² Bayley: *Phil. Mag.*, January, 1882.

and the sodium-potassium cycle involves also seven elements ; and for this reason, and because in the succeeding cycles analogous groups of seven elements are repeated, almost all tabular expressions of the atomic progression have been set in a septenary form. But these arrangements, by unduly emphasizing the septenary character of the periodic change, have perhaps somewhat obscured the more important and fundamental cyclical features of the progression. Before attempting to substantiate this assertion, however, it is necessary to consider the nature of the higher cycles which are complex, and to show that the properties of any element are more profoundly modified by position in the cycle than by position in the septenary series.



Assuming that hydrogen is the first element of an incompletely known cycle which we may call the first, then the lithium-sodium cycle becomes the second and the sodium-potassium cycle becomes the third. Beyond this point the cycles are complex, and the fourth contains seventeen elements, of which the first, potassium, is completely analogous with sodium ; the second element, calcium, with magnesium ; and the third, scandium, with aluminum ; for sodium and potassium both conform

to the alkali metal type, calcium and magnesium to the alkaline earth metal type, and aluminum and scandium to the type of the earth metals; but the analogies between silicon and titanium, and between phosphorus and vanadium, are less perfect, while the analogies between oxygen and chromium and between chlorine and manganese are very much less pronounced. The analogies between the latter pairs, indeed, appear to consist chiefly in structural resemblances between the compounds of the respective elements, due to the valency or atomicity impressed upon the septenary series as a primary law of its formation. The analogies between the elements of the septenary series entirely constituting the second and third simple cycles, and the elements constituting the first portion of the fourth cycle, a compound cycle, are perfect therefore only in the first, second, and third elements of each series respectively, and become fainter in the later members. Now the elements between which complete analogy exists are those which have analogous positions in the cycle, and the elements between which incomplete analogy exists are those which have not analogous cyclic position, but merely analogous serial position. The region of the third cycle—occupied by sodium, magnesium, and aluminum—corresponds to the region occupied by potassium, calcium, and scandium in the fourth cycle for each group of elements occupies the front portion of its cycle, whereas silicon, phosphorus, and sulphur in the third cycle occupy a region posterior to the point of lowest atomic volume, while titanium, vanadium, and chromium occupy a region anterior to the point of lowest atomic volume in the fourth. Neglecting for the moment the position and properties of the three intermediate elements, iron, nickel, and cobalt, and passing to the consideration of the second septenary series, which completes the fourth cycle, and to comparison of this with the third cycle, we see that analogy fails, or is chiefly structural, between copper and sodium, between zinc and magnesium, between gallium and aluminum, but becomes more pronounced between selenium and sulphur, and perfect between bromine and chlorine. The structurally analogous copper and sodium have nothing in common except serial position, and the fully analogous bromine and chlorine have similar cyclic position; chlorine fails to find a complete analogue in manganese which has not analogous

regional position, but finds it in bromine, because both occur at the end of the cycle. To make this clearer it is necessary to study more closely the architecture of the simple and complex cycles. The increment of atomic weight occupied by the series lithium-sodium is 15.98; the increment from sodium to potassium is 16.05; the increment from potassium to iron is 16.86; the increment from copper to rubidium is 22; the increment from rubidium to ruthenium is 16.2; and the increment from silver to cesium is 25.04. The increments for the series constituting the simple cycles, and for the series occurring in the first portions of the fourth and fifth cycles, is, therefore, about 16 (or 17), and the increment for the series occurring in the posterior halves of the fourth and fifth cycles is 22 and 25. If we proceed to consider the nature of the sixth cycle, we are met at the outset by a difficulty, for since no alkali metal of higher atomic weight than cesium has yet been discovered, it is not easy to fix the upper limit of the cycle.

