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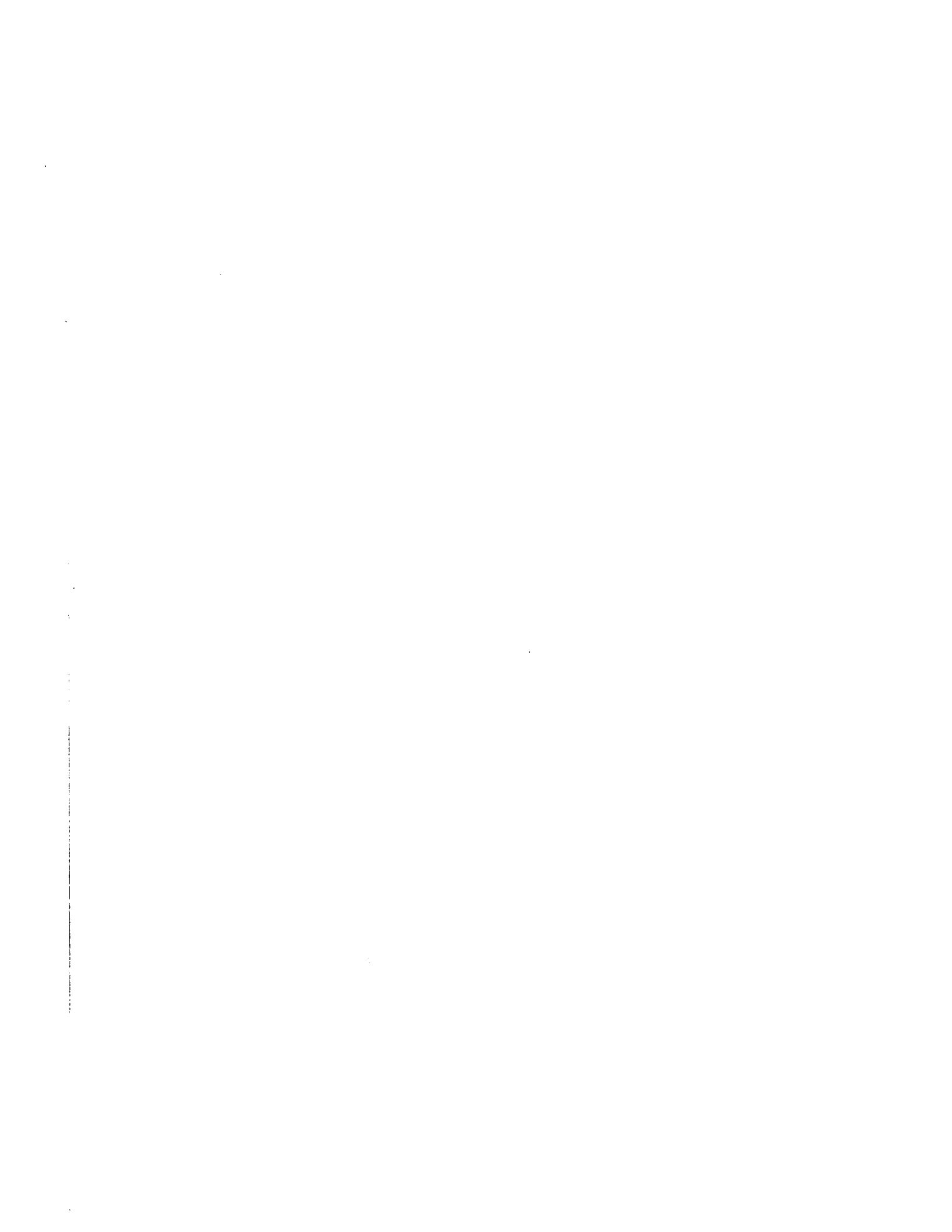
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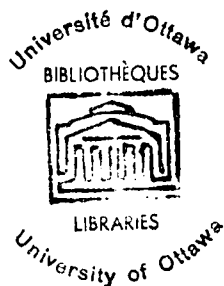


**SOME THERMODYNAMIC PROPERTIES OF IONS
IN AQUEOUS SOLUTION**

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30 May, 1958.



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PREFACE

The concept of partial molal properties is of great value in providing some additional basis for a better understanding of the theory of ionic interactions in aqueous media. In the case of entropies, several equations have been proposed to correlate the values for various types of ions with the charge of the ion, the radius, and other parameters. However, with the building of an absolute scale of ionic entropies and the convincing evidence pointing to a dependence of the entropies on the square of the charge, all these equations, except the most recent one, proposed by Laidler for monatomic ions, have lost their meaning. We have, therefore, in the light of this evidence, investigated the entropies of the inorganic oxy-anions in order to obtain a new equation.

In the case of partial molal volumes of ions, it seems that there has been no interest in the problem for its own sake. Our present purpose was therefore to obtain a reliable set of values for both monatomic ions and inorganic oxy-anions, and to analyze the dependence of these volumes on the various properties of the ions.

The greater part of this thesis has been published in the Canadian Journal of Chemistry under the titles:

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I. Dependence on Charge and Radius. Can. J. Chem. 34, 1209 (1956)

II. An Empirical Equation for Oxy-Anions. Can. J. Chem. 35, 207 (1957).

The Entropies of Ions in Aqueous Solution.

II. An Empirical Equation for Oxy-Anions. Can. J. Chem. 35, 202 (1957).

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ABSTRACT

Some methods of obtaining the partial molal entropies of ions are reviewed, and the equations proposed for monatomic ions are discussed. The entropies of oxy-anions in aqueous solution are shown to obey the following relationship

$$S_{\text{abs}}^{\circ} = 40.2 + \frac{3}{2} R \ln m - 27.2 \frac{z^2}{0.25 nr} .$$

In this equation, S_{abs}° is the partial molal entropy relative to a value of -5.5 e.u. for the proton, m is the molecular weight, z the number of charges on the ion, n the number of charge-bearing ligands, and r is equal to $r_{12} + 1.40$, where r_{12} is the interatomic distance between the central atom and the surrounding oxygens, and 1.40 is the van der Waals radius of oxygen. The significance of the empirical equation is discussed.

The density data for aqueous solutions of electrolytes have been analyzed, and the partial molal volumes at infinite dilution have been calculated. The values are shown to be additive, and a set of volumes for individual ions has been prepared, based arbitrarily on a value of zero for the hydrogen ion. It is shown that for a given value of the charge, the volumes vary linearly with the cube of the ionic crystal radii, and that for a given radius, they vary with the first power of the charge. In the case of monatomic cations the equation obeyed is

$$V_{+} = 16 + 4.9 r^3 - 20 z_{+}$$

while for monatomic anions it is

$$V_{-} = 4 + 4.9 r^3 - 20 z_{-} .$$

If the volume of the hydrogen ion is taken as -6.0 ml. instead of zero, the same equation is obeyed for both monatomic cations and anions, namely

$$\bar{V}'_{\pm} = 16 + 4.9 r^3 - 26 |z_{\pm}| .$$

In the case of oxy-anions, the volumes relative to a value of -6.0 ml. for the proton are represented by the equation

$$\bar{V}'_{-} = 58.8 + 0.89 (0.25 nr)^3 - 26 |z_{-}| ,$$

where r , as with entropies, is given by $r_{12} + 1.40$. These empirical equations are explained in terms of a simple model for ions in solution and the significance of the effective radius used for oxy-anions is discussed.

The importance of these equations is discussed with reference to their application to reactions involving ions in aqueous solution.

INTRODUCTION

Although the values for the partial molal entropies of ions in aqueous solution have been known for a few decades, attempts to accurately correlate them as a function of the atomic or molecular weight (m) of the ion, of its charge (z), of its radius (r) and, in the case of complex ions, of the number of ligands (n), are quite recent.

Powell and Latimer (1), by inspection of the data available on ionic entropies, found it possible to write the following general equation for the entropies of aqueous monatomic ions:

$$[1] \quad \bar{S}_{\text{conv}}^{\circ} = \frac{3}{2} R \ln m + 37 - 270 \frac{z}{r_e^2}$$

Here, $\bar{S}_{\text{conv}}^{\circ}$ refers to conventional entropies, i.e. entropies arbitrarily based on a value of zero for the proton, and r_e the effective ionic radius, is the Pauling (2) ionic crystal radius with an added correction of 2 Å in the case of cations, and 1 Å in the case of anions.

A similar expression has been obtained by Cobble (3) for oxygenated anions:

$$[2] \quad \bar{S}_{\text{conv}}^{\circ} = \frac{3}{2} R \ln m + 66 - 81 \frac{z}{\rho}$$

However, in contrast with Equation [1], this equation involves an inverse dependence on the first power of the effective radius ρ , which is related to the interatomic distance (r_{12}) between the central atom and the peripheral oxygens (2) by a suitable structural constant f :

$$\rho = \frac{r_{12}}{f}$$

These structural parameters are obtained by dividing the calculated value of r_{12} by the values of ρ necessary to fit Equation [2].

Using a different approach, Connick and Powell (4) have also developed an empirical expression for the entropies of oxygenated anions. Upon examination of the values of these entropies, they noticed that the entropies are approximately the same for ions of the same charge and the same number of oxygen atoms, but that they become about 46.5 e.u. more negative for each additional negative charge, and about 13.0 e.u. more positive for each additional oxygen surrounding the central atom. Consequently they proposed that the partial molal entropy of an oxy-anion could be fairly well estimated from the empirical relation

$$[3] \quad S_{\text{conv}}^{\circ} = 43.5 - 46.5 (z - 0.28 n)$$

where n is the number of charge-bearing ligands.

The entropies of aqueous complex ions other than oxy-anions have also been studied, and empirical expressions have been proposed by Cobble (5) and by George and co-workers (6), although fewer data are available for these ions.

It must be noted that in all these equations the entropy values are arbitrarily based on a value of zero for the proton. Recently, however, Gurney (7) has proved quite convincingly the entropy of the proton to be -5.5 e.u., and therefore the above relationships, which involve a linear dependence of the entropy on the first power of the charge, and, in certain cases, an inverse dependence on the square of a corrected radius, have no fundamental validity, arising from the choice of arbitrary entropies and from the use of arbitrarily corrected radii.

