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The Radii of Spherical Ions

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A set of most probable ionic radii have been formulated using a combination of deduction from r_0 values and experimental electron density maps. The relationship of the new radii to the free energies of hydration of gaseous ions is discussed.

Introduction

It was shown by Bragg [1] in 1920 that the alkali metal halides behaved as though each of their component ions had a characteristic radius. For example, the differences between the shortest interatomic distances [2], r_0, in the rubidium and the potassium halides are nearly constant, whatever the halide:

	r_0, Å		r_0, Å	Δr_0, Å
RbF	2.82	KF	2.67	0.15
RbCl	3.29	KCl	3.15	0.14
RbBr	3.43	KBr	3.30	0.13
RbI	3.67	KI	3.53	0.14

It is quite evident that individual ionic radii are not obtained directly from the experimental data, r_0. Several methods have been suggested [3–8] by means of which ionic radii may be deduced. Consequently, several sets of radii are described currently, and for some ions the given values differ appreciably.

It is desirable to have a reliable set of ionic radii, in order that the evaluations of free energies of hydration of ions and of repulsion potentials in ionic crystals may be carried out. In this paper, some of the previous assignments of ionic radii are discussed, and a set of most probable ionic radii are postulated. In addition, interesting correlations with experimental free energies of hydration of uni-electrovalent ions are noted.

Previous Radii Assignments

Most of the alkali halides have the "NaCl" type-structure: it is very easy to show that, if the anions are close-packed, the radius of the anion is $r_0/\sqrt{2}$. Landé [3] assumed this degree of contact in the case of lithium iodide, but without direct proof. Wasastjerna [4] obtained ionic radii of isoelectronic alkali metal and halide ions by dividing the r_0 values in the proportion of the fourth root of their polarizabilities, which in turn, were derived by an empirical subdivision based upon the refractive indices of the corresponding salts. Goldschmidt [5] extended Wasastjerna's table of radii, using the values of $r(\mathrm{F}^-)$ and $r(\mathrm{O}^{2-})$ as standards.

Pauling's ionic radii [6] were evaluated by dividing the r_0 values for certain salts composed of pairs of isoelectronic ions in the inverse ratio of their effective nuclear charges, Z, for example:

$$r_0(\mathrm{NaF}) = r(\mathrm{Na}^+) + r(\mathrm{F}^-) = 2.31$$
$$Z(\mathrm{Na}^+) = 6.48$$
$$Z(\mathrm{F}^-) = 4.48$$

whence $r(\mathrm{Na}^+) = 0.9\,(4)$ and $r(\mathrm{F}^-) = 1.3\,(7)$ Å. The determination of the effective nuclear charges involved calculations on free atoms; the radius of the lithium ion was obtained by the subtraction $r_0(\mathrm{Li_2O}) - r(\mathrm{O}^{2-})$. Similar radii have been compiled by Zachariasen [7], using Goldschmidt's value of $r(\mathrm{Cl}^-)$ as a standard. Morris [8] has listed radii of alkali metal and halide ions deduced from the values of $r(\mathrm{Na}^+)$ and $r(\mathrm{Cl}^-)$ obtained from electron density maps [9, 10] of sodium chloride.

Table 1. *Ionic radii assignments*, Å

	Goldschmidt [5]	Pauling [6]	Zachariasen [7]	Morris [8]	New radii (this work)
Li^+	0.78	0.60	0.68	0.93	0.86
Na^+	0.98	0.95	0.98	1.17	1.12
K^+	1.33	1.33	1.33	1.49	1.44
Rb^+	1.49	1.48	1.48	1.64	1.58
Cs^+	1.65	1.69	1.67	1.83	1.84
Be^{2+}	0.34	0.31	0.30	—	—
Mg^{2+}	0.78	0.65	0.65	—	0.87
Ca^{2+}	1.06	0.99	0.94	—	1.18
Sr^{2+}	1.27	1.13	1.10	—	1.32
Ba^{2+}	1.43	1.35	1.29	—	1.49
Ra^{2+}	—	1.40	1.37	—	1.57
H^-	1.54	2.08	—	—	1.39
F^-	1.33	1.36	1.33	1.16	1.19
Cl^-	1.81	1.81	1.81	1.64	1.70
Br^-	1.96	1.95	1.96	1.80	1.87
I^-	2.20	2.16	2.19	2.04	2.12
O^{2-}	1.32	1.40	1.46	—	1.25
S^{2-}	1.74	1.84	1.90	—	1.70
Se^{2-}	1.91	1.98	2.02	—	1.81
Te^{2-}	2.11	2.21	2.22	—	1.97
NH_4^+	—	1.48	—	—	1.66
Ag^+	1.13	1.26	—	—	1.27
Tl^+	1.49	1.40	—	—	1.54
Cd^{2+}	1.03	0.97	—	—	1.14
Co^{2+}	0.82	0.74	—	—	0.88
Fe^{2+}	0.83	0.76	—	—	0.90
Mn^{2+}	0.91	0.80	—	—	0.93

