states of a system, experimentally observable changes of state can be discussed consistently in terms of processes proceeding through unattainable states.

Let us define the processes

$$M(ss) \longrightarrow M^{z+}(aq) + z[e^-](aq) \qquad (\alpha_+)$$

$$X(ss) + z[e^-](aq) \longrightarrow X^{z-}(aq) \qquad (\alpha_-)$$

$$M(ss) + zH^+(aq) \longrightarrow M^{z+}(aq) + \frac{z}{2}H_2(g) \qquad (\beta_+)$$

$$X(ss) + \frac{z}{2}H_2(g) \longrightarrow X^{z-}(aq) + zH^+(aq) \qquad (\beta_-)$$

$$^1/_2H_2(g) \longrightarrow H^+(aq) + [e^-](aq) \qquad (\gamma)$$

$$M(ss) \longrightarrow M^*(aq) + z[e^-](aq) + z[+](aq) \qquad (\delta_+)$$

$$X(ss) + z[e^-](aq) \longrightarrow X^*(aq) + z[-](aq) \qquad (\delta_-)$$

$$M^*(aq) + z[+](aq) \longrightarrow M^{z+}(aq) \qquad (\epsilon_+)$$

$$X^*(aq) + z[-](aq) \longrightarrow X^{z-}(aq) \qquad (\epsilon_-)$$

For reasons explained in Appendix B, the above processes are defined to involve no net transport of charge across a phase boundary.

The quantities used in the Introduction can be defined by the following relations where $Y^0_{ss}$ is the value of $Y$ for the element in its standard state and the other subscripts refer to the above processes. Absence of a sign in the subscript means that the equation is valid for both cations and anions.

$$\bar{Y}^0 = Y^0_{ss} + \Delta\bar{Y}^0_\alpha \qquad (A1)$$

$$\bar{Y}^0_{con} = Y^0_{ss} + \Delta\bar{Y}^0_{\beta_+} - (z/2)Y^0_{H_2} \quad \text{(cation)} \qquad (A2)$$

$$\bar{Y}^0_{con} = Y^0_{ss} + \Delta\bar{Y}^0_{\beta_-} + (z/2)Y^0_{H_2} \quad \text{(anion)} \qquad (A3)$$

$$\bar{Y}^0_H = {}^1/_2Y^0_{H_2} + \Delta\bar{Y}^0_\gamma \qquad (A4)$$

$$\bar{Y}^0_{neut} = Y^0_{ss} + \Delta\bar{Y}^0_\delta \qquad (A5)$$

$$\bar{Y}^0_{el} = \Delta\bar{Y}^0_\epsilon \qquad (A6)$$

The processes are also defined to satisfy the equations

$$\alpha_+ = \beta_+ + z\gamma \qquad (A7)$$

$$\alpha_- = \beta_- - z\gamma \qquad (A8)$$

$$\alpha = \delta + \epsilon \qquad (A9)$$

Hence eq. 1–3 in the Introduction follow directly.

## Appendix B

**Treatment of Interfacial Potentials.**—Special problems arise when the above equations are applied to the properties free energy and enthalpy. Estimation of $\bar{F}^0_{neut}$ and $\bar{H}^0_{neut}$ from experimental data seems to require use of properties of gaseous ions.

Let $e^-(0)$ refer to gaseous electrons in a hypothetical state having zero values for kinetic energy, entropy, and free energy. Let $Z$ be the electrostatic potential of an aqueous phase relative to a gas in contact with it. Frumkin[24] has suggested that orientation of water dipoles will make $Z$ negative by some tenths of a volt, but no really satisfactory method of experimental measurement is known.

Process $\delta_+$ can be separated into the following component processes. Free energy changes are given in parentheses, and $\Delta F^0_{ion}$ and $\Delta F^0_{neut}$ have been defined previously.[1]

$$M(ss) \longrightarrow M^{z+}(g) + ze^-(0) \qquad (\Delta F^0_{ion}) \qquad (B1)$$

$$M^{z+}(g) \longrightarrow M^*(g) + z[+](g) \qquad (-z^2e^2/2r) \qquad (B2)$$

$$M^*(g) \longrightarrow M^*(aq) \qquad (\Delta F^0_{neut}) \qquad (B3)$$

$$z[+](g) \longrightarrow z[+](aq) \qquad (NzeZ) \qquad (B4)$$

$$ze^-(0) \longrightarrow z[e^-](aq) \qquad (-NzeZ) \qquad (B5)$$

Similar component processes can be written to define process $\delta_-$ involving an anion.