In a recent paper, Laidler (8) showed that the entropy changes for reactions of various ionic types indicate that the absolute entropy of

ions (related to a value of -5.5 e.u. for the proton) must depend on z^2 . The equation he proposes refers explicitly to monatomic ions:

$$[4] \quad S_{\text{abs}}^{\circ} = 10.2 + \frac{3}{2} R \ln m - 11.6 \frac{z^2}{r_u} .$$

Here, m is the atomic weight of the ion, z the valency, and r_u the univalent radius as defined by Pauling (2). In view of the applicability of an equation involving $\frac{z^2}{r}$ to the entropies of monatomic ions, we have attempted to develop a similar expression for inorganic oxy-anions.

In contrast to partial molal entropies, comparatively little work has been done on partial molal volumes of ions, although these are of some considerable theoretical and practical interest, particularly with reference to the effects of pressure on equilibria and rates. Owen and Brinkley (9) and Fajans and Johnson (10) have collected values for certain ions, and a few others have been quoted from time to time. The significance of these values has occasionally been discussed, but no attempt appears to have been made to analyze the volumes with a view to seeing how they depend on the valence (z) of the ion, the crystal radius (r) and other factors. Our investigation has therefore been concerned with obtaining a more complete and reliable set of values for monatomic ions and oxygenated anions, and showing empirically how the volumes of these ions vary with the charge, the size, and the number of ligands, if any.

SOURCE OF EXPERIMENTAL DATA

I. Partial Molal Entropies

Several methods are available for measuring the standard entropies of ions. One of these is an electrochemical method. If the standard potential of an electrode is known at two or more temperatures, the entropy change can be calculated using

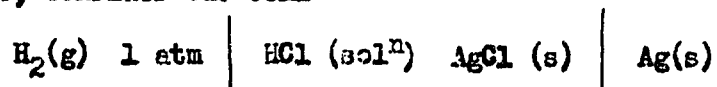
$$\Delta S = n \mathcal{F} \left(\frac{\partial \epsilon}{\partial T} \right)_p$$

which, for a substance in its standard state, takes the form

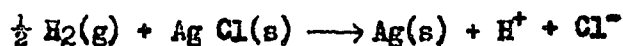
$$[5] \quad \Delta S^\circ = n \mathcal{F} \frac{d\epsilon^\circ}{dT}$$

the constant pressure condition being omitted as unnecessary (since the work is carried out at atmospheric pressure); in Equation [5], n is the number of electrons transferred during the process and \mathcal{F} is the Faraday.

For example, consider the cell



for which the overall reaction is



and the standard entropy change is

$$[6] \quad \Delta S^\circ = S_{\text{H}^+}^\circ + S_{\text{Cl}^-}^\circ + S_{\text{Ag(s)}}^\circ - \frac{1}{2} S_{\text{H}_2(\text{g})}^\circ - S_{\text{AgCl(s)}}^\circ$$

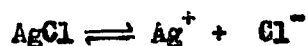
where S_{Ag}° , $S_{\text{H}_2(\text{g})}^\circ$, $S_{\text{AgCl(s)}}^\circ$ can be determined from heat capacity measurements based on the third law of thermodynamics. Since $\frac{d\epsilon^\circ}{dT}$ is known, therefore, upon combining Equations [5] and [6], we obtain the following expression ($n = 1$ in this case):

$$[7] \quad S_{\text{H}^+}^\circ + S_{\text{Cl}^-}^\circ = \mathcal{F} \frac{d\epsilon^\circ}{dT} + \frac{1}{2} S_{\text{H}_2(\text{g})}^\circ + S_{\text{AgCl(s)}}^\circ - S_{\text{Ag(s)}}^\circ$$

which gives the sum of the standard partial molal entropies of the hydrogen

and chloride ions. If, by convention, the entropy of the hydrogen ion is taken as zero, it is possible to calculate the entropy of the chloride ion, and from this, to build a relative scale of standard ionic entropies.

An alternative method of determining partial molal entropies of ions involves the use of solubility data. As an example, consider the solid salt AgCl in equilibrium with its ions in a saturated solution:



In such a reaction, the equilibrium constant is equal to the solubility product, K_s , at a pressure of 1 atmosphere, and hence the standard free energy change is given by

$$[8] \quad \Delta G^\circ = -RT \ln K_s$$

However, before calculating the entropy change, ΔH° is also required.

It is calculated in the following way. The total heat content of the products in their standard states is $H_{\text{Ag}^+}^\circ + H_{\text{Cl}^-}^\circ$ which is equivalent to \bar{H}_2° , the standard partial molal heat content of the solute AgCl in solution; the standard heat content of the reactant, which consists of pure solid AgCl at a pressure of 1 atmosphere, is identical with the molar heat content (H_{AgCl}) of the solid salt. Therefore it is seen that

$$[9] \quad \Delta H^\circ = (H_{\text{Ag}^+}^\circ + H_{\text{Cl}^-}^\circ) - H_{\text{AgCl}}$$

Since \bar{H}_2° is the partial molal heat content of the solute, it follows that ΔH° , in this case, is equal to the differential heat of solution. But the solution in question is a very dilute solution so that the differential heat of solution is equal to the integral heat of solution per mole. Now that ΔG° and ΔH° are known, ΔS° for the process may be calculated from the relation

$$[10] \quad \Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T} = \bar{S}_2^\circ - S_s$$

where \bar{S}_2° is the standard partial molal entropy of the salt in solution

and S_s is the molar entropy of the solid salt. But the standard partial molal entropy of the solute in solution may be taken as the sum of the partial molal entropies of the constituent ions, that is

$$\bar{S}_2^{\circ} = S_{\text{Ag}^+}^{\circ} + S_{\text{Cl}^-}^{\circ},$$

so that

$$[11] \quad S_{\text{Ag}^+}^{\circ} + S_{\text{Cl}^-}^{\circ} = \frac{\Delta H^{\circ} - \Delta G^{\circ}}{T} + S_{\text{AgCl}}$$

Here again, if the standard entropy of either of the ions and that of the solid salt are known, the entropy of the other ion may be calculated. If this is not possible, only a relative scale of ionic entropies can be obtained.

The weakness of these two methods comes from the arbitrary nature of the division of the entropy changes, measurable only for the electrolyte as a whole, into separate ionic values. Gurney (7), by a very ingenious procedure involving the use of the B-coefficients of viscosity, succeeds in obtaining the absolute entropy of the proton and hence, in building an absolute scale of ionic entropies. The B-coefficients of viscosity is a constant which appears in the following equation:

$$[12] \quad \eta = \eta_0 (1 + A \sqrt{c} + Bc)$$

where η is the viscosity of the solution, η_0 the viscosity of the solvent, c the concentration of the solute, and A and B constants characteristic of the solute. This equation states that a solute alters the viscosity of a solvent in two ways: the first effect is due to the electrostatic forces between the ions and is accounted for by the term $A \sqrt{c}$; the second effect, given by the term Bc , represents the contributions from the "co-spheres of the ions" (co-sphere of the ion referring to the little spherical portion of solvent which encloses

the ion and which is somewhat modified by the presence of the ion); in a dilute solution, the solvent between the co-spheres of the ions is unmodified, but the co-spheres of each positive and negative ion contribute to a change in the viscosity. In aqueous solutions, at room temperature, the B-coefficient is positive for the majority of ions; for some, however, it is negative, and for these ions the viscosity is the lowest. But the lower the viscosity, the higher the mobility, in other words, the greater the disorder. Since the entropy of any system is to be regarded as some measure of the degree of disorder, Gurney examined the available data to see whether a decrease in viscosity was in fact accompanied by an increase in entropy, and vice-versa. Figure 1 (a), which is a plot of the B-coefficients of viscosity from Table I against the conventional partial molal entropies from Table II, could hardly be more striking and convincing. It is noticed that the points for the positive ions lie about a straight line while the points for the negative ions lie about a nearly parallel straight line, but, in both cases, the ions with the largest ionic entropies are those with negative B-coefficients of viscosity. In view of the fact that the entropy values of Table II are conventional, i.e. all based on $\bar{S}_{H^+}^{\circ} = 0$, it is not surprising that the points for the positive and the negative ions lie about separate straight lines. If $\bar{S}_{H^+}^{\circ}$ were assigned a value of -5.5 e.u. instead of 0.0 e.u., the value of each positive ion would be diminished by 5.5 e.u. while the value of each negative ion would be increased by the same amount, so that the sum for any ion pair retains the same value, namely the value derived from the experimental data. When these "absolute" ionic entropies (from Table III) are plotted against the B-coefficients of viscosity, the result shown in Figure 1 (b) is obtained. The points for the atomic ions of both signs now lie about a single straight line.