New Radii Assignments

The most direct approach to the assignment of individual ionic radii, although of limited applicability, is the geometrical method of Landé. The alkali halide in which the anions are most likely to be in contact is lithium iodide [3]. This postulate leads to the following example deductions:

$$r(\mathrm{I}^-) = 2.12\ \text{Å}$$
$$r(\mathrm{Na}^+) = 1.12\ \text{Å}$$
$$r(\mathrm{Cl}^-) = 1.70\ \text{Å}\,.$$

It is interesting to note, and it has not been pointed out previously, that the electron density section $\varrho(XY0)$ given by Schoknecht [10] leads also, as near as can be estimated graphically, to the results $r(\mathrm{Na}^+) = 1.12$ Å and $r(\mathrm{Cl}^-) = 1.70$ Å. It seems reasonable, therefore, to set up a table of ionic radii based upon these values. Only those simple salts in which the coordination number is six or more have been considered, since these are the ionic compounds.

In structures of lower coordination number, in layer structures and in molecular structures, not only are the bonds partially directional, but often no unique r_0 distance obtains. It is, of course, always possible to postulate a radius for any atomic species. However, unless the electrons are sensibly localised, the radius is not, in general, characteristic of the ion in different environments. Table 1 lists also the new radii, which are believed to be correct to about ± 1%. It can be shown that a similar set of radii are obtained on the assumption that $\mathrm{Li_2Te}$ forms a close-packed structure.

Discussion

The new radii differ significantly from those given by previous investigators. Bearing in mind the possible errors associated with the detailed interpretation of electron density maps obtained by Fourier summation [11, 12], the agreement gained from the independent approaches used in assigning the new radii is surprisingly good. It has not been found necessary to make an allowance for the change in coordination number between the “NaCl” and the “CsCl” type-structures.

The new radii are comparable with those adopted by Fumi and Tosi [13] in calculating the repulsion potential term in the crystal energy equation, for alkali halides. It would not be reasonable, however, to offer the agreement between the calculated crystal energies and the corresponding thermodynamically derived values as evidence for the correctness of the radii: the thermodynamic (Born-Haber cycle) calculation involves the electron affinity of the halogen atom, and the best estimate of this quantity is obtained through the calculated crystal energies.

Bernal and Fowler [14] determined the enthalpies of hydration, ΔH_h, of gaseous ions by dividing the experimental enthalpies of hydration of ion-pairs, taking $\Delta H_h(\mathrm{K}^+, g) = \Delta H_h(\mathrm{F}^-, g)$: at that time, $r(\mathrm{K}^+) = r(\mathrm{F}^-)$ was assumed, Table 1 (Column 1). With the new radii of Table 1 (Column 5), both $r(\mathrm{Na}^+) \simeq r(\mathrm{F}^-)$ and $r(\mathrm{Cs}^+) \simeq r(\mathrm{Br}^-)$, and using the Bernal/Fowler approach, the data of Table 2 were obtained; the entropies of hydration, ΔS_h, were taken from Bockris and Conway [15]. It can be seen that the data are in good agreement with the experimental results of Randles [16].

The free energies of hydration of the alkali metal and the halide ions are represented by the equation

$$-\Delta G_h = 89.4(1/r) + 20.7\,, \qquad \text{kcal/mol} \tag{1}$$

with an average deviation of 1–2 kcal/mol. This result lends support to the new radii values, taking into account that the free energy of hydration of simple uni-electrovalent ions is almost wholly Coulombic in nature [14]. From the appropriate thermodynamic cycles, the enthalpy of hydration of the gaseous hydrogen ion, $\Delta H_h(\mathrm{H}^+, g)$, has been evaluated as -264 ± 3 kcal/mol.

Table 2. *Free energies and enthalpies of hydration of gaseous ions, kcal/mol*

	Randles [16]	This work	
	$-\Delta G_h$	$-\Delta G_h$	$-\Delta H_h$
Li^+	122	124	134
Na^+	98	99	107
K^+	81	82	87
Rb^+	76	75	80
Cs^+	68	72	76
F^-	99	102	111
Cl^-	71	75	80
Br^-	65	69	73
I^-	57	59	62

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