ATOMIC NUMBERS AND ATOMIC CHARGES.

BY FERNANDO SANFORD.

IN a paper entitled "Untersuchungen ueber das System der Grundstoffe" (Lund, 1913), Rydberg has undertaken to show that the properties of the elements which determine their positions in the periodic series may be calculated from the number which represents the order of their occurrence in this series. Thus he says:[1]

"In the system of Mendelejeff all the elements are arranged in a single series, and each element is distinguished from all others by its place in this series. This signifies that *a single independent variable suffices to completely determine each element.* According as a quantity to be determined varies continuously or discontinuously must the independent variable pass through the continuously increasing series of all numbers or the discontinuous series of the positive whole numbers. In the case before us one cannot doubt that the properties of the elements vary discontinuously from element to element. Continuous variation in the properties of the elements may, indeed, occur, but only in consequence of a continuous change in temperature, pressure, and the like, of the same element. Between the individual elements there is no continuous transition.

"We are accordingly led to the adoption of the series of the positive whole numbers as the independent variable for the system of the atoms."

Rydberg then undertakes to show that the characteristics of the atoms upon which the periodic law was based may be calculated by means of the mathematical relations between their atomic numbers. He does not propose any physical explanation of these numerical relations.

Such a physical relation is suggested in a discussion by A. van den Broek, entitled Die Radioelemente, das periodische System und die Konstitution der Atome.[2] van den Broek concludes from the change in atomic weight of the elements produced by radioactive changes that, in general, the atomic weight changes from atom to atom in the periodic series by about two units, and that the deviations from this law are accidental.[3] He also assumes that each change in atomic weight is

[1] Translation by present writer.

[2] Phys. Zeitsch., XIV., 32 (1913).

[3] See article by present writer in Jour. Am. Chem. Soc., XXXIII., 1349 (August, 1911) and Theo. Wulf, Phys. Zeitsch., XII., 497 (1911).

accompanied by the gain or loss of a definite electrical charge, hence the positive sub-atom or nucleus of an elementary atom should carry a charge proportional to the serial number of the atom in the chemical series. This hypothesis gives a physical significance to the atomic numbers which Rydberg regards as the descriptive characteristics of the elements.

Previous to this Rutherford[1] and Barkla[2] had concluded from the scattering of α-particles and of X-rays that the elementary atom carries a positive charge which is proportional to half its atomic weight. van den Broek concludes that the atomic number should be substituted for half the atomic weight in the above hypothesis.

In the recent work which has been done upon the spectra of the X-rays given off by various elements when these are bombarded by cathode rays it has been found that in its high frequency radiation as in its visible radiation each element has a characteristic spectrum. The work of the Braggs, of Mosely and Darwin and, more recently, of Mosely has shown that the X-ray spectra of the different elements are very similar; that they are, in general, characterized by five lines of much greater intensity than the rest of the spectrum, and that corresponding lines in the spectra of different elements may be identified. When the relative frequencies of these lines are determined by reflection from the same analyzing crystal, it has been found that this vibration frequency is greater the higher the atomic weight of the element.

In his paper in Phil. Mag., XXVII., 703 (1914), Mosely has extended his measurements on X-ray frequencies to include all the elements from aluminium to gold, and has related the frequencies of corresponding lines in different spectra to the serial numbers of the respective atoms in Mendelejeff's table. He concludes that the vibration frequency of the line α (α being the line of lowest frequency in the X-ray line spectra of the elements) varies as the quantity $(N - k)^2$, where k is a constant and N is the serial number of the element, aluminium being taken as 13.

Mosely then concludes from a discussion of Rutherford's theory of atomic structure that the change in frequency of the vibrating electrons which produce this line must be due to a change in the magnitude of the positive charge on the nucleus of the atom. He states his conclusions as follows:

1. Every element from aluminium to gold is characterized by an integer N which determines its X-ray spectrum. Every detail in the spectrum of an element can therefore be predicted from the spectra of its neighbors.

[1] Phil. Mag., XXI., 669 (1911).
[2] Ibid., XXI., 648 (1911).

2. This integer N, the atomic number of the element, is identified with the number of positive units of electricity contained in the atomic nucleus.

3. The atomic numbers for all the elements from Al to Au have been tabulated on the assumption that N for Al is 13.

4. The order of the atomic numbers is the same as that of the atomic weights, except where the latter disagrees with the order of the chemical properties.

5. Known elements correspond with all the numbers between 13 and 79 except three. There are here three possible elements still undiscovered.