TABLE I

B-coefficients of viscosity
of some simple ions

H ⁺	+ 0.07 ₀
Li ⁺	+ 0.14 ₇
Na ⁺	+ 0.08 ₆
K ⁺	- 0.00 ₇
Cs ⁺	- 0.04 ₅
Ag ⁺	+ 0.09 ₁
NH ₄ ⁺	- 0.00 ₇
Cl ⁻	- 0.00 ₇
Br ⁻	- 0.03 ₂
I ⁻	- 0.08 ₀
OH ⁻	+ 0.12

TABLE II

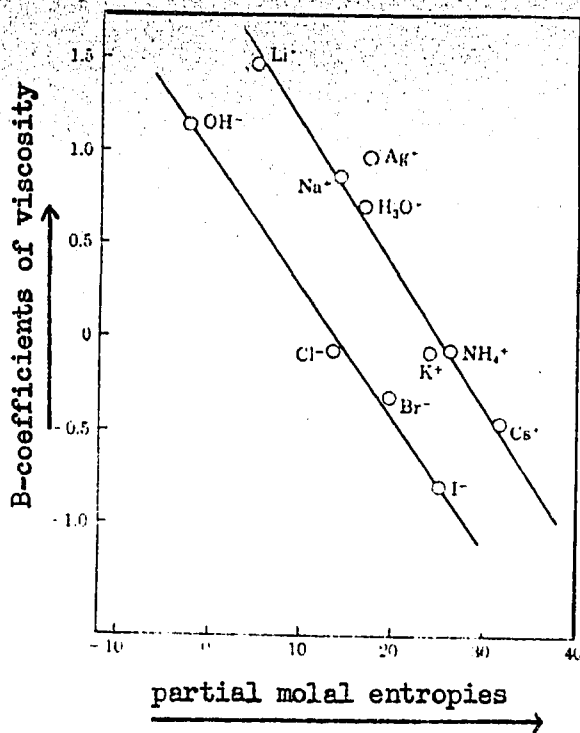
Conventional partial molal entropies
of some simple ions

0.00 e.u.
4.7
14.0
24.2
31.8
17.5
26.4
13.5
19.7
25.3
-2.5

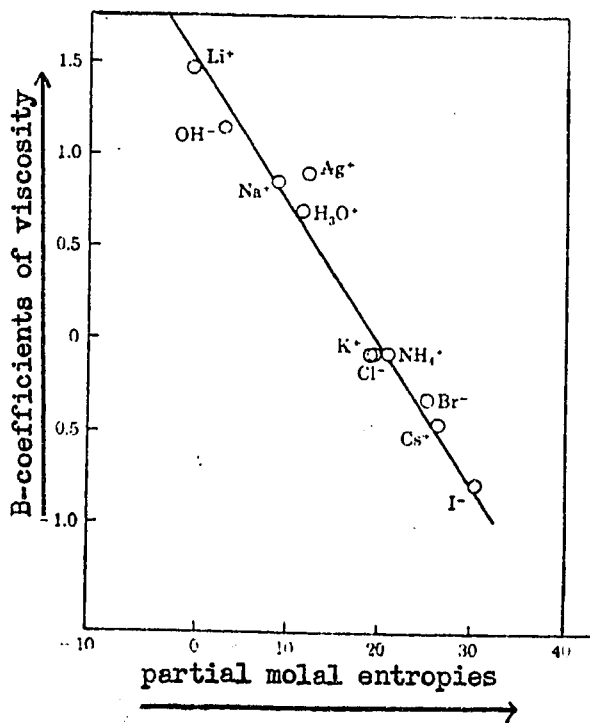
TABLE III

Absolute partial molal entropies
of some simple ions

-5.5 e.u.
-0.8
8.5
18.7
26.3
12.0
20.9
19.0
25.1
30.8
3.0



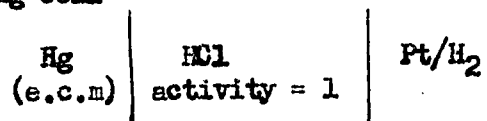
(a) on scale of 0.0 e.u. for $\bar{S}_{H^+}^0$



(b) on scale of -5.5 e.u. for $\bar{S}_{H^+}^0$

Figure 1. Plots of the B-coefficients of viscosity against the partial molal entropies for some simple ions.

It is of interest to note that Lee and Tai (11) have devised a method of determining the absolute entropy of the proton. They studied the following cell



where Hg (e.c.m.), i.e. Hg polarized to capillary maximum, refers to the potential at which the surface tension is maximum and at which there is no voltaic potential at the interface (since there is no net charge at the interface); the potential difference should therefore arise only from $\text{H}^+ \mid \text{H}_2$. From this, the standard partial molal entropy of the proton was found to be - 5.4 e.u., a value which compares very well with that derived by Gurney.

II. Partial Molal Volumes

An accurate and convenient method of evaluating partial molal volumes makes use of apparent molal volumes, which are capable of direct experimental determination. If V is the volume of a mixture consisting of n_1 moles of solvent and n_2 moles of solute ($n_1 > n_2$), then the apparent molal volume, Φ_v , of the solute is given by

$$\Phi_v = \frac{V - n_1 V_1}{n_2}$$

since, of course,

$$[13] \quad V = n_1 V_1 + n_2 \Phi_v$$

Combining this equation with the following equation

$$[14] \quad \bar{v}_2 = \left(\frac{\partial V}{\partial n_2} \right)_{T, P, n_1}$$

which defines the partial molal volume of constituent 2, i.e., the solute, we obtain the expression:

$$[15] \quad \bar{V}_2 = n_2 \left(\frac{\partial \varphi_r}{\partial n_2} \right) + \varphi_r$$

From Equation [15] we see that \bar{V}_2 can be determined by measuring φ_r at various concentrations and extrapolating to zero concentration where it becomes equal to \bar{V}_2 . For ionic solutes, the Debye-Huckel theory predicts (12) that φ_r should vary linearly with the square root of the concentration, and many results have confirmed this relationship (9, 13, 14, 15; see, however, Reference 16); the extrapolation is therefore based on this observation.

The determination of the apparent molal volume at a number of different concentrations is based on density measurements at these concentrations. Consider one litre of pure solvent (of density d_0) to which are added X moles of solute (of molecular weight M_2), thus forming a solution of

$$[16] \quad \begin{array}{ll} \text{volume} & V = (1 + X \varphi_r) \text{ litres,} \\ \text{concentration} & c = \frac{X}{1 + X \varphi_r} \text{ moles/litre,} \\ \text{and density (gm./ml.)} & \end{array}$$

$$[17] \quad d = \frac{1000 d_0 + X M_2}{(1 + X \varphi_r) 1000} .$$

Rearranging Equation [17] and converting φ_r into ml./mole, we get:

$$[18] \quad \varphi_r = \frac{M_2}{d_0} - \frac{1000}{d_0} \left(\frac{d - d_0}{\varepsilon} \right) .$$

There exist extensive data (17)(18) for densities of aqueous solutions of electrolytes, and the apparent partial molal volumes were calculated from such densities using the formula [18]. The procedure to obtain the partial molal volumes at infinite dilution then consisted in plotting these \bar{V}_∞ values against \sqrt{c} and extrapolating to zero \sqrt{c} . The values obtained in this manner are shown in Table IV. This table includes most of the salts for which reliable data are available and which are known to be fully ionized and unhydrolyzed in dilute solutions. Compounds of B, Be, Hg (ic), and Hg (ous), and salts such as FeCl_3 and ThCl_4 , are not included because there is evidence that they are not completely ionized in solution, while the following salts are omitted because there is evidence that they do not ionize to form simple ions: Cd halides, Au halides, and Sn (ous) and Sn (ic) halides. For example, the fact that the cadmium halides do not behave as normal electrolytes is most clearly shown by the fall in the molecular conductivity with increasing concentration as compared with that of normal di-univalent salts such as $\text{Cd}(\text{NO}_3)_2$ and MgCl_2 ; electromotive force measurements indicate that this abnormality is due to the imperfect dissociation of the simple halide, i.e. to the presence of CdX_2 , CdX^+ , and to the formation of the complex anions CdX_3^- and CdX_4^{2-} . No reliable data appear to be available for salts of Tl^{+++} , In^{+++} and Ga^{+++} .

In an extremely dilute solution, there will be a large quantity of solvent that is not near any ion or modified by any ion; in this solution, the co-spheres of the ions will not overlap except in those very rare cases where two ions happen to be near to each other. If the volume of such a solution could be measured, the contributions from the co-spheres of the positive ions would be independent of the

TABLE IV
PARTIAL MOLAL VOLUMES OF IONIC SOLUTES (ml/mole)

Solute	\bar{V}_{solute}	Solute	\bar{V}_{solute}
HCl	18.1*	AgF	-3.1
LiCl	17.1*	AgNO ₃	28.3*
LiBr	24.0*	MgCl ₂	15.3*
LiI	35.6*	CaCl ₂	18.5*
LiOH	-6.3*	SrCl ₂	18.0*
NaCl	16.6*	BaCl ₂	23.9*
NaBr	23.5*	Cd(NO ₃) ₂	38.0*
NaI	35.1*	ZnSO ₄	-7.6
NaOH	-6.8*	Pb(NO ₃) ₂	42.5
Na ₂ SO ₄	11.5*	FeCl ₂	13.8
Na ₂ S	-10.6	FeBr ₂	23.0
KF	6.6*	FeSO ₄	-11.9
KCl	26.8*	CoCl ₂	10.8
KBr	33.7*	CoBr ₂	23.8
KI	45.3*	Co(NO ₃) ₂	30.6
KOH	3.4*	CoSO ₄	-4.2
KNO ₃	38.0*	NiSO ₄	-10.1
K ₂ SO ₄	31.9*	Al(NO ₃) ₃	43.0
RbCl	31.8*	AlCl ₃	12.9
RbBr	38.7*	LaCl ₃	16.0*
RbI	50.3*	Fe(NO ₃) ₃	49.7
CsCl	39.2*	Fe(NO ₃) ₃	36.5 ⁺
CsBr	46.1*	CrCl ₃ (violet)	13.9
CsI	57.7*	ThCl ₄	17.8
TlF	10.5	Th(NO ₃) ₄	62.6

* Quoted by Owen and Brinkley (9)

+ From Landolt-Börnstein (18); all other values from the International Critical Tables (17).

contributions from the co-spheres of the negative ions; in other words, the volumes would be the sums of the contributions for individual ions. The additivity of partial molal volumes of ions is demonstrated in Table V.

On the basis of this property, it is possible to build scales of ionic volumes. Various procedures for splitting the values for salts into ionic contributions have been suggested (10) (19), but since none is above criticism, the arbitrary procedure [also employed by Owen and Brinkley (9)] has been used of taking the value for the proton as zero. Based on this convention, our set of volumes, which confirm Owen and Brinkley's values where they are given, is shown in Table VIII for monatomic ions, and in Table IX for oxy-anions. The values in those tables can readily be converted into values based on another standard; thus, if the volume of the proton is actually X instead of zero, the values for cations will be raised by z_+X , where z_+ is the valence; the values for anions will similarly be lowered by z_-X , where z_- is the absolute value of the valence of the ion (e.g. + 2 in the case of S^{2-}).