The ionic hydration process is usually written

$$M^{z+}(g) \longrightarrow M^{z+}(aq) \qquad (B6)$$

The above equations indicate that the electrostatic contribution to the free energy of this process contains a term involving an unknown interfacial potential in addition to the usual terms involving dielectric properties of the medium. These effects can be eliminated if eq. B6 is avoided and if hydration of gaseous ions is always defined to involve a process of the type

$$M^{z+}(g) + ze^-(0) \longrightarrow M^{z+}(aq) + z[e^-](aq) \qquad (B7)$$

$$M^{z+}(g) + z[-](g) \longrightarrow M^{z+}(aq) + z[-](aq) \qquad (B8)$$

$$X^{z-}(g) + z[+](g) \longrightarrow X^{z-}(aq) + z[+](aq) \qquad (B9)$$

(24) A. Frumkin, *J. Chem. Phys.*, **7**, 552 (1939).

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[CONTRIBUTION FROM THE DEPARTMENT OF PHYSICAL AND INORGANIC CHEMISTRY OF THE UNIVERSITY OF NEW ENGLAND, ARMIDALE, N.S.W., AUSTRALIA]

# The van der Waals Radii of Gaseous Ions of the Noble Gas Structure in Relation to Hydration Energies

BY R. H. STOKES

RECEIVED SEPTEMBER 6, 1963

In comparing experimental free energies of hydration of ions with calculations from electrostatic models, the self energy of the gaseous ion is the dominant term. The crystal radius is not appropriate for the calculation of this term. The van der Waals radius calculated from that of the isoelectronic noble gas by the quantum mechanical scaling principle is a reasonable alternative and leads to excellent agreement with the experimental data for ions of the noble gas structure. The model used for the ion in solution is consistent with the known dielectric properties of water.

## Notation

$\mu$, chemical potential of ionic species
$\Delta\mu_h$, Gibbs free energy of hydration per mole
$\epsilon$, dielectric constant (relative permittivity)
el, electrostatic contribution
$r_E$, "equivalent electrostatic radius" of ion
$r_V$, van der Waals radius
$r_C$, crystal radius (Pauling)
$z$, valency of ion (signed)
$Z$, atomic number of ion
$S$, screening constant for outermost electron shell of ion or noble gas atom
$\Delta\bar{F}^0$, standard free energy change

## Introduction

The failure of the Born equation

$$-\Delta\mu_h^{el} = \frac{Nz^2e^2}{2r}\left(1 - \frac{1}{\epsilon}\right) \qquad (1)$$

to represent the electrostatic contribution to observed free energies of hydration of ions is well known. Using the crystal radius of the ion for $r$, agreement can be produced only by either: (a) reducing the value of $\epsilon$ to values much lower than the expected value for "irrotationally bound" water. Thus the work of Hasted,

*et al.*,[1] has shown that water molecules "irrotationally bound" at the surface of an ion should have a dielectric constant $\epsilon_{irr} \approx 5$, while eq. 1 demands values as low as 1.3 for multivalent ions. Noyes[2] explains such low values by the proposal that near ions like $Al^{+3}$ "even the electronic polarization of water is becoming saturated." This, however, would demand a marked drop in the optical refractive index below that of water, which is not observed. (b) Assuming[3] that the cation in solution is surrounded by a "cavity" extending for about 1 Å. beyond the ion, in which the dielectric constant is unity, *i.e.*, that of a void. This is not acceptable on physical grounds, as it is not consistent with the small or negative apparent molar volumes of the smaller cations, nor is it easy to see how such a cavity could remain stable under the strong ion–dipole forces operating.

In this paper it is argued that the failure of eq. 1 is due primarily to the fact that the crystal radius is not appropriate for the calculation of the electrostatic self energy of the ion *in vacuo*. An alternative choice, the van der Waals radius, leads to excellent agreement.