The usual arrangement of the elements in odd and even series, such as Mendeléeff's original classification or Brauner's modification of it, show three septenary series and an intermediate group between cesium and osmium, and the increment of 57 in atomic weight corresponding to this space is just about what would be required for twenty-four elements. Commencing with potassium and writing its higher analogues in a line, we obtain the sequence potassium, copper, rubidium, silver, cesium, in which each alkali metal is followed by a subfamily analogue, and, unless other conditions intervene in the sixth cycle, the unknown element of atomic weight c. 156 should be an analogue of copper and silver, and the unknown element of atomic weight c. 170 should be an alkali metal and the first member of a seventh cycle. But as every alkali metal is preceded by a halogen (neglecting the argon family), and succeeded by an alkaline earth metal, it also follows that the element of atomic weight 170 should be similarly accompanied. Reasoning also from analogy, we must suppose that the unknown halogen is somewhat less negative than iodine, because negativity decreases with atomic weight in the halogen family, and the unknown alkali metal and the alkaline earth metal must be more positive than cesium and barium, respectively, because positivity increases with atomic

weight in the highly positive families. It also seems necessary, from analogy, to assume the existence of an intermediate group between 152 and 154, but in all other instances, both lower and higher, in the atomic progression the intermediate groups are preceded not by basic earth metals (such as samarium), but by elements such as chromium and manganese, molybdenum and (—c. 100), and tantalum and tungsten, which form oxides of a pronounced acidic character. If, therefore, there is a cycle stretching from cesium to the position of atomic weight 170, it must differ essentially from compound cycles below it and the compound cycle above it. We may now profitably turn to a consideration of the curves of atomic volume in the various cycles. It was first pointed out by L. Meyer that atomic volume has a periodic variation, and the curves given in the accompanying figure are essentially identical with those drawn in his "Modern Theories of Chemistry."

It is evident that atomic volume is a cyclical function. Each cycle, simple or compound, shows a loop, and all truly analogous elements occupy similar positions on the curves. The alkali metals have high atomic volumes, and occupy the top of the curves; the alkaline earth metals invariably occur on the downward flanks. The earth metals occur lower down on the same flank, and in the fourth and fifth angles they immediately precede the elements (titanium, vanadium, chromium, manganese), (zirconium, niobium, molybdenum, —), which form acidic oxides. The intermediate groups occupy the troughs of the curves, and the series copper-bromine, silver-iodine, gold-bismuth occur on the rising posterior portion of the curves. If, then, the element of atomic weight c. 170 is an alkali metal, it is reasonable to conclude that it has a high atomic volume and that curve of atomic volume indicated by the upper dotted line must exist, even if it does not follow—however probable it may appear—that this curve need necessarily be as steep as it is drawn. The curves of atomic volume present very remarkable regularities, using the word curve to mean the collection of straight lines drawn from point to point. Thus the lines drawn from chlorine to potassium, from bromine to ruthenium, and from iodine to cesium, are almost exactly parallel, as are some other lines of similar character.

In the earlier diagrams, before the atomic volume of cesium was determined, the line from iodine to cesium was assumed to occupy a position in accordance with this parallelism, and the facts when determined justified the assumption, and for these reasons it seems permissible to use this method of drawing parallel lines as a means of forecasting the atomic volumes of elements as yet undiscovered. Now, whether we draw the upper or the lower dotted curve, in which latter case the metal (atomic weight c. 170) would not be a perfect analogue of sodium and potassium, it appears necessary to believe in the existence of a halogen and an alkaline earth metal, and also of a group of intermediate elements of the iron or platinoid type, followed by a series commencing with a true analogue of copper and silver. It is a significant fact that, although a number of elements are assigned to positions between atomic weight 150 and the atomic weights of tantalum and tungsten, there has as yet been described no element corresponding to the hypothetical intermediate group, or to the supposed halogen, alkali metal, or alkaline earth metal. On the other hand, the numerous elements between atomic weight 150 and tantalum which have been described are elements of a purely earth-forming type, separable from well-located earths, such as scandium, yttrium, and lanthanum, which they closely resemble, only by repeated fractional precipitations or similar methods. So far research has not rendered it possible to assign definite atomic weights to the majority of these rare earth metals, and much of the brilliant laborious work done upon them by Crookes and others has tended rather to bewilderment, yttrium and samarium, and several other rare earth metals, having been shown to be complex bodies; but accepting the usual location of these metals provisionally, it would seem that $Tb > Er > Tm > Yb$ fall just where the hypothetical alkali metal of atomic weight c. 170 would require to be placed, and that with these four elements there is a regular but small progression from greater to less basicity in the order given, which is what we might expect if the sixth cycle stretches from cesium to about atomic weight 233 with a long flank on the anterior (descending) portion of its curve of atomic volume occupied by a series of rare earth metals. This conception of the cyclic progression eliminates the unsym-

metrical dotted curve, and substitutes a cycle of approximately symmetrical dimensions. The cyclical increments then appear as