TABLE V
ADDITIVITY OF PARTIAL MOLAL VOLUMES OF IONS

	Cl		Br		I
Li	17.1	← 6.9 →	24.0	← 11.6 →	35.6
	↑		↑		↑
	-0.5		-0.5		-0.5
	↓		↓		↓
Na	16.6	← 6.9 →	23.5	← 11.6 →	35.1
	↑		↑		↑
	10.2		10.2		10.2
	↓		↓		↓
K	26.8	6.9	33.7	← 11.6 →	45.3

PARTIAL MOLAL ENTROPIES: EMPIRICAL EQUATIONS

I. Monatomic Ions

Although the equation for the entropies of monatomic ions has been developed by Laidler, part of his paper will here be summarized in some detail since it has an important and direct bearing on the work we did on the partial molal entropies of oxy-anions.

In this paper (8), Laidler discusses the theoretical and experimental evidence pointing to a dependence of entropies on the square of the charge. Born (21), assuming that ions behave like conducting spheres of charge ze (e is the charge on the electron) and radius r , found the electrostatic part of the entropy to be

$$[19] \quad S_{el} = \frac{z^2 e^2}{2rD} \frac{d \ln D}{dT}$$

where D is the dielectric constant. For ions in aqueous solution at 25°C, S_{el} is given by

$$[20] \quad S_{el} = 9.42 \frac{z^2}{r} \text{ e.u.}$$

if the value of r is in Å. The experimental evidence, which also points to a dependence on z^2 is the following. In the reaction



the entropy change, if one neglects, to a rough approximation, size effects, will be related to

$$(Z_C^2 + Z_D^2) - (Z_A^2 + Z_B^2) = z^2$$

if ionic entropies depend on z^2 , but it will be related to

$$(Z_C + Z_D) - (Z_A + Z_B) = z$$

if ionic entropies depend on z . Laidler applied this test to a number of reactions, and his results are shown in Table VI. It is seen that,

TABLE VI
Entropy Changes for Reactions of Various Ionic Types

Reaction	$\sum z$	$\sum z^2$	ΔS (e.u.)
1. $C_6H_5OH + OH^- \rightarrow C_6H_5O^- + H_2O$	0	0	- 8.2
2. $C_6H_5NH_2 + H_3O^+ \rightarrow C_6H_5NH_3^+ + H_2O$	0	0	1.4
3. $2H_2O \rightarrow H_3O^+ + OH^-$	2	2	- 18.7
4. $NH_4OH \rightarrow NH_4^+ + OH^-$	2	2	- 18.9
5. $H_2CO_3 + H_2O \rightarrow H_3O^+ + HCO_3^-$	2	2	- 22.9
6. $HSO_4^- + H_2O \rightarrow H_3O^+ + SO_4^{2-}$	2	4	- 26.3
7. $HCO_3^- + H_2O \rightarrow H_3O^+ + CO_3^{2-}$	2	4	- 35.0
8. $HPO_4^- + H_2O \rightarrow H_3O^+ + PO_4^{3-}$	2	6	- 43.0
9. $UOH^{3+} \rightarrow U^{4+} + OH^-$	2	8	- 52.0
10. $ClO_4^- + 2H^+ + 2Fe^{2+} \rightarrow ClO_3^- + H_2O + 2Fe^{3+}$	0	8	- 73.5
11. $MnO_4^- + 5Fe^{2+} + 8H^+ \rightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$	- 2	20	- 213.6
12. $Cr_2O_7^{2-} + 3Ti^{2+} + 14H^+ \rightarrow 2Cr^{3+} + 3Ti^{3+} + 7H_2O$	-4	24	- 248.6
13. $Cr_2O_7^{2-} + 6Fe^{2+} + 14H^+ \rightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O$	-4	30	- 339.2
14. $2MnO_4^- + 5Ti^{2+} + 16H^+ \rightarrow 2Mn^{2+} + 5Ti^{3+} + 8H_2O$	-4	30	- 359.2

in many cases, prediction of S from z would yield the wrong sign, but that there is a close correlation between S and z^2 (see also Figure 2 which is a plot of S against z^2). Such a correlation over a wide range of reaction types strongly indicates that the ionic entropy is a function of z^2 .

On the basis of these conclusions, Laidler has proposed the following new empirical equation for the entropies of monatomic ions:

$$[4] \quad S_{\text{abs}}^{\circ} = \frac{3}{2} R \ln m + 10.2 - 11.6 \frac{z^2}{r_u}$$

where m is the atomic weight of the ion, z the valency, and r_u the univalent radius given by Pauling (2). A plot of $S_{\text{abs}}^{\circ} - \frac{3}{2} R \ln m$ against $\frac{z^2}{r_u}$ is shown in Figure 3; the mean deviation here is 4.8 e.u.

The first two terms of Equation [4] make up the non-electrostatic part of the entropy and correspond to the free motion of ions in a free volume of 0.73 \AA^3 ; the last term represents the electrostatic part of the entropy and is consistent with Equation [20] which is based on Born's electrostatic model for ions in solution, although the coefficient is slightly but significantly different from that predicted by the Born equation. This is discussed in more detail in a later paper by Laidler and Pegis (21), who developed a higher approximation treatment than that obtained from the simple Born model, by the application of the theories of the dielectric constant of water and of its variation with field strength to the case of monatomic ions in aqueous solution.

II. Oxy-anions

The Data

The conventional partial molal entropies of a number of oxy-anions (22), based on a value of zero for the proton, are shown in the second

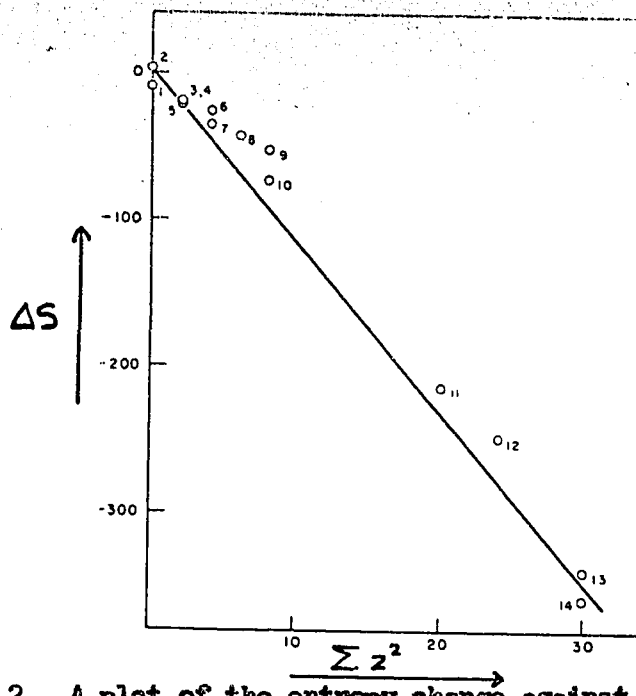


Figure 2. A plot of the entropy change against $\sum z^2$ for reactions of various ionic types. The numbers refer to the reactions listed in Table VI.

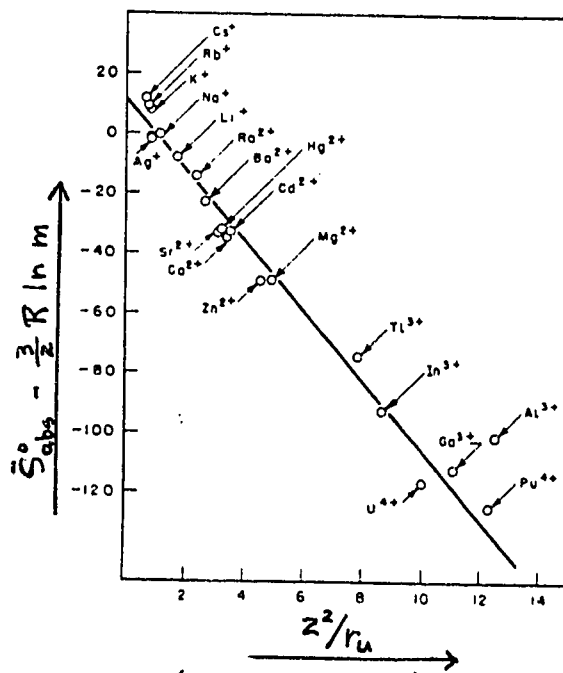


Figure 3. A plot of $(S^{\circ}_{\text{abs}} - \frac{3}{2} R \ln m)$ against $\left(\frac{z^2}{r_u}\right)$.

column of Table VII. These have been converted into absolute entropies by the addition of $5.5 |z_-|$, where $|z_-|$ is the number of negative charges on the ion, and the results are shown in the third column.

Also shown in the table are the values of r_{12} , the distance between the center of the central atom and the center of the surrounding oxygen atoms; these values have been derived from Pauling's covalent radii (2). The fourth column of Table VII shows the values of $r_{12} + 1.40$; since 1.40 \AA is the van der Waals radius of oxygen, the distance $r_{12} + 1.40$ represents the radius of a sphere that completely circumscribes the anion.

An Empirical Equation

An inspection of Table VII reveals that the entropy decreases as the charge increases, but increases as the interatomic distance and the number of charge-bearing ligands increase. Further examination shows that the entropy shows a dependence on z^2/r , where $r = r_{12} + 1.40$. Figure 4 shows a plot of $\bar{S}^{\circ}_{\text{abs}}$ against z^2/r , and it is seen that the points are grouped according to the number of charge-bearing ligands, n . There is no grouping in terms of the total number of ligands.

Since it is the number of charge-bearing ligands that is important, it follows that the distribution of charges plays an important role. An attempt was made to correlate the entropies with dipole moments as well as with z^2 , but this proved unsuccessful. One can only make estimates of the dipole moments of ions, but one knows that the moments for certain symmetrical ions (e.g. SO_4^{--} , PO_4^{--} , NO_3^-) must be zero. Even for these ions of zero moment there is still a grouping with respect to the number of charge-bearing ligands. More is therefore involved than the dipole moment.

