2. BOILING POINT AND ATOMIC SIZE

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One of the authors (G.R.S.) has discovered a simple relation[1] (Somayajulu, 1956) that the boiling points and quite a few other properties of halogens and also of a series of analogous halogen compounds, are linear with the sum of the effective atomic number, Z' where $Z' = Z-S$, Z being the atomic number of the halogens in the molecule and S is a screening constant whose value is zero for F and Cl, 13 for Br and 23 for I. Following on the above clue it has been found,

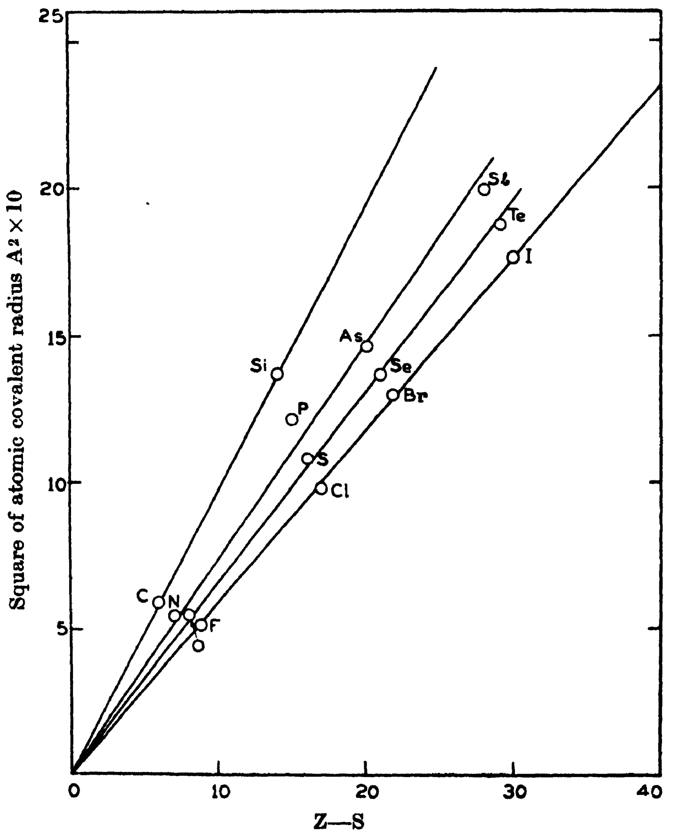
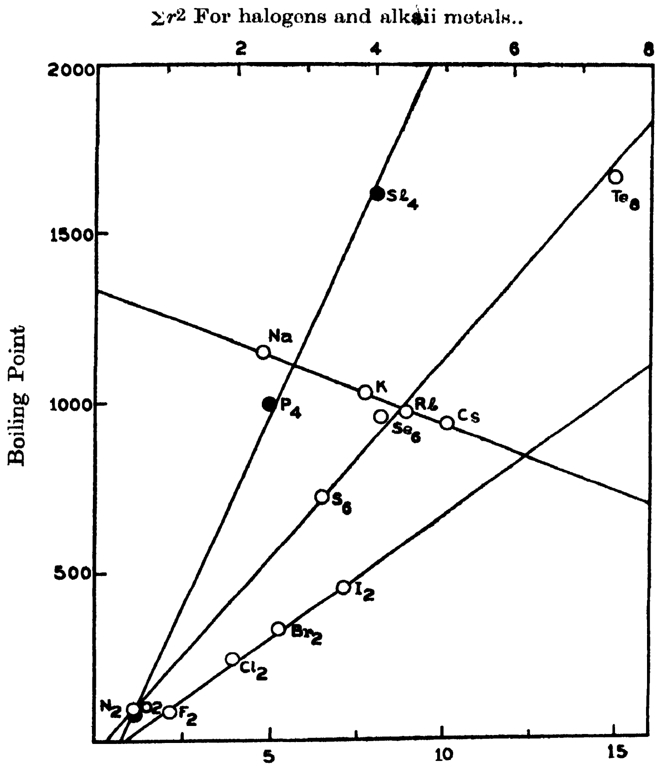


Fig. 1. Plots of square of atomic covalent Radii *vs.* $Z-S$.

as shown in figure 1, that the squares of the covalent radii are also linear with Z' for the following sequences, (i) F, Cl, Br and I, (ii) O, S, Se and Te and (iii) N, P, As and Sb, using the same sequence of values of S as given by Somayajulu for all the above three groups of four elements. The most striking feature of these straight lines is that they pass through the origin which leads to a few rather unexpected conclusions as discussed below. All data for covalent radii, r, have been taken from the latest compilation by Schomaker and Stevenson (1941).

Size of the Covalent Atom:—Assuming that the effective atomic number, Z' represents the net nuclear charge of the atom insofar as it determines the physical properties as described by Somayajulu (*1956*), the most obvious conclusion is that the normal induction per unit surface area for all atoms in the same group of the periodic table is the same and increases with increase in group number or electro- negativity within th esame period. It thus appears that the covalent size of an atom is predominantly determined by its effective nuclear charge, $Z'e$



Σr^2 For O_2, S_6, Se_6, Te_8, N_2, P_4 & Sb_4.

Fig. 2. Plots of boiling point *vs.* $p\Sigma r^2$.

such that it attains the same effective normal induction per unit area for all members of the same group. Alternatively, since $\epsilon Z'/r^2$ is the field strength on the surface of an atom due to its effective nuclear charge, we can as well say that all atoms of the same group have on their surface the same effective field trength owing to their nuclear charge, and the field strength increases with increasing group number. This is a rather unusual conclusion whose full significance, particularly with reference to the electronegativity scale is yet to be elucidated.

Boiling Point and Atomic Size—Combining figure 1 with Somayajulu's findings, as summarised in the opening paragraph, we immediately see that the boiling point of the halogens and similar halogen compounds should be linear with the sum total of the surface area of the halogens in the molecule. This is shown in figure 2 curve A for halogens. It would be seen that an excellent straight line is obtained. The obvious conclusion is that the boiling points of similar halogen compounds are determined by the sum of the surface area of the constituent atoms. This is further corroborated by plotting the available data for other groups. Thus, curve B shows that O_2, S_6 and Se_6 being the states in which they occur near their boiling points, also give a good straight line. Curve C shows that the relationship is also valid for N_2, P_4 and Sb_4 (datum for As is not available). It thus appears established that the boiling points of elements are simply related to the sum total of the surface area of the constituent atoms in the molecule.

The above relationship also holds good fairly well (curve D) for the alkali metal sequences Na, K, Rb and Cs; but here the slope is reversed. This interesting behaviour is however, understandable from figure 2. From curves A, B and C we find that the slope increases with decreasing periodic group number and so, in this case the slope has become much more than a right angle. In fact, we can reasonably expect from the above trend that somewhere around the middle groups of the periodic table these B. P. versus r^2 curves may be just steeper than a right angle as a result of which the first members are likely to show very high boiling points. This is in agreement with the well-known occurrence of high boiling elements, viz., B, Si, etc., in this region. It is thus seen that the trend in boiling points in various groups of the periodic table, though apparently irregular, forms part of a common plan depending on the size and nuclear charge for the whole periodic table ; an explanation of the whole plan itself however, is yet to be found.

Schomaker V. and Stevenson, D. P. 1941, *J. Amer. Chem. Soc.* **63**, 37.
Somayajulu, G. R. 1956. *Ind. Jour. Phys.* **30**, 258, the foregoing note.