6. The frequency of any line in the X-ray spectrum is approximately proportional to $A(N - b)^2$, where A and b are constants.

Mosely does not give a table of frequencies of the same line for all the elements he has examined, but on page 709 of his paper he gives curves showing both the wave-length and the square root of the frequency of many of these lines plotted against the atomic numbers. These curves are very approximately straight lines. It accordingly seems that whether the charge of the positive nucleus of an atom is, or is not, proportional to the atomic number, N, the frequencies of the principal lines of the X-ray spectra are proportional to the squares of these atomic numbers.

The present writer has published several papers in this journal and in others, beginning in 1911,[1] in which it has been shown that the product of the atomic weight of an element multiplied by the migration velocity of its ion in the electrolysis of dilute water solutions gives a number which has been shown to be related to all the properties of elements and their compounds which depend upon affinity or cohesion, as well as to many optical properties and to the dielectric constants of several of the elements. It may accordingly be worth while to compare the atomic constants calculated in this way with the atomic charges which van den Broek and Mosely infer from the atomic numbers.

Since the ionic mobilities given by different investigators differ by considerable quantities, I have used in this comparison only the elements and the ionic velocities given in Kaye and Laby's Tables. Mobilities are there given for twenty elements. These elements with their atomic numbers as given by Rydberg,[2] and their atomic charges as calculated by me, assuming the charge on the hydrogen ion as 5, are given in the table below.

[1] PHYS. REV., XXXII., 512 and 518; XXXV., 276; N. S., I., 211 and 446. Astrophys. Jour., XXXV., 1; XXXVI., 255.

[2] Since Rydberg introduces two hypothetical numbers between hydrogen and helium, Mosely's atomic numbers are each two less than the number for the same atom as given by Rydberg. This will make no difference in the curves plotted for the present article.

Table I.

Element.	N	Chg.	Element.	N	Chg.
H............	1	5	Br...........	37	84.9
Li............	5	3.6	Rb...........	39	91.2
F............	11	14.6	Sr...........	40	71.5
Na...........	13	15.7	Ag...........	49	91.6
Mg..........	14	17.3	Cd...........	50	83.8
Cl...........	19	36.5	I.............	55	132.5
K............	21	39.6	Cs...........	57	142
Ca...........	22	32.5	Ba...........	58	119.4
Cu...........	31	46.7	Tl............	83	212
Zn...........	32	47.6	Pb...........	84	199.4

It will be seen from the above table that while the atomic charges increase as the atomic numbers increase they do not increase at the same rate for the univalent and divalent ions. This has been shown elsewhere

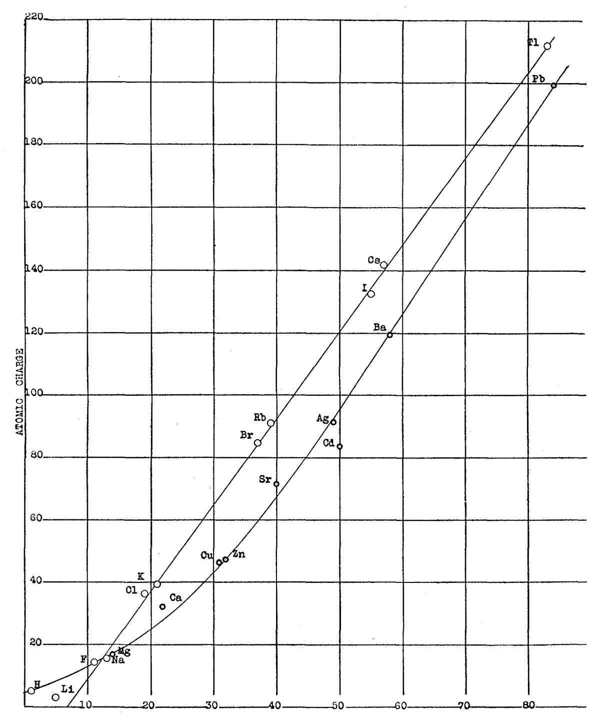

Fig. 1.

for all the other properties which seem to depend upon the atomic charges. The relation of these two sets of charges to the atomic numbers are shown graphically by the two curves in Fig. 1.

It will be seen from these curves that a straight line relation exists between the atomic charges of the univalent ions and their corresponding atomic numbers, and hence that these charges may be accurately calculated from the atomic numbers. This does not seem to be so generally true of the divalent elements, though these, with the exception of cadmium, lie on a smooth curve which does not differ much from a straight line for the elements heavier than calcium. The case of cadmium does not necessarily furnish an exception, since it is known that cadmium salts are usually made up of complex molecules which ionize by successive steps, so that in solutions of finite concentration both ions usually contain cadmium. This makes the determination of the transference number for cadmium very difficult, if not impossible, and would regularly make it appear too low, as is indicated by its atomic charge.