TABLE VII

CONVENTIONAL AND ABSOLUTE ENTROPIES OF OXY-ANIONS

Ion	\bar{S}^0_{conv} (e.u.)	\bar{S}^0_{abs} (e.u.)	Interatomic distance (r_{12}) (Å)	r (Å)	\bar{S}^0_{abs} $-(3/2)R \ln m$	$0.25 nr$	$\frac{z^2}{0.25nr}$
ClO^-	10.0	15.5	1.70	3.10	3.8	0.77	1.30
NO_2^-	29.9	35.4	1.24	2.64	24.0	1.32	0.76
BO_2^-	20	25.5	1.37	2.77	14.3	1.38	0.72
ClO_2^-	24.1	29.6	1.52	2.92	17.1	1.46	0.68
AlO_2^-	25	30.5	1.54	2.94	18.4	1.47	0.68
HCO_3^-	22.7	28.2	1.26	2.66	16.0	1.33	0.75
HSO_3^-	26	31.5	1.39	2.79	18.4	1.39	0.72
HSeO_3^-	30.4	35.9	1.63	3.03	21.5	1.51	0.66
H_2PO_4^-	21.3	26.8	1.55	2.95	13.2	1.47	0.68
H_2AsO_4^-	28	33.5	1.75	3.15	18.8	1.57	0.64
NO_3^-	35.0	40.5	1.24	2.64	28.2	1.98	0.50
ClO_3^-	39.0	44.5	1.48	2.88	31.3	2.16	0.46
BrO_3^-	38.5	44.0	1.68	3.08	29.6	2.38	0.43
HSO_4^-	30.3	35.8	1.50	2.90	22.2	2.17	0.46
ClO_4^-	43.2	48.7	1.52	2.92	35.0	2.92	0.34
MnO_4^-	45.4	50.9	1.69	3.09	36.7	3.09	0.32
ReO_4^-	50	55.5	1.90	3.30	39.1	3.30	0.30
CO_3^{--}	-12.7	-1.7	1.26	2.66	-13.9	1.99	2.01
SO_3^{--}	-7	4.0	1.39	2.79	-9.1	2.09	1.91
SeO_3^{--}	3.9	14.9	1.70	3.10	0.5	2.32	1.72
HPO_4^{--}	-8.6	2.4	1.55	2.95	-11.2	2.21	1.81
HASO_4^{--}	0.9	11.9	1.75	3.15	-2.8	2.36	1.69
SO_4^{--}	4.1	15.1	1.50	2.90	1.5	2.90	1.38
SeO_4^{--}	5.7	16.7	1.65	3.05	1.9	3.05	1.31
CrO_4^{--}	9.2	20.2	1.60	3.00	6.1	3.00	1.33
MoO_4^{--}	14	25.0	1.83	3.23	9.9	3.23	1.24
WO_4^{--}	15	26.0	1.95	3.35	9.6	3.35	1.19
PO_4^{---}	-52.0	-35.5	1.55	2.95	-49.1	2.95	3.06
AsO_4^{---}	-34.6	-18.1	1.75	3.15	-32.8	3.15	2.86

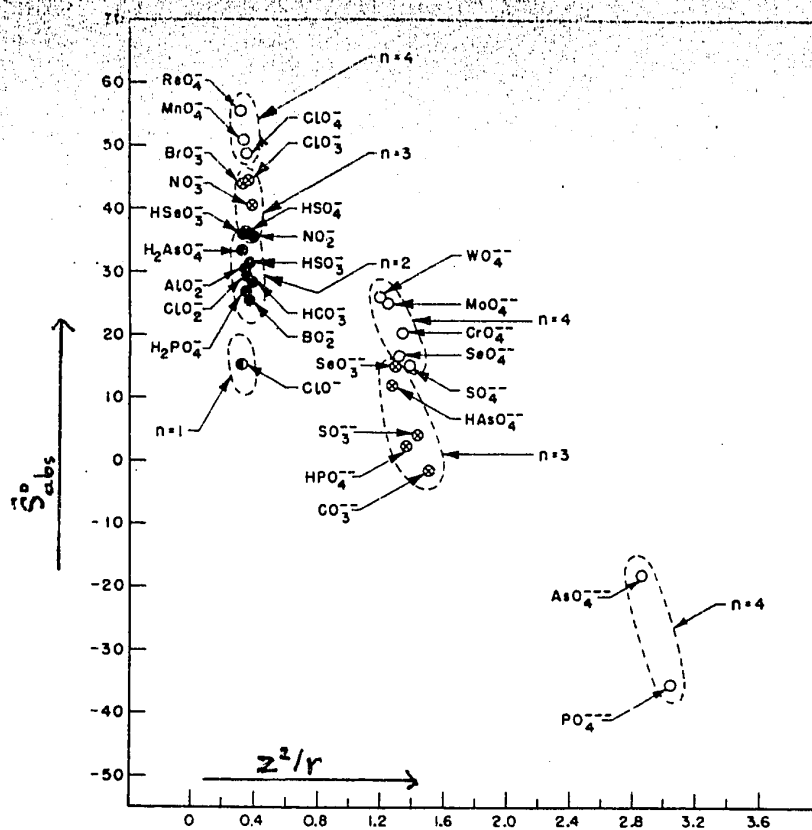


Figure 4. A plot of \bar{S}_{abs}^0 against z^2/r , where $r = r_{12} + 1.40$. The points are seen to be grouped according to the number of charge-bearing ligands, n .

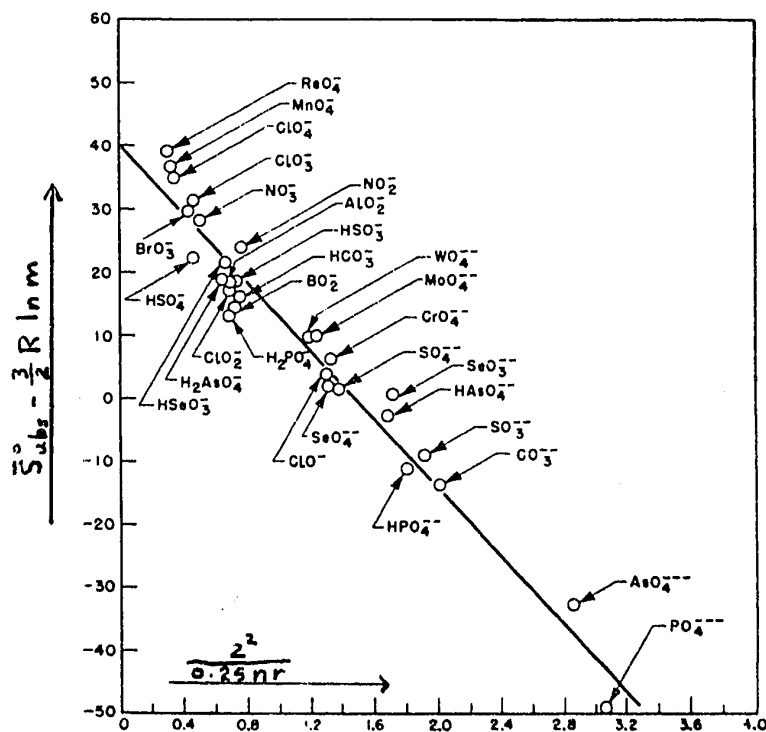


Figure 5. A plot of $(\bar{S}_{abs}^0 - \frac{3}{2} R \ln m)$ against $\frac{z^2}{0.25 nr}$.

The groups corresponding to the different values of n can be brought together if the effective radius r ($r = r_{12} + 1.40$) is multiplied by n ; in other words, if the entropies are plotted against z^2/rn . As with the monatomic ions, the correlation is improved if one subtracts from the entropies the quantity $\frac{3}{2} R \ln m$, where m is the molecular weight. This term is related to the non-electrostatic contribution to the entropy. Values of $(\bar{S}_{\text{abs}}^{\circ} - \frac{3}{2} R \ln m)$ are shown in Table VII, and are plotted against $\frac{z^2}{0.25 nr}$ (also listed in Table VII) in Figure 5. The use of $\frac{z^2}{0.25 nr}$ instead of z^2/mr is purely a matter of convenience. For ions like SO_4^{--} , for which n is 4, $\frac{z^2}{0.25 nr}$ becomes z^2/r , while r is correspondingly reduced for values of n of less than 4.

The points in Figure 5 are seen to lie close to a straight line. By the method of least squares the equation of the line was found to be

$$[21] \quad \bar{S}_{\text{abs}}^{\circ} = 40.2 + \frac{3}{2} R \ln m - 7.2 \left(\frac{z^2}{0.25 nr} \right)$$

with a mean deviation of 3.6 e.u.

The use of r_{12} in place of r was also investigated, but the correlation was then not quite as satisfactory.

Discussion

Equation [21] is seen to be of the same general form as Equation [4], which was obtained for monatomic ions. It again consists of a non-electrostatic part $(40.2 + \frac{3}{2} R \ln m)$ and an electrostatic part, the final term. The correlation is again with z^2 rather than with z .

The relationships expressed in Equation [21] may be explained on the basis of a very simple model. The ions with four charge-bearing ligands may conveniently be regarded as standard, and for them $0.25 nr$ represents the radius of the circumscribing sphere. If, for example,

n is 2, the radius appearing in the denominator, $0.25nr$, is one half the radius of the circumscribing sphere; the behavior of such an ion (as far as entropy is concerned) is therefore equivalent to that of an ion having half the radius of the circumscribing sphere. This is not surprising, since for such an ion the water molecules have much more access to the charge-bearing centers.

The fact that it is the number of charge-bearing ligands that counts, and not the total number of ligands, is of some special interest and significance. As far as the electrostatic contribution to the entropy is concerned it is evidently only the total charge and the distribution of charges that are important. For the ions under consideration a non-charge-bearing ligand can be only an OH group, and the empirical equation implies that the presence or absence of an OH group is immaterial as far as entropy is concerned. That this is really the case from the experimental point of view is revealed by an inspection of Figures 4 and 5 in which it may be seen, for example, that the ions $H_2AsO_4^-$, HSO_3^- , and ClO_2^- , with very similar z^2/r values, have almost identical entropies; this is so in spite of the fact that the ions contain 2, 1, and 0 non-charge-bearing ligands (OH) respectively. These OH groups will, of course, behave very much like the OH groups in the surrounding water molecules. It is true that they should contribute some non-electrostatic entropy, but such a contribution is very small and is partly taken into account in the $\frac{3}{2} R \ln n$ term.

PARTIAL MOLAL VOLUMES, EMPIRICAL EQUATIONS

I. Monatomic Ions.

Dependence on Charge and Radius.