**Electrostatic Self Energies of Ions.**—In electrostatic models of the hydration of ions, the free energy of hydration is considered as made up of a part $\Delta\mu_h^{el}$ arising from the change in self energy of the ion on transfer from the gaseous standard state to water, and a small component $\Delta\mu_S$ corresponding to the nonelectrostatic part of the free energy of solution of the ion.

The electrical part should clearly be written

$$\Delta\mu_h^{el} = \mu_{aq}^{el} - \mu_{gas}^{el} \qquad (2)$$

In the electrostatic models, the actual ion is conceptually replaced by a sphere having a radius $r_E$ such that

$$\mu^{el} = Nz^2e^2/2r_E\epsilon = 166.0z^2/r_E\epsilon \text{ kcal. mole}^{-1} \text{ Å.} \qquad (3)$$

where $\epsilon$ is the relevant dielectric constant. All previous treatments of this model have tacitly or explicity accepted the assumption that $r_E$ in both phases is the crystal radius. Since Pauling's crystal radii are commonly used, his words[4] on their meaning are worth quoting here:

"Since the electron distribution function for an ion extends indefinitely, it is evident that no single characteristic size can be assigned to it. Instead the apparent ionic radius will depend on the physical property under discussion and will differ for different properties."

Now it is certain that the ions in a crystal are under strong compressive forces. When an ion is isolated in the gas phase, the outer parts at least of its electron distribution will expand considerably. Approximate quantum mechanical calculations show that in a free univalent ion a considerable fraction of one electronic charge lies outside the crystal radius. If we propose to replace the actual ion, as far as its effects on the space outside it are concerned, by a sphere of equivalent electrostatic radius $r_E$, we must clearly take a radius outside which the electron density is inappreciable. This is, however, too indefinite a concept for practical utility. Instead I propose the use of the van der Waals radius, which for ions of the noble gas structure can be given a quite precise meaning as follows.

**van der Waals Radii of Noble Gas Atoms.**—The crystal radii of the solidified noble gases have been determined by X-ray diffraction; Wyckoff's[5] values are given as $r_C$ in Table I. Since these crystals are held together only by very weak forces, $r_C$ should form a good approximation to the required radius. Another method of estimating the size of these atoms comes from the fact that both transport and equilibrium properties of the noble gases can be described with good accuracy[6] using a Lennard-Jones 6–12 interaction for the mutual potential energy of a pair of atoms. The van der Waals radius may then be taken as half the distance at which the minimum potential energy given by this function occurs. The values denoted $r_{L-J}$ in Table I are the means of several values for each substance, differing only slightly, obtained from both the second virial coefficient and the viscosity parameters tabulated by Hirschfelder, Curtiss, and Bird.[6] Agreement between these and the crystal radii is good except in the case of helium, where complications due to quantum interactions occur. For all the others, we take for $r_V$ the mean values from Table I.

TABLE I

VAN DER WAALS RADII OF NOBLE GAS ATOMS

$r_C$ = crystal radius. $r_{L-J}$ = one-half distance of minimum potential energy in the Lennard-Jones 6–12 potential expression for the gas, $r_V$ = mean value used in this paper for gaseous ions.

| | He | Ne | Ar | Kr | Xe |
|---|---|---|---|---|---|
| $r_C$/Å. | 1.78 | 1.598 | 1.916 | 2.017 | 2.210 |
| $r_{L-J}$/Å. | 1.43 | 1.568 | 1.920 | 2.021 | 2.267 |
| $r_V$/Å. | .. | 1.583 | 1.918 | 2.019 | 2.239 |

**van der Waals Radii of Ions of the Noble Gas Structure.**—The corresponding radii $r_V$ of isolated ions of the noble gas structure can now be calculated from those of the isoelectronic noble gases, using the quantum mechanical scaling principle. This principle states that within an isoelectronic sequence of ions or atoms, any characteristic radius $r'$ associated with a given electron is inversely proportional to the effective atomic number $(Z - S)$, where the screening parameter $S$ is constant for the isoelectronic sequence. Here we are concerned with electrons in closed (sp) shells, for which Slater's[7] rules give the values of $S$: He sequence, $S = 0.30$; Ne sequence, $S = 4.15$; Ar sequence, $S = 11.25$; Kr sequence, $S = 27.75$; Xe sequence, $S = 45.75$. Using these values, and fixing the constant of proportionality by the data for the noble gas atoms in Table I, the van der Waals radii of the ions are obtained (Table II). The self energy of spheres of radius $r_V$ *in vacuo* is then calculated by eq. 3 with $\epsilon = 1$ (Table III, column d).