Since the frequencies of corresponding lines in the X-ray spectra of the elements may be calculated from the atomic numbers, it follows that for the monovalent elements, at least, they may be calculated from the atomic charges determined in electrolysis.[1] It does not necessarily follow, however, that the charges of the ions determined in electrolysis are the same as the charges of the positive atomic nuclei in the Rutherford atom. In fact, they cannot be the same, since the charges calculated for the halogen ions in electrolysis are electronegative.

The distinction between the properties of the electropositive and electronegative atoms has been shown in many ways by the present writer, though it is now seen that the magnitude of both kinds of charges may be calculated from the atomic numbers. Thus, while all the properties depending upon cohesion have been shown to be quantitatively related to the atomic charges, the magnitude of cohesion increases with the increase of the negative atomic charge but decreases with the increase of the positive atomic charge. This relation, which has been shown in previous papers, may also be exhibited by plotting the magnitude of such properties as compressibility, melting point, boiling point, critical temperature, hardness, and the like, against the atomic numbers of the elements. Thus, Fig. 2 shows graphically the relation of the melting points of the alkali metals and of the electronegative halogen elements to their respective atomic numbers. I have previously shown that the melting points of the alkali metals may be calculated

[1] In this connection it may be mentioned that in Astrophysical Journal, XXXVI., 255 (Oct., 1912), the present writer has shown that the convergence frequencies in the spectral series of a number of elements may be calculated from their atomic charges. It follows that these may also be calculated from the atomic numbers, and that the frequencies of the visible spectra as well as the X-ray spectra may be shown to be related through the atomic numbers or atomic charges.

from their atomic charges as accurately as they can be measured. They may also be calculated to a high degree of approximation from the equation $(N+3)(T-275) = 1{,}497$, where N is Rydberg's atomic number and T is the melting point, absolute.

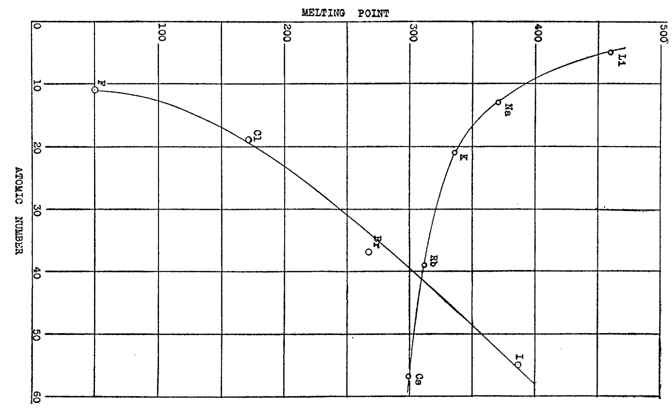

Fig. 2.

A similar relation between atomic numbers and melting points may be shown for many closely related groups of elements, but while within a given group the melting point is higher the more electronegative the

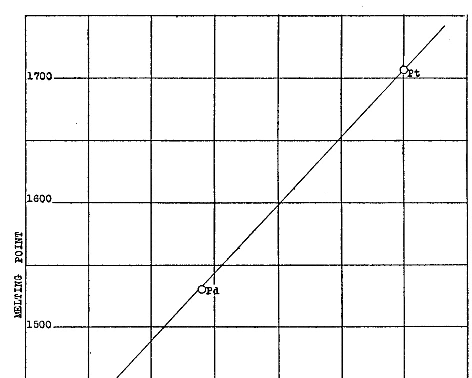

Fig. 3.

element, the melting point may either increase or decrease with the atomic number, as is shown in Fig. 2. Examples of the increase of melting point with the increase of the atomic number in metals may be shown in the three similar groups, iron, ruthenium, osmium; nickel, palladium, platinum; cobalt, rhodium, irridium. This relation for nickel, palladium and platinum is shown graphically in Fig. 3. The melting points used are those given in Kaye and Laby's Tables. Within each set of triplets from which the above elements are taken, on the contrary, the melting point decreases as the atomic number increases.

The above considerations make it seem to the writer that while the electrical properties of the elementary atoms are in some manner closely related to their respective serial numbers, it is not probable that these numbers represent in all cases the magnitudes of the electropositive charges of the sub-atoms.

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