In Table VIII is listed a set of partial molal volumes of monatomic ions; these values have been obtained from the partial molal volumes of ionic solutes given in Table IV. Table VIII also includes the crystal radius of the ions, as given by Goldschmidt (23). It is obvious from an inspection of this table that the charge on the ion has an important effect on its partial molal volume. For a given radius, each unit of charge lowers the volume by approximately 20 ml. In order to elucidate the effects of charge and radius the procedure was to determine the effect of radius for groups of constant charge, and then to study the charge effect separately. The monatomic cations present the most complete set of data, and it was found by trial that the volumes of these vary linearly with the cube of the crystal radii, the slope of the plot of \bar{V}_+ against r^3 being 4.9. The same relationship was found to apply to the other classes of ions.

In order to determine the dependence on z the values of $\bar{V}_+ - 4.9 r^3$ were plotted against z . The result, shown in Figure 6, demonstrates clearly that \bar{V}_+ varies linearly with z . The intercept is 16 ml. and the slope -20, so that the empirical equation suggested by the results is

$$[22] \quad \bar{V}_+ = 16 + 4.9 r^3 - 20 z_+ .$$

A similar plot for the anions is shown in Figure 7. Here the data are less extensive (there is only one point for $|z_-| = 2$) but the values are consistent with the same slope of -20, which leads to an

TABLE VIII
PARTIAL MOLAL VOLUMES OF MONATOMIC IONS

$$(\bar{v}_{H^+} = 0)$$

Ion	$r(\text{\AA})$	$\bar{v}_{ion} \left(\frac{\text{ml}}{\text{mole}} \right)$	Remarks
Li^+	0.78	-1.0	From Owen and Brinkley (9)
Na^+	0.98	-1.5	" "
K^+	1.33	8.7	" "
Rb^+	1.49	13.7	" "
Cs^+	1.65	21.1	" "
Ag^+	1.13	-1.0	" "
Tl^+	1.49	14.7	From TLF
H_3O^+	1.70	18.0	From Owen and Brinkley (9)
Mg^{++}	0.78	-20.9	" "
Ca^{++}	1.06	-17.7	" "
Sr^{++}	1.27	-18.2	" "
Ba^{++}	1.43	-12.3	" "
Cd^{++}	1.03	-20.6	From $\text{Cd}(\text{NO}_3)_2$
Pb^{++}	1.32	-16.1	From $\text{Pb}(\text{NO}_3)_2$
Zn^{++}	0.83	-22.1	From ZnSO_4
Fe^{++}	0.83	-25.3	Average from $\text{FeCl}_2, \text{FeBr}_2, \text{FeSO}_4$
Co^{++}	0.82	-24.6	Average from $\text{CoCl}_2, \text{CoBr}_2, \text{Co}(\text{NO}_3)_2, \text{CoSO}_4$
Ni^{++}	0.78	-24.6	From NiSO_4
Mn^{++}	0.80	-18.3	From MnBr_2
Al^{+++}	0.83	-43.1	Average from AlCl_3 and $\text{Al}(\text{NO}_3)_3$
La^{+++}	1.22	-38.3	From LaCl_3
Fe^{+++}	0.67	-44.6	From $\text{Fe}(\text{NO}_3)_3$ -average of (17) and (18)
Cr^{+++}	0.65	-40.4	From CrCl_3 (violet)
Th^{++++}	1.10	-54.6	From ThCl_4 and $\text{Th}(\text{NO}_3)_4$
OH^-	1.40	-5.3	From Owen and Brinkley (9)
F^-	1.33	-2.1	" "
Cl^-	1.81	18.1	" "
Br^-	1.96	25.0	" "
I^-	2.20	36.6	" "
S^{--}	1.84	-7.6	From Na_2S

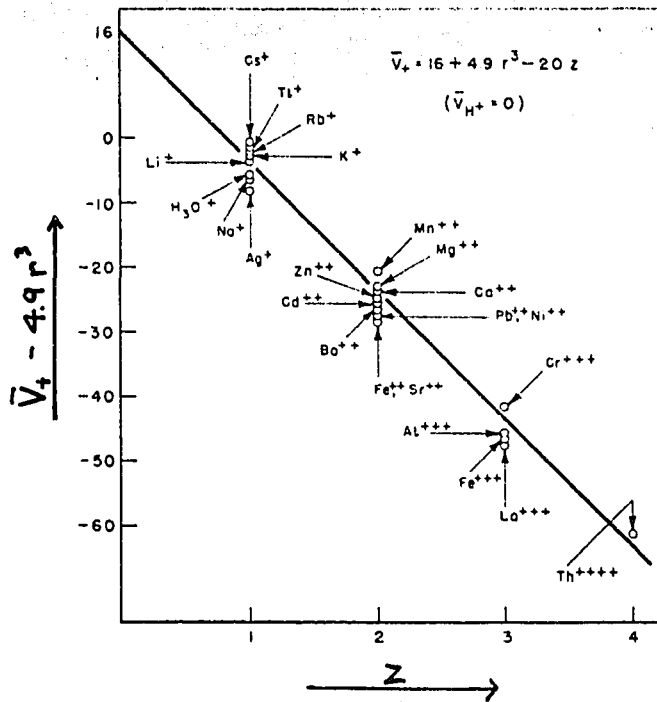


Figure 6. A plot of $(\bar{V}_+ - 4.9 r^3)$ against z for monatomic cations.

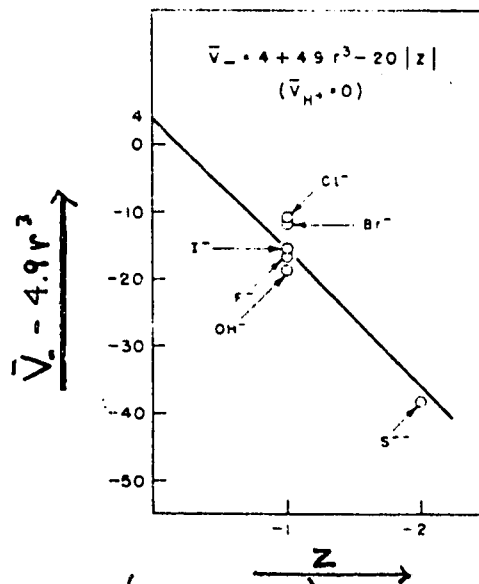


Figure 7. A plot of $(\bar{V}_- - 4.9 r^3)$ against z for monatomic anions.

intercept of 4. The empirical relationship obtained is thus

$$[23] \quad \bar{V}_- = 4 + 4.9 r^3 - 20 |z_-| .$$

The applicability of these relationships is further demonstrated in Figures 8 and 9, which show plots of $\bar{V} + 20 |z|$ against r^3 . The linearity observed is quite satisfactory, the mean deviation of the volumes being 2.4 ml. in the case of the cations and 2.7 ml. in the case of the anions. Such deviations may be explained in part by errors in the volumes (as high as 5 ml. in the case of some of the polyvalent ions), and perhaps more importantly in terms of errors in the crystal radii. These latter errors are of course highly magnified by cubing the radii. There are quite serious discrepancies between the crystal radii listed by Goldschmidt (23) and by Pauling (2), notably in the case of lithium for which the values are 0.78 Å and 0.60 Å respectively. In the present work the Goldschmidt values were found to give better correlations, and have therefore been used. In similar work on entropies (8), the univalent radii were found to give the best correlations, and there was little to choose between the Goldschmidt and Pauling values, presumably because $\frac{1}{r}$ was involved instead of r^3 .

The empirical equations for cations and anions are seen to differ only in the constant term. This, however, is only a reflection of the arbitrariness in the choice of zero as the value for the proton. The two equations can be brought together if the values for all of the univalent cations are lowered by $\frac{1}{2} (16-4) = 6$ ml., and those for the univalent anions are raised by the same amount.

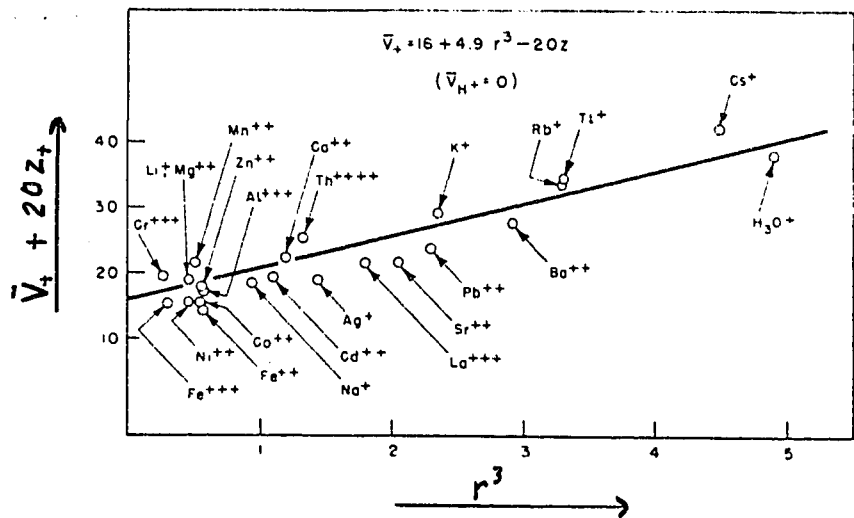


Figure 8. A plot of $(\bar{V}_+ + 20 z_+)$ against r^3 for monatomic cations.

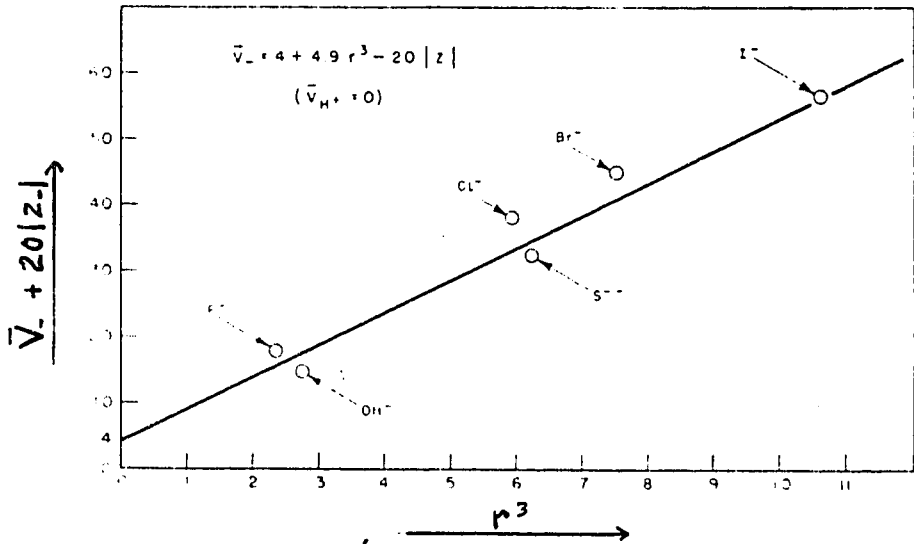


Figure 9. A plot of $(\bar{V}_- + 20 |z_-|)$ against r^3 for monatomic anions.