TABLE II

VAN DER WAALS RADII (ÅNGSTROMS) OF NOBLE GAS TYPE ATOMS AND IONS IN THE GASEOUS STATE

(Calculated from $r_V$ of Table I and the quantum mechanical scaling principle; see text)

| $O^{-2}$ | $F^-$ | $Ne^0$ | $Na^+$ | $Mg^{+2}$ | $Al^{+3}$ |
|---|---|---|---|---|---|
| 2.405 | 1.909 | 1.583 | 1.352 | 1.180 | 1.046 |
| $S^{-2}$ | $Cl^-$ | $Ar^0$ | $K^+$ | $Ca^{+2}$ | $Sc^{+3}$ |
| 2.726 | 2.252 | 1.918 | 1.671 | 1.480 | 1.328 |
| $Se^{-2}$ | $Br^-$ | $Kr^0$ | $Rb^+$ | $Sr^{+2}$ | $Y^{+3}$ |
| 2.665 | 2.298 | 2.019 | 1.801 | 1.625 | 1.481 |
| $Te^{-2}$ | $I^-$ | $Xe^0$ | $Cs^+$ | $Ba^{+2}$ | $La^{+3}$ |
| 2.956 | 2.548 | 2.239 | 1.997 | 1.802 | 1.642 |

**A Model for Ions in Aqueous Solution.**—It has recently been pointed out[8] that the fact that the enthal-

(1) J. B. Hasted, D. M. Ritson, and C. H. Collie, *J. Chem. Phys.*, **16**, 1 (1948).

(2) R. M. Noyes, *J. Am. Chem. Soc.*, **84**, 513 (1962).

(3) W. M. Latimer, K. S. Pitzer, and C. M. Slansky, *J. Chem. Phys.*, **7**, 108 (1939).

(4) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1944.

(5) R. G. Wyckoff, "Crysta) Structures," Interscience Publishers, Inc., New York, N. Y.

(6) J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, "Molecular Theory of Gases and Liquids," John Wiley and Sons, Inc., New York, N. Y., 1954.

(7) J. C. Slater, *Phys. Rev.*, **36**, 57 (1930).

(8) S. W. Benson and C. S. Copeland, *J. Phys. Chem.*, **67**, 1194 (1963).

TABLE III

CALCULATION OF FREE ENERGIES OF HYDRATION AND COMPARISON WITH EXPERIMENTAL VALUES

| (a) Ion | (b) $r_V$ | (c) $r_C$ | (d) $\mu_{vac}^{el}$ | (e) $\mu_{aq}^{el}$ | (f) $\Delta\mu_S$ | (g) $-\Delta\mu_h$ (calcd.) | (h) $-\Delta\mu_h$ (exptl.) | (i) Diff., % |
|---|---|---|---|---|---|---|---|---|
| $Na^+$ | 1.352 | 0.95 | 122.8 | 15.1 | 4.3 | 103.4 | 101.8 | +1.6 |
| $K^+$ | 1.671 | 1.33 | 99.3 | 9.9 | 3.9 | 85.5 | 84.1 | +1.7 |
| $Rb^+$ | 1.801 | 1.48 | 92.2 | 8.7 | 3.5 | 80.0 | 79.0 | +1.3 |
| $Cs^+$ | 1.997 | 1.69 | 83.1 | 7.3 | 3.2 | 72.6 | 71.3 | +1.8 |
| $Mg^{+2}$ | 1.180 | 0.65 | 563 | 103 | 4.3 | 455 | 463 | −1.7 |
| $Ca^{+2}$ | 1.480 | 0.99 | 449 | 65 | 3.9 | 380 | 388 | −2.0 |
| $Sr^{+2}$ | 1.625 | 1.13 | 409 | 56 | 3.5 | 349 | 348 | +0.3 |
| $Ba^{+2}$ | 1.802 | 1.35 | 369 | 39 | 3.2 | 326 | 322 | +1.2 |
| $Al^{+3}$ | 1.046 | 0.50 | 1428 | 308 | 4.3 | 1116 | 1114 | +0.2 |
| $Sc^{+3}$ | 1.328 | .81 | 1125 | 182 | 3.9 | 939 | 952 | −1.4 |
| $Y^{+3}$ | 1.481 | .93 | 1009 | 156 | 3.5 | 849 | 872 | −2.6 |
| $La^{+3}$ | 1.642 | 1.15 | 910 | 123 | 3.2 | 784 | 792 | −1.0 |
| $F^-$ | 1.909 | 1.36 | 87.0 | 1.6 | 4.3 | 81.1 | 83.4 | −2.8 |
| $Cl^-$ | 2.252 | 1.81 | 73.7 | 1.2 | 3.9 | 68.6 | 70.0 | −2.0 |
| $Br^-$ | 2.298 | 1.95 | 72.2 | 0.9 | 3.5 | 67.8 | 63.1 | +7.4 |
| $I^-$ | 2.548 | 2.16 | 65.1 | 0.8 | 3.2 | 61.1 | 54.2 | +13.0 |