Cycle II.	Cycle III.	Cycle IV.	Cycle V.	Cycle VI.
c. 16	c. 16	46(3 × 16)	47(3 × 16)	94(6 × 16)

and the position of lowest atomic volume, which in the lower cycles occurs near the middle of the curve, occupies in the sixth cycle a position nearer to the end. In these measurements of the length of the cycles, we have taken the increments of atomic weight from one alkali metal to the next higher in progression, but it does not necessarily follow that this is the proper method. For if the elements have been produced, as was suggested by Sir William Crookes, during the cooling of some primal form of matter—the protyle—we may imagine that after the genesis of each cycle had been completed, and the halogen had been formed, there came a turning-point in the evolution, probably marked by the development of an element of the argon type, after which the course of atomic genesis again set in the direction of alkali-metal formation. If so, then clearly the cycle commenced at this turning-point, but the first element of the new series may not have been formed immediately. The conditions at the commencement of the cycle may not have permitted of the coherence of the newly condensed material into the atomic form, and the first element of the new cycle may, as it were, have had to wait until the attractive force of the condensed protyle had time to gather. Some such conception might explain a lateness in the appearance of an element like argon, endowed with little or no affinity; for if the element were all the while forming in a kind of nebulous intermediate condition, and if, as it appears, atomic weight is a function chiefly or wholly of the temperature at the moment of atomic formation, such an element might not take the atomic form until after the commencement of the next cycle. This, however, assumes some sort of connection between the attraction of the primal molecules for each other and the chemical affinity of the completed atom. Before we can attempt to fix the true dimensions of the cycles in accordance with this hypothesis, we must cast about for evidences of definite arithmetical dimensions in other regions of the cycles than the beginnings. The point of lowest atomic volume seems to be another definite turning-point in the cyclic

changes; and taking carbon as representing this point in the second cycle, and iridium the similar point in the (large) sixth, we get an interval of atomic weight of 180.5. Dividing this by 12 we obtain 15.04, and adding this number to the atomic weight of carbon (11.97) the sum is 27.01, the atomic weight of aluminum (27.02), the element of lowest atomic volume in this cycle. By adding to aluminum (27.01) the expression 15.04×2 , we obtain 57.09, which is between iron (55.9) and nickel (58.6) and the addition of 15.04×2 again gives 102.24, which is very near the atomic weight of ruthenium (102.7); and adding 15.04×6 to 102.24 gives 192.48, which is the atomic weight of iridium. Now assuming this dimension 15.04 to represent the true dimension of a simple cycle, and adding it to lithium, we have $7.01 + 15.04 = 22.05$, between fluorine and sodium, as the initial or turning-point for Cycle III. In like manner, $22.05 + 15.04$ gives 37.09, between chlorine and potassium, as the initial-point of Cycle IV; $37.09 + 15.04 \times 3$ gives 82.21 between bromine and rubidium, for the corresponding point of the fourth cycle, and $82.21 + 15.04 \times 3$ gives 127.33, between iodine and cesium for the sixth cycle. If the sixth cycle is a large cycle $127.33 + 15.04 \times 6$ indicates 217.57 as its probable terminating point. If the cyclic dimensions be fixed in this manner, the point of lowest atomic volume in the various cycles occurs in the second or third at the one-third distance, and in the fourth and fifth at the four-ninths distance from the initial point of the cycles. Thus:

$$\begin{aligned} \text{Li } 7.01 + \frac{15.04}{3} &= 12.01 \text{ (C = 11.97),} \\ 22.05 + \frac{15.04}{3} &= 27.02 \text{ (Al = 27.01),} \\ 37.09 + \frac{15.04}{3} \times 4 &= 57.13 \text{ (Fe = 55.9; Ni = 58.6),} \\ 82.21 + \frac{15.04}{3} \times 4 &= 102.25 \text{ (Ru = 102.7),} \\ 127.33 + \frac{15.04}{3} \times 13 &= 192.46 \text{ (Ir = 192.5).} \end{aligned}$$

It may be assumed that the actual turning-point of lowest atomic volume may not be occupied by an element having the atomic weight corresponding to the temperature existing when the evolutionary crisis arrived.