This means that the new standard is $\bar{V}_{H^+} = -6$ ml., and accordingly the values must be lowered for all cations by $6 z_+$ and raised for all anions by $6 |z_-|$. If we define a new partial molal volume by $\bar{V}_+^1 = \bar{V}_+ - 6 z_+$, equation [22] is transformed into

$$[24] \quad \bar{V}_+^1 = 16 + 4.9 r^3 - 26 z_+.$$

A similar procedure converts equation [23] into

$$[25] \quad \bar{V}_-^1 = 4 + 4.9 r^3 - 14 |z_-|.$$

These equations are not in general identical, but become so for the particular case of $|z_-| = 1$. There is actually only one ion (S^{--}) for which $|z_-|$ is other than unity, so that with the exception of this case we may well apply the general equation

$$[26] \quad \bar{V}_\pm^1 = 16 + 4.9 r^3 - 26 |z_\pm|$$

to both cations and anions. Figure 10 shows a plot of $(\bar{V}_\pm^1 + 26 |z_\pm|)$ against r^3 . The correlation is satisfactory, and even the point for S^{--} is not too badly off the line. The mean deviation in this case is 2.7 ml.

Discussion

The physical significance of the empirical equations that have been developed is not hard to understand. The volume occupied by an ion in aqueous solution may be considered to be made up of two terms: (1) a term related to the intrinsic volume of the ion itself, and (2) a term related to the electrostriction of water molecules in the neighborhood of the ion. On the simplest view the first of these terms would simply be $\frac{4}{3} \pi r^3$, which works out to be $2.5r^3$ ml. per mole, where r is expressed in angstroms. The item that actually

appears in the equation is $4.9 r^3$, the numerical factor being approximately twice as great. The difference may be due to several causes. In the first place, the crystal radii are significantly smaller than the true radii owing to the distortion of the electronic orbitals in the crystal; if it is supposed, however, that the ionic radii in solution are 25% larger than in the crystal, the two terms correspond. Secondly, as indicated by the analysis of the entropies of ions (8), there is a free volume (of about 0.7 \AA^3) associated with the ions in solution, and this must be added to the apparent volumes. These two factors seem to be quite sufficient to account for the apparent discrepancy between the coefficients of r^3 .

In this connection, it is of interest to note that Lee (24), on the basis of the partial molal volumes of uni-univalent electrolytes in aqueous solution, has proposed the equation

$$[27] \quad V = 1.87 (V_+ + V_-) - 20.7$$

where V_+ and V_- are the volumes of the ions in the crystals.

Our equations [22] and [23] lead to

$$[28] \quad V = \bar{V}_+ + \bar{V}_- = 20 + 4.9 (r_+^3 + r_-^3) - 20(z_+ + |z_-|).$$

For the special case of a uni-univalent electrolyte this equation becomes, with $V_+ = 2.5 r_+^3$ and $V_- = 2.5 r_-^3$,

$$[29] \quad V = 1.96 (V_+ + V_-) - 20.$$

This equation closely resembles that of Lee.

It may be noted in conclusion that the present treatment makes no explicit reference to ionic hydration. The electrostriction terms in the empirical equations do in a sense cover the effects of hydration, but in our view the concept of ionic hydration has not proved to be a particularly useful one. The electrical field in the neighborhood of an ion falls continuously with increasing distance,

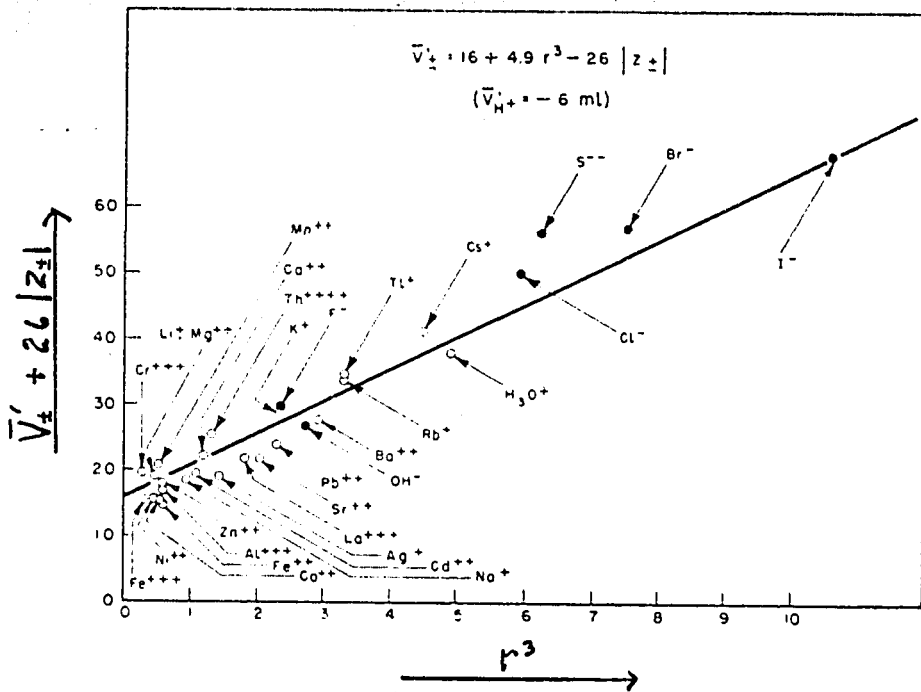


Figure 10. A plot of $(\bar{V}_z + 26 |z_{\pm}|)$ against r^3 for both monatomic cations and anions.

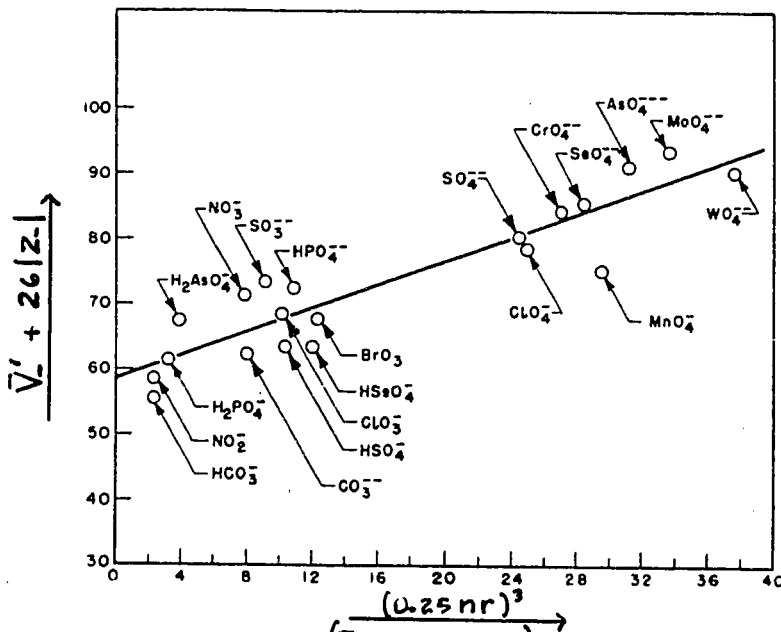


Figure 11. A plot of $(\bar{V}_z + 26 |z_{\pm}|)$ against $(0.25 nr)^3$.

and it is therefore arbitrary to regard some of the water molecules as associated with the ion and others not. It is no doubt for this reason that different methods of measuring ionic hydration numbers lead to such widely different results.

II. Oxy-anions

Empirical Equation

Since the equation correlating the partial molal volumes of all monatomic cations and anions,

$$[26] \quad \bar{V}'_{\pm} = 16 + 4.9 r^3 - 26 |z_{\pm}|,$$

is made up of two parts, one related to the intrinsic volume of the ion and the other to the electrostriction of the water molecules surrounding the ion, an equation representing the volumes of the oxy-anions should also consist of the same two terms.

These volumes, both on the scale of $\bar{V}'_{H^+} = 0$ and $\bar{V}'_{H^+} = -6.0$ ml, are listed in Table IX; they have been calculated from density data (17) and agree with the few values given by Owen and Brinkley (9). The problem with oxy-anions is to define a suitable effective radius and to elucidate the effect of charge-bearing ligands. Since the use of $0.25nr$ [where n is the number of charge-bearing ligands and r the sum of the Pauling (2) interatomic distance, r_{12} , and the van der Waals radius of the oxygen atom] was very suitable in the case of entropies (8), we have attempted to employ it here as an effective radius. These values of $0.25nr$ are also included in Table IX. From the study of the variation of the volumes with the cube of this radius and with the charge, we arrived at the following equation for the volume related to the value of -6.0 ml. for the protons:

