

Letters to the Editor

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1. BOILING POINT AND OTHER PHYSICAL PROPERTIES OF THE HALOGENS AND HALIDES

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Some regularities have been already observed for many physical properties of halides. We have, however, found that most of the physical properties of halogens and of halides can be treated from a common basis. It has been found that in a sequence of compounds of the general formula RX_n , where X stands for any halogen and R is any atom (may be a halogen itself) or a group of atoms, many physical properties are linearly related to the sum of the effective atomic numbers of the halogen atoms in RX_n ; in other words, there exists a relationship of the type

$$P = a\Sigma(Z-S) + b = a\Sigma Z' + b$$

where P is the property in question, a and b are constants for any particular series of molecules, and Z' is the effective atomic number of X, the summation being carried over all the X's; Z' is equal to $Z-S$ where Z is the atomic number, and S is a constant characteristic for each halogen (the significance of which is not yet quite clear) and has the value 0 for fluorine and chlorine, 13 for bromine and 23 for iodine.

We first illustrate the above relationship from available boiling point data. Taking R to be a halogen itself, the boiling points of all compounds of the type X_2 , viz., F_2 , FCl, Cl_2 , ClBr, Br_2 , ICl, IBr and I_2 , have been plotted in figure 1 against the summation of the effective atomic numbers of the two atoms constituting the X_2 molecule and it would be seen that all the points fall in a straight line. Similar behaviour is also exhibited (figure 1) by twenty-one tetrahalides of silicon and also by twelve tetrahalides of carbon for which data are available.

An exactly similar relation is also obtained with the same Z' values for halogens for the boiling points of a multitude of other sequences, viz., monohalides

of H (with the exception of HF), R (alkyl or aryl), Si H₃, etc., dihalides of CH₂, C₂H₄, SiR₂, Hg, etc., trihalides of B, N, P, As, Sb, (excepting SbF₃), Bi, PO, PS, CH, SiH, SiR, etc. tetrahalides of Ti, Ge, Sn (excepting TiF₄ and SnF₄), etc., and so on.

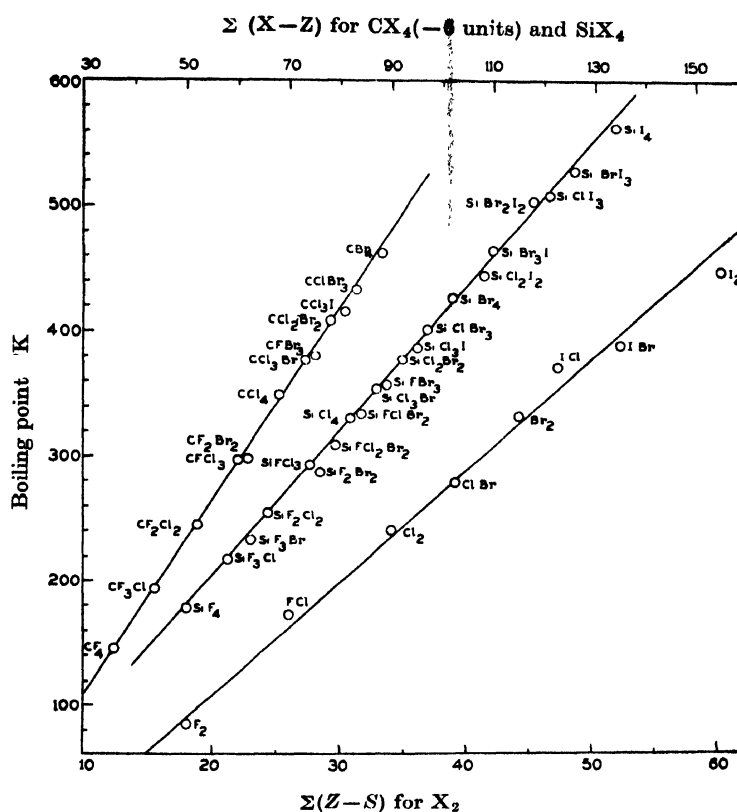


Fig. 1. Boiling point vs. summation effective atomic number diagram.

Linear relationships have also been found to exist between several other properties such as polarisability, refractivity, square of atomic covalent radius (*vide* the other note appearing herewith), van der Waals volume, atomic volume, parachor, Pascal's constant, etc., on the one hand and Z' on the other for halogens. In fact, all sequences, of the type RX_n we have tried so far and which are

too numerous to mention here, have shown this regularity and we present in figure 2 a few typical illustrations for halogens.