pies of solution of most ionic crystals are small or zero must mean that the forces acting on ions in water are quite close to those in the crystal; aqueous ions should therefore be "compressed" to much the same extent as those in crystals. In the crystal, compression appears to have gone so far that minor changes from one crystal to another do not have any appreciable effect on the crystal radius, for a nearly additive set of individual ionic radii can be deduced. It is therefore reasonable to attribute to the ion in aqueous solution the crystal radius $r_C$. Microwave studies[1,9] of the dielectric constant depression for aqueous electrolytes indicate that near the larger halide ions the water has nearly its normal bulk dielectric constant, but near cations a number of water molecules are "irrotationally bound" so that orientation of their permanent dipoles cannot make its normal large contribution to the dielectric constant. Water in this state appears to have a minimum dielectric constant of about 5, estimated from the infrared refractive index and the microwave data. Around the cation, the dielectric constant rises from 5 at the "surface" of the ion to its bulk value of 78 at a distance of one or two molecular diameters.

We therefore adopt the following model for the aqueous ion: The ion itself is a sphere of the crystal radius $r_C$. Univalent cations are surrounded by a layer of 2.8 Å. thickness, in which the effective dielectric constant $\epsilon_{eff}$ is given by $\frac{1}{\epsilon_{eff}} = {}^1/_2\left(\frac{1}{5} + \frac{1}{78}\right)$ from which we obtain as a round value $\epsilon_{eff} = 9$. Doubly and trebly charged cations are taken to have two such layers, of total thickness 5.6 Å. (except $Ba^{+2}$, for which only one layer is assumed since there is a variety of evidence that this ion is less hydrated than the other group IIA ions).

On this model the self energy of a mole of ions at infinite dilution is given by

$$\mu_{aq}^{el} = \frac{Nz^2e^2}{2}\left[\frac{2nr_w}{r_C(r_C + 2nr_w)\epsilon_{eff}} + \frac{1}{\epsilon(r_C + 2nr_w)}\right] \quad (4)$$

where $2nr_w$ is the thickness of $n$ layers of water molecules around the ion, $r_C$ is the crystal radius, $\epsilon$ is the normal bulk dielectric constant, and $\epsilon_{eff}$ the effective dielectric constant of the bound water. Putting $\epsilon_{eff} = 9$, $\epsilon = 78.3$, and $2nr_w = 0$ for univalent anions, 2.8 Å. for univalent cations and $Ba^{+2}$, and 5.6 Å. for multiply charged cations, 4 becomes

$$X^-: \ \mu_{aq}^{el} = \frac{2.12}{r_C} \quad (5)$$

$$M^+ \text{ and } Ba^{+2}: \ \mu_{aq}^{el} = 166z^2\left[\frac{0.3111}{r_C(r_C + 2.8)} + \frac{0.01276}{r_C + 2.8}\right] \quad (6)$$

$$M^{+2}, M^{+3}: \ \mu_{aq}^{el} = 166z^2\left[\frac{0.6222}{r_C(r_C + 5.6)} + \frac{0.01276}{r_C + 5.6}\right] \quad (7)$$

In eq. 5–7 energies are in kcal. mole$^{-1}$ and radii in Å. Values calculated by these equations form column e of Table III.