TABLE IX

PARTIAL MOLAL VOLUMES AND EFFECTIVE RADII OF OXY-ANIONS

Ion	\bar{V} conv	\bar{V}'	r_{12}	0.25m	Source of \bar{V} conv
NO_2^-	26.5	32.5	1.24	1.32	NaNO_2 and KNO_2
H_2PO_4^-	29.4	35.4	1.55	1.47	NaH_2PO_4 and KH_2PO_4
H_2AsO_4^-	35.5	41.5	1.75	1.57	NaH_2AsO_4
HCO_3^-	23.5	29.5	1.26	1.33	NaHCO_3 , KHCO_3 and (9)
ClO_3^-	36.4	42.4	1.48	2.16	LiClO_3 , NaClO_3 , KClO_3 , and (9)
BrO_3^-	35.6	41.6	1.68	2.38	NaBrO_3 , KBrO_3 , and (9)
HSO_4^-	31.4	37.4	1.50	2.17	NaHSO_4 , KHSO_4 , H_2SO_4 and (9)
HSeO_4^-	31.4	37.4	1.65	2.29	H_2SeO_4
NO_3^-	29.3	35.3	1.24	1.98	HNO_3 , KNO_3 , and (9)
SO_3^{--}	9.5	21.5	1.39	2.09	Na_2SO_3 and K_2SO_3
HPO_4^{--}	8.3	20.3	1.55	2.21	Na_2HPO_4
CO_3^{--}	-1.7	10.3	1.26	1.99	Na_2CO_3 , K_2CO_3 and (9)
ClO_4^-	46.4	52.4	1.52	2.92	HClO_4 , NaClO_4 , and NH_4ClO_4
MnO_4^-	43.2	49.2	1.69	3.09	KMnO_4 and (9)
SO_4^{--}	16.4	28.4	1.50	2.90	Li_2SO_4 , K_2SO_4 , $(\text{NH}_4)_2\text{SO}_4$ and (9)
SeO_4^{--}	21.5	33.5	1.65	3.05	Na_2SeO_4 and K_2SeO_4
CrO_4^{--}	20.3	32.3	1.60	3.00	Li_2CrO_4 , Na_2CrO_4 , K_2CrO_4 and (9)
MoO_4^{--}	29.5	41.5	1.83	3.23	Na_2MoO_4 and K_2MoO_4
WO_4^{--}	26.3	38.3	1.95	3.35	Na_2WO_4 and K_2WO_4
AsO_4^{--}	-14.9	3.1	1.75	3.15	Na_3AsO_4

$$[30] \quad \bar{V}_1 = 58.8 + 0.89(0.25nr)^3 - 26|z_-| .$$

A plot of $(\bar{V}_1 + 26|z_-|)$ versus $(0.25nr)^3$ appears in Figure 11 and the mean deviation in the volume is 3.5 ml. The corresponding equation for \bar{V}_- (related to zero for the proton) is

$$[31] \quad \bar{V}_- = 58.8 + 0.89 (0.25nr)^3 - 32|z_-| .$$

Discussion

Although the radius ($r = r_{12} + 1.40$) is corrected empirically to take into account the effect of the charge-bearing ligands, the effective radius thus obtained is easily visualized. The ion with four charge-bearing ligands is taken as the standard and its effective radius is r . As the number of charge-bearing ligands decreases the effective radius is reduced in the same proportion; hence

$$r_e = \frac{3}{4}r \text{ if } n = 3,$$

$$r_e = \frac{1}{2}r \text{ if } n = 2,$$

$$r_e = \frac{1}{4}r \text{ if } n = 1.$$

The ligands ($-OH$) which cannot have a charge are discarded as they make no more contribution to the volume than if they belonged to the water molecules surrounding the ion.

An effective radius may be calculated by considering only the volumes of the atoms involved, i.e.

$$[32] \quad r_{\text{calc}} = \sqrt[3]{r_{\text{covalent}}^3 (\text{central atom}) + n(1.40)^3}$$

(where 1.40 Å is the van der Waals radius of O). If this r_{calc} and the r_e obtained empirically are compared, they are found to agree very closely for $n = 3$; r_{calc} is smaller than r_e when $n = 4$ but is larger when $n = 2$ or 1. These differences arise in part from the

uncertainty in the radii of the atoms combined to form oxy-anions owing to a certain amount of interpretation. Moreover, depending on the number of atoms involved, there is some dead space unavailable to water molecules, and this dead space is included in r_0 but not in r_{calc} .

It is interesting to note that the coefficient of $|z|$ is the same in Equation [30] as in Equation [26]. The $|z|$ term is related in both cases to the electrostriction of the water molecules in the neighborhood of the ion, and the fact that two empirical equations, obtained independently for two types of ions, agree in the coefficient of this term is very probably more than a coincidence: it is an indication that the scale on which the volumes are based is an absolute scale and hence that -6.0 ml. is the true partial molal volume of the proton. On the scale where $\bar{V}_{H^+} = 0$, the coefficient of $|z|$ is -20 for monatomic cations but -32 for oxy-anions. The coefficient of $|z|$ for the monatomic anions should also be -32, which it is not (it is -20). However, it must be pointed out that all the monatomic anions are univalent with the exception of S^{2-} , so that the accuracy of the slope in a plot of $(\bar{V}_- - 4.9r^3)$ against z depends solely on the accuracy of the volume of the volume of S^{2-} ; if it were not for S^{2-} the slope, which is the coefficient of $|z|$, could have any value. There are several reasons for doubting the accuracy of $\bar{V}_{S^{2-}}$: (1) it is derived from the partial molal volume of only one solute, Na_2S ; (2) if an attempt is made to bring together monatomic cations and anions, S^{2-} does not agree with the general equation, thus leading to the conclusion that this equation applies only to monatomic cations and univalent monatomic anions; (3) the equation

for oxy-anions points to a dependence on $-26 |z_-|$ for \bar{V}' and on $-32 |z_-|$ for \bar{V} , and all monatomic anions except S^- can be made to fit such a dependence. The evidence thus points to -6.0 ml. as the absolute volume of the proton.

The coefficients of r^3 do not correspond, but this was not expected since the two r 's are different, one being the crystal radius, and the other being derived empirically.

III. Other Equations

Very recently, there appeared a paper (25) also concerned with the problem of ionic volumes for its own sake. The author, I. G. Hepler, proposes, for monatomic ions, the following equation:

$$[33] \quad \bar{V}_{ion} = Ar^3 - B \frac{z^2}{r}$$

according to which the volume consists of two terms. The first term, a positive contribution to the ionic volume, is proportional to the cube of the crystal radius of the ion and represents the volume of the spherical cavity, in the water, containing the ion; the constant A has been evaluated as 5.3 for cations and 4.6 for anions. The second term is the decrease in volume caused by electrostriction, i.e. by compression of the solvent molecules around the ions; here again, the constant B was found to have a different value for cations and anions: 4.7 in the first case and 19 in the second.

Although the difference in the B constants for cations and anions can be understood, - since it is possible for anions to interact with the water molecules by the formation of hydrogen bonds, - the difference in the A constants is not so easily seen. It must

be pointed out that the average of Hepler's A values is very near to 4.9, which is the coefficient for r^3 in our equation [26].

From the figures inserted in (25), it would seem that Equation [33] approximates very closely the accepted values for the ionic volumes. However, these plots are rather misleading since they involve, for example, $\frac{\bar{V}_{ion}}{r^3}$ as abscissa. If we plot $(\bar{V}_{ion} - Ar^3)$ against $\frac{z^2}{r}$, we find that the correlation, except for anions, is in fact not quite as good as the other plots suggested: the average deviation from the straight line is about 6 ml. With our equation, this deviation was less than 3 ml.

Hepler's equation has the advantage of being the result of a theoretical derivation and of containing only two parameters, in comparison with three in our equation. However, our equation fits the data much better than his. Furthermore, a least squares analysis of the following equation

$$[34] \quad \bar{V} = Ar^3 + B \frac{z^2}{r} + C \frac{z}{r} + Dz$$

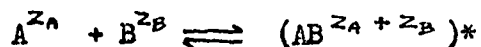
gives

$$A = 8.40; B = 0.40; C = 9.21; D = -21.07,$$

the average deviation in \bar{V} being slightly less than 3 ml. This simply indicates that, empirically, the volumes depend very little on a term involving $\frac{z^2}{r}$.

GENERAL DISCUSSION

It is of interest to note that the ionic entropies depend on z^2 while the volumes depend on z . In view of this fact, the entropies and volumes of activation, which are the entropy and the volume changes referring to the activation process



are expected to depend on Δz^2 and Δz respectively.

For the entropies of activation (ΔS^*), Δz^2 is seen to be equal to $2 z_A z_B$. However, a kinetic analysis (26) of a reaction between ions in aqueous solution shows that ΔS^* should be given by the approximate relationship

$$[35] \Delta S^* = -10 z_A z_B$$

which has been verified experimentally (26). Equation [35] therefore provides further evidence in favour of a dependence of entropies on the square of the charge.

The volume of activation (ΔV^*) is expected to be small if the ions are of the same sign (Δz being zero in this case); but if the reacting ions are of opposite sign, a positive volume of activation is expected since Δz is negative; while a negative ΔV^* is expected when neutral molecules form an activated complex in which there is a separation of charges (since Δz is positive). Such a behaviour has also been verified experimentally (27).

In other words, the entropies and volumes of activation can be explained on the basis of the electrostriction theory. If, in the course of the activation process, there is an intensification of

the electrical field (as when ions of the same sign come together, or when neutral molecules unite to form a polar substance), there will be an increase in the binding of solvent molecules, and hence a negative ΔS^* and ΔV^* . On the other hand, if the electrical field is weakened during the activation reaction (as when two ions of opposite sign come together), there will be a release of bound water molecules and, as a result, ΔS^* and ΔV^* will be positive.

Partial molal volumes are also of interest with reference to the effects of pressure on equilibrium constants and on reaction rates (28, 29), since these effects depend respectively upon over-all volume changes (ΔV) and upon volumes of activation (ΔV^*). From the following equations, derived by van't Hoff (30),

$$[36] \left(\frac{\partial \ln k}{\partial p} \right)_T = - \frac{\Delta V}{RT}$$

and

$$[37] \left(\frac{\partial \ln k}{\partial p} \right)_T = - \frac{\Delta V^*}{RT} ,$$

it is seen that the problem of understanding pressure effects on equilibria and rates reduces to one of understanding the volume changes that occur in the over-all reaction or in the activated process.

CLAIMS TO ORIGINAL RESEARCH

1. The partial molal entropies of the inorganic oxy-anions have been analyzed from the point of view of the factors on which they depend.
2. An equation correlating the entropies of these oxy-anions has been found.
3. A reliable set of partial molal volumes for the monatomic cations and anions and the inorganic oxy-anions has been obtained, and these values have been investigated.
4. Equations correlating the volumes of both the monatomic ions and the oxy-anions have been found.

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