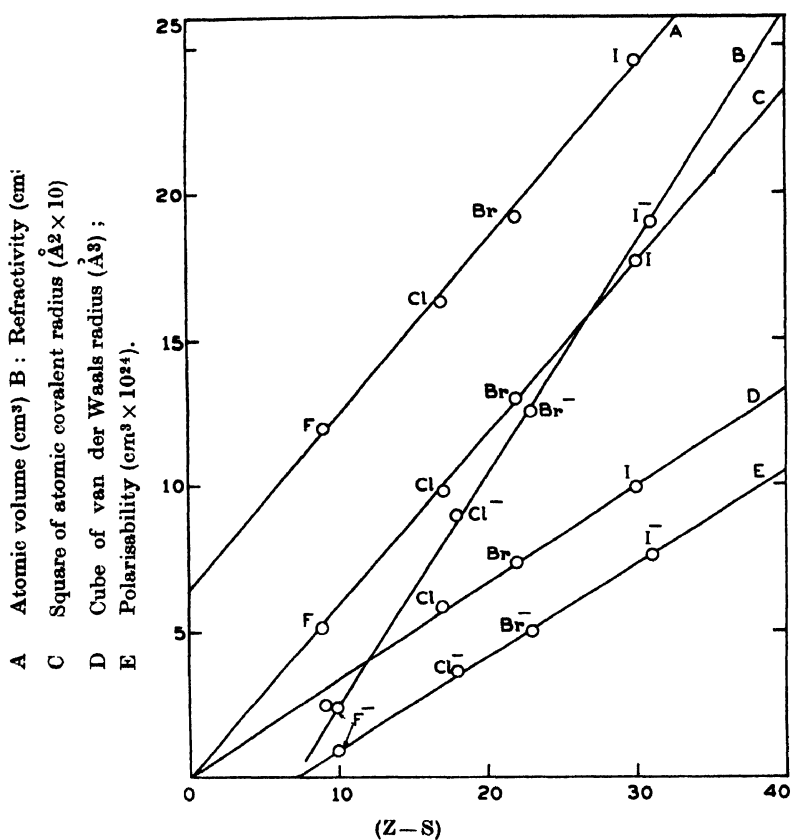


Fig. 2. Plots of some physical properties of halogens and their ions vs. $(Z-S)$.

The regularities reported above for halogens also apply to other similar sequences of elements and the most surprising thing is that practically the same set of S -values as found for F, Cl, Br and I has also been found to hold good for corresponding elements in the following sequences, viz., (i) O, S, Se and Te, (ii) N, P, As and Sb, (iii) C, Si, Ge and Sn, (iv) B, Al, Ga and In, (v) Mg, Ca, Sr and Ba, (vi) Na, K, Rb and Cs and (vii) Ne, Ar, Kr and Xe, with respect to at least

some physical properties of these elements and their compounds. A few typical illustrations are shown in figure 3.

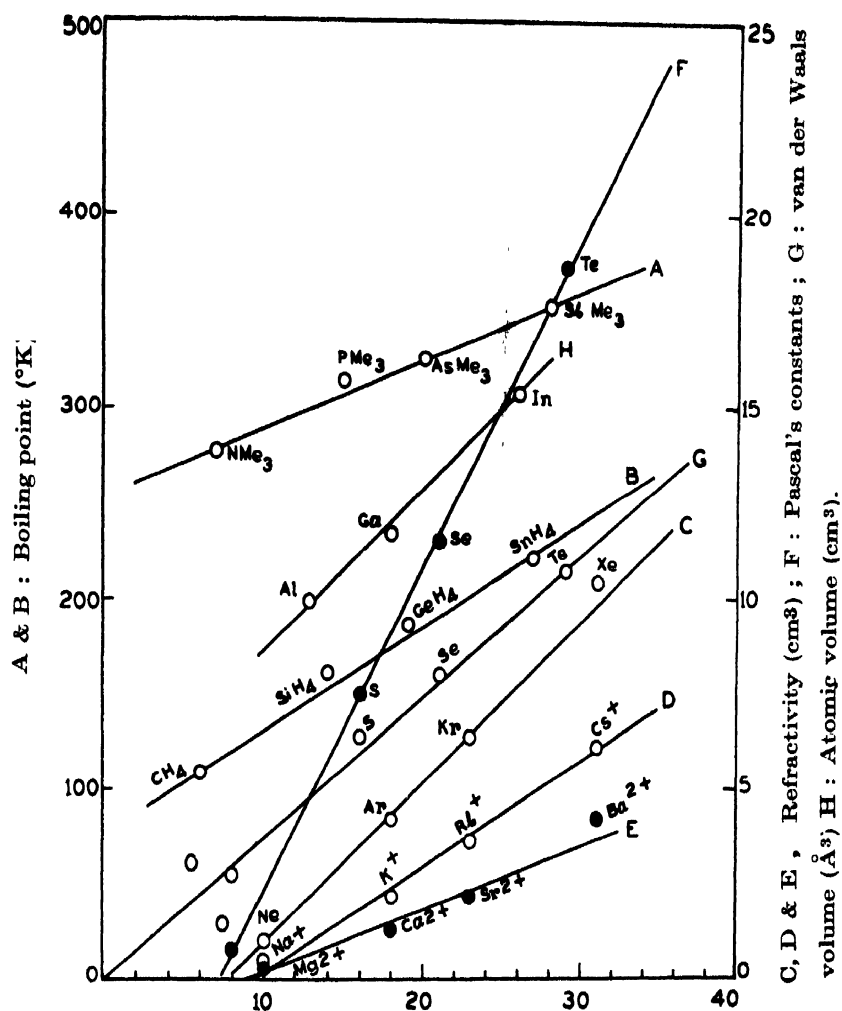


Fig. 3. Plots of some physical properties vs. $(Z-S)$ for various sequences.

A detailed account of the above relationships will appear elsewhere.

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