**Comparison with Experiment.**—To estimate the small term $\Delta\mu_S$ representing the nonelectrostatic part of the free energy of solution of the ions, the values for the isoelectronic inert gas are assumed, using Noyes'[2] selection of the data. Then we have

$$\Delta\mu_h(\text{calcd.}) = \mu_{aq}^{el} - \mu_{vac}^{el} + \Delta\mu_S \quad (8)$$

the values being given in Table III, column f.

The experimental values are derived from Noyes'[2] extensive recent compilation. He gives conventional values (his $\Delta F°_{con}$) which are separate ionic values relative to $\Delta\mu_h = -364.0$ for the hydrogen ion. The absolute ionic values are related to these by

$$\Delta F°_{con} = \Delta\mu_h(\text{ion}) - z\Delta F°_H \quad (9)$$

where $z$ is the signed valency of the ion. Noyes presents arguments in favor of assigning to the constant $\Delta F°_H$ the value +104.8 kcal. mole$^{-1}$; other authors have preferred different values; *e.g.*, Kortüm and Bockris[10] use 100.3, and Verwey[11] 123.0. Here, the value of 100.0 kcal. mole$^{-1}$ has been used. This quantity ($\Delta F°_H$) is the free energy change in the hypothetical reaction

$${}^1/_2H_2(g) \longrightarrow H_{aq}^+ + e^-(g)$$

The standard states throughout this paper are those used by Noyes, *viz.*, ideal gas at 1 atm. fugacity, and the "hypothetical molal" aqueous solution of unit activity and unit molal activity coefficient. The values calculated from the experimental data with $\Delta F°_H = 100.0$ kcal. mole$^{-1}$ are given in Table III, column g. Agreement is excellent for all the cations, averaging 1.5%. For the anions, the discrepancies for bromide and iodide are rather large, but scarcely damaging.

Lithium and beryllium ions have not been included in Tables II and III because of the disagreement between the two methods of determining the van der Waals radius of helium. Using the two alternatives in Table I one obtains the results in Table IV for the free energies of hydration of the isoelectronic ions. These bracket the experimental values.

(9) G. H. Haggis, J. B. Hasted, and T. J. Buchanan, *J. Chem. Phys.*, **20**, 1452 (1952).

(10) G. Kortüm and J. O'M. Bockris, "Textbook of Electrochemistry," Elsevier Press, New York, N. Y., 1951.

(11) E. J. W. Verwey, *Chem. Weekblad*, **37**, 530 (1940).

TABLE IV

COMPARISON OF CALCULATED HYDRATION ENERGIES FOR $Li^+$ AND $Be^{+2}$ USING ALTERNATIVE RADII FROM TABLE I FOR HELIUM TO DETERMINE THEIR VAN DER WAALS RADII

(a) $r_{He} = 1.78$ Å; (b) $r_{He} = 1.43$ Å; $\mu$ in kcal. mole$^{-1}$

| | $-\Delta\mu_h$ (calcd.)(a) | $-\Delta\mu_h$ (calcd.)(b) | $-\Delta\mu_h$ (exptl.) |
|---|---|---|---|
| $Li^+$ | 114 | 154 | 125.6 |
| $Be^{+2}$ | 554 | 779 | 591 |

Fluoride ion presents a special problem. The value for the free energy of hydration tabulated by Noyes appears to be consistent with the present model (Table III). This value, however, was calculated from the data for gaseous fluoride ion in the National Bureau of Standards Circular 500; more recent work[12] shows fairly conclusively that this entry is wrong. Revision leads to a free energy of hydration (on the present scale) of $-98$ kcal. mole$^{-1}$ for fluoride ion. This cannot be accounted for on the present model, since it is numerically greater than the self energy of the ion *in vacuo*. The discrepancy is made worse if we assume, as is probable for this anion on the evidence of its mobility and dielectric constant depression, a layer of partially immobilized water molecules around it. This would increase its self energy from the value of 1.6 kcal. shown in Table III to about 10 kcal. mole$^{-1}$, making the calculated hydration energy about $-73$ kcal. mole$^{-1}$. Thus the free energy of aqueous fluoride ion appears to be between 17 and 25 kcal. mole$^{-1}$ lower than can be explained on the electrostatic model. A reasonable explanation of this could lie in the formation of several "hydrogen bonds" between the fluoride ion and the water molecules surrounding it. In other terms, the "proton affinity" of fluoride ion is high compared with the other halide ions.

