General and Inorganic Chemistry

Metallic radii of nonmetals

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Experimental data are used to determine the atomic volumes and radii of the elements of subgroups IV—VIIA in the structures of metallic phases at high pressures. Metallic radii of nonmetals are compared with values based on Pauling and Goldschmidt calculations.

Key words: high-pressure phase, metallic structure, atomic radii, coordination number.

Studies of structural transformations of substances at high pressures are very important for crystallochemistry. The use of new objects, such as elements of groups IV—VIIA, offers a way to complete the systematization of metal structures and their geometric parameters including atomic radii. Calculations of metallic radii of nonmetals from the available experimental data make it possible to consider the validity of conventional crystallochemical rules, including the effect of the coordination numbers of atoms on bond length.

Back in 1926—1928, Goldschmidt derived a linear relation between the atomic radius (r) and the coordination number based on studies of the structures of polymorphous modifications of elements:

$$r_{12} = 1.03r_8 = 1.04r_6 = 1.12r_4\,, \qquad (1)$$

where the subscripts denote the coordination numbers.

Comparing the bond lengths in molecules and crystals of univalent metals [1,2] makes it possible to find the relation between r_{12} and r_1. From linear interpolation, the correspondig values for other coordination numbers can be derived:

$$r_{12} = 1.14r_3 = 1.16r_2 = 1.18r_1\,. \qquad (2)$$

The two relations evidently supplement the rules obtained by Goldschmidt.

Pauling [4] suggested another way to calculate atomic radii based on changes in coordination number:

$$r_{(n)} = r_{(1)} - 0.3\,\log n\,, \qquad (3)$$

where n is the ratio of the valence (z) to the coordination number; r_1 and r_n are the radii of single and multiple (n) bonds, correspondingly. Applying this equation, it should be kept in mind, according to Pauling, that

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Table 1. Atomic parameters of elements for coordination number 6

Element	r_4[3]/Å	$r_{(1)}$/Å	Structure β-Sn, V_a/Å^3	r_6/Å experimental	 (1)	 (3)
Si	1.176	1.173	15.8[5], 15.93[6]	1.29	1.266	1.284
Ge	1.225	1.242	19.0[5], 16.76[7]	1.34	1.319	1.353
Sn	1.405	1.421	27.0[3]	1.54	1.513	1.532
Element	r_3[8,9]/Å	$r_{(1)}$/Å	Structure β-Po, V_a/Å^3	r_6/Å experimental	 (1,2)*	 (3)
P	1.125	1.10	15.2[9]	1.24	1.233	1.190
As	1.258	1.210	21.41[8], 20.44[10]	1.38	1.379	1.385
Sb	1.454	1.391	30.20[11]	1.56	1.594	1.566
Bi	1.536	1.510	35.38[12]	1.64	1.684	1.685
Element	r_2[13,14]/Å	$r_{(1)}$/Å	Structure β-Po, V_a/Å^3	r_6/Å experimental	 (1,2)**	 (3)
Se	1.185	1.17	20.51[15]	1.37	1.322	1.313
Te	1.433	1.37	31.14[16], 30.94[17]	1.57	1.598	1.513

* Calculated according to the relation: $r_6 = (1.14/1.04)r_3$.

** Calculated according to the relation: $r_6 = (1.16/1.04)r_2$.

Table 2. Parameters of elements for coordination numbers 8 and 12

Element	V_a/Å^3 Cubic close packing	r_{12}/Å experimental	 (1)	 (3)
Si	15.1[5], 14.33[6]	1.375	1.317	1.374
	Body-centered lattice	r_8/Å experimental	 (1,2)	 (3)
Sb	26.88[11]	1.63	1.609*	1.604
Bi	31.73[12]	1.73	1.700*	1.723
Se	20.47[15]	1.49	1.334**	1.351
Te	30.46[16]	1.70	1.614**	1.551

* Calculated according to the relation: $r_8 = (1.14/1.03)r_3$.

** Calculated according to the relation: $r_8 = (1.16/1.03)r_2$.

the value of z coincides with the group number for the A-subgroup elements of the Periodic Table. The subgroups VIIA and VIIIA are an exception; for these elements $z = 6$. For halogens, chalcogens, B, C, N, P, and O, the valences correspond to the conventional values, whereas for the IB—VB subgroup elements, z has fractional values, which decrease by one (Ref. 4, p. 403) on passing from subgroup IB (5.56) to the neighboring groups (4.56, 3.56, *etc.*).

