Covalent and Crystal Radii of Non-transition Elements

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Summary The ratio, crystal radius:covalent radius, for the Group constants of non-transition elements is shown to be an exponential function of one half of the Group number.

ALTHOUGH the radius of an atom or of an ion is a function of its environment, a covalent radius is assigned to each atom, and a crystal radius to each ion. The crystal radii of Groups I and II are stable whereas those for many elements of Group IV—VII are hypothetical and are calculated from quantum-mechanical considerations. Here the two radii are compared.

It was shown[1] for the elements in each Group (Table 1)

TABLE 1

Groups of elements

Group	Elements
0	He, Ne, Ar, Kr, Xe
I	Li, Na, K, Rb, Cs
II	Be, Mg, Ca, Sr, Ba
III	B, Al, Ga, In, Tl
IV	C, Si, Ge, Sn, Pb
V	N, P, As, Sb, Bi
VI	O, S, Se, Te
VII	F, Cl, Br, I

that there is a log–log relationship between covalent radius and atomic number (Z) as expressed in Equation (1),

$$r = kZ^s \qquad (1)$$

where r is the covalent radius (Å), Z is the atomic number, and k and s are constants for each Group as shown in Table 2.

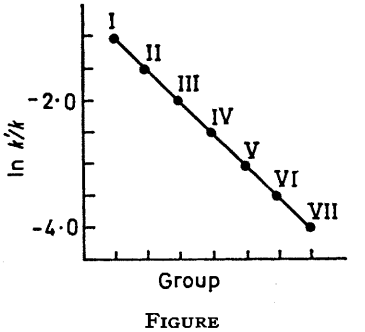
TABLE 2

Constants for Equation (1)[a]

Group	k(Å)	s	k'(Å)	s'
I	1·10	0·18	0·41	0·36
II	0·59	0·30	0·14	0·56
III	0·58	0·21	0·081	0·56
IV	0·50	0·25	0·046	0·66
V	0·44	0·27	0·025	0·77
VI	0·37	0·33	0·012	0·98
VII	0·34	0·34	0·0061	1·11

[a] Calculated for Equation (1) from experimental data.

Now the crystal radii[2] are compared for each Group. A log–log plot between crystal radius and Z for the elements in each Group yields the relationship of Equation (1), and the constants k' and s' for each Group are shown in Table 2.



FIGURE

Whereas both constants, k and k', decrease from I to VII, the k' values decrease at a greater rate. This is shown in the Figure, which is a plot of $\ln k'/k$ against Group number. The data are fitted into Equation (2), in which the ratio of the constants, k'/k (for any Group) is an exponential function of one half of the Group number ($a = 0{\cdot}61$, $b = 0{\cdot}5$, and G is group number).

$$k'/k = a \exp(-b\mathrm{G}) \qquad (2)$$

The decrease in k and in k' values from I to VII can be explained by a decrease in covalent radius and in crystal radius, respectively, with increasing Z. The effect is greater for the k' values because the atoms have lost valence electrons in attaining cationic states equal to their respective Group numbers.

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[1] J. Elson, *Chem. Comm.*, 1969, 898.
[2] L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N.Y., 1960, 3rd edn., p. 514.