The striking success of the model in accounting for the hydration energies of cations, including multiply charged ones, justifies the claim that the present method of calculating self energies of gaseous ions is a marked advance on the use of the crystal radii.

**Some Comments on the Model.**—The transfer of the ion from the gas state to solution is envisaged as being carried out directly rather than through a discharge–transfer–recharge process, since the latter is difficult to visualize for actual ions which can be "neutralized" only by conversion to atoms, and raises some difficult problems about the solvation of electrons. The direct transfer really involves the question of the energy for moving the ion through the interfacial potential at the water surface, as discussed by Randles.[12] This term is $zeV$ where $V$ is the interfacial potential, a constant at constant temperature even though its actual value is still in doubt. A term with the necessary dependence on the charge of the ion has been introduced *via* the quantity $z\Delta F^\circ_H$ of eq. 9, which may be taken to include the interfacial potential term. This term appears only when separate ionic values are discussed, and may be thought of as a penalty for using quantities not determinable by direct experiment. It vanishes when we consider either energies of electrically equivalent numbers of cations and anions together, or energy differences between equivalent amounts of ions of the same sign.

While the model proposed gives a very satisfactory account of the free energy of hydration, it cannot be expected to deal adequately with the entropy. The entropy of the gaseous ion does not involve an electrostatic term and is fully calculable from the Sackur–Tetrode equation; but that of the aqueous ion will involve the change with temperature of several of the quantities in eq. 4. Only that of $\epsilon$ is known, and its contribution is probably the least important. One could of course estimate the changes in $n$ or $r_w$ with temperature needed to produce agreement, but this would not constitute an explanation of the entropy of hydration. For this more sensitive test, detailed consideration of the modes of motion of water molecules near the ion would be required in addition to the relatively crude electrostatic approximation for more remote molecules. Dr. L. G. Hepler is currently working on this problem and on that of the free energy of transfer of ions between different solvents.

The reduction in size of the ion on solution in water would appear to require a compression energy which has been disregarded in this paper. This question is discussed for the closely related case of the formation of an ionic crystal from gaseous ions in the following paper, and the answer suggested in that case is probably relevant, *mutatis mutandis*, to the present situation. In brief, the ions are not compressed; rather, as a necessary consequence of the virial theorem, they shrink in the wash.

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(12) J. E. B. Randles, *Trans. Faraday Soc.*, **52**, 1573 (1956).

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[CONTRIBUTION FROM THE DEPARTMENT OF PHYSICAL AND INORGANIC CHEMISTRY, OF THE UNIVERSITY OF NEW ENGLAND, ARMIDALE N.S.W., AUSTRALIA]

# Crystal Lattice Energies and the Electrostatic Self Energies of Gaseous Ions

BY R. H. STOKES

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The self energies of gaseous ions, calculated from their van der Waals radii by the method of a previous paper, show a striking correlation with crystal lattice energies. For ions of the noble gas electronic structure, the lattice energy of a crystal in which the cations and anions have equal van der Waals radii is simply the negative of the self energy of the gaseous ions. For ions of unequal size, the difference between these two energies is a linear function of the radius ratio of the gaseous ions; a single slope characterizes large groups of crystals. A tentative explanation of these observations is suggested in terms of a simple electrostatic model taking account of the deformation of the ions in the crystal.

## Introduction

The writer has recently shown[1] that it is possible to calculate the van der Waals radii of gaseous ions of the noble gas structure from data on the noble gases themselves. Consideration of the electrostatic self energies of the gaseous ions calculated by treating the ion as a sphere of charge $ze$ having the van der Waals radius $r^v$

(1) R. H. Stokes, *J. Am. Chem. Soc.*, **86**, 979 (1964).