Relations (1) and (3) show that the first calculation method envisages a constant relative increase in the atomic radius as the coordination number increases within the indicated range, while the second method gives a constant absolute value for the increase. Experimental data obtained at high pressures make it possible to choose the proper approach for the calculation of atomic radii at high coordination numbers from single-bond covalent radii.

Table 1 lists the calculated covalent radii for single bonds (r_1) of the elements belonging to subgroups IVA—VIA according to Pauling (Ref. 4, p. 403) and the experimental radii for the same elements: r_4 for coordination number 4 (Si, Ge, Sn), r_3 for coordination number 3 (P, As, Sb, Bi), r_2 for coordination number 2 (Se, Te) and the corresponding references. Table 1 also contains the mole volumes of the high-pressure phases for one atom in a unit cell (V_a) extrapolated to normal pressure. From these volumes, the averaged atomic radii of elements with coordination number 6 are derived and compared with r_6 obtained from the structural data of the initial phases according to (1), (2) and from r_1 according to (3). The averaging was necessary because, for example, in white tin, each atom has four neighbors at a distance of 3.016 Å and two neighbors at a distance of 3.175 Å.

Table 1 shows that the average deviation of r_6 calculated from relations (1)—(2) and (3) from the experimental radii for the high-pressure phases is the same for both of the calculation techniques.

It is of interest to verify whether the two methods are suitable for higher coordination numbers, which characterize phases existing at the highest pressures currently attainable for the specific elements. Table 2 presents the experimental data and the calculated values for metallic structures with coordination numbers 8 and 12.

As can be seen from Table 2, for high coordination numbers the efficiency of the methods suggested by Goldschmidt and Pauling is approximately three times worse than for octahedral coordination. And the latter method gives the maximum error for Se and Te (as for coordination number 6). Taking into account that Pauling did not determine the metallic valences for these elements (Ref. 4 gives 2 for z), it seems reasonable to minimize the calculation errors in Eq. (3) for Se and Te by varying the value of z.

Agreement between the calculated atomic radii and the experimental results is observed for the following effective valences of the chalcogens:

1) for coordination number 6, $z = 1.29$; this means that about one third of the valence electrons are delocalized and two thirds are involved in the formation of the covalent bond;

2) for coordination number 8, $z = 0.66$; this means, on the contrary, that one third of the valence electrons take part in the formation of covalence bonds and two thirds are delocalized.

The result can be proved experimentally.

The introduction of the corrections outlined above makes the Pauling method somewhat more preferable for the calculations of nonmetal atomic radii in metallic structures than that of Goldschmidt. It should be kept

Table 3. Recommended values of metallic radii

Element	r_{12}/Å	Element	r_{12}/Å
Si	1.38	P	1.33
Ge	1.43	As	1.48
Sn	1.58	Sb	1.66
Bi	1.78	Cl	(1.26)
S	(1.41)	Br	1.41
Se	1.55	I	1.62
Te	1.75		

Note. The extrapolated values are presented for S and Cl, because their metallic states have not been realized yet.

in mind, however, that the Goldschmidt relation bears one parameter, while that of Pauling involves two parameters, namely, the effective valence and the single-bond radius.

The metallic radii for Br and I are given below; no relevant information could be found in the literature. The transition of Br from the molecular structure to a body-centered[18] lattice at 80 GPa decreases the mole volume by 2.8 %. Extrapolating this drop in the volume to normal pressure, the decrease in the atomic volume of Br from 31.88 Å^3 for the molecular structure[19] to 30.99 Å^3 for the body-centered metallic lattice can be obtained. Therefore, it can be inferred that the r_8 radius of Br is 1.36 Å.

On transition from the molecular to the metallic type of structure at 21 GPa, the radius of iodine, extrapolated to normal pressure, shows[20] an increase from 1.357 to 1.62 Å for coordination number 12 ; that is, 4 + 8.

These experimentally found radii can be compared with those calculated according to relations (1) and (2) using the following bond lengths[21] in the molecular crystal of Br_2 and I_2 : r_8 (Br) = 1.317 and r_{12}(I) = 1.602 Å. Strictly speaking, relation (3) cannot be used for the calculation, because neither the effective halogen valencies for the metallic state nor the values for $r_{(1)}$ are available. Using the experimental radii for Br and I atoms (coordination numbers 8 and 12, correspondingly), the single-bond radii of Br and I for the conventional valences can be calculated as 1.09 and 1.30 Å, correspondingly. Thus, based on the Pauling method, r_{12}(Br) = 1.41 Å.

Table 3 presents the recommended values of the metallic radii for nonmetals (with coordination number 12).

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