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EMPIRICAL CONSIDERATIONS OF ENTROPY I. THE ENTROPIES OF THE OXY-ANIONS AND RELATED SPECIES

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James W. Cobble

February 3, 1953

Berkeley, California

EMPIRICAL CONSIDERATIONS OF ENTROPY

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Department of Chemistry and Chemical Engineering
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ABSTRACT

The partial molal entropies for oxy-anions and related species have been correlated as a function of the charge, interatomic distance and certain structural factors. An equation is given by which the entropy for unknown species can now be estimated fairly accurately. In the few cases where the method does not give good agreement, the data are open to suspicion as indicated by other independent observations. Some applications and extensions of the method are indicated for future study.

*This work was performed under the auspices of the AEC.

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INTRODUCTION

Powell and Latimer¹ have recently demonstrated that it is possible to correlate the entropies of the monatomic aqueous ions in a simple manner as a function of their mass, charge, and crystalline radii. The correlation is so striking that it suggested the possibility that a similar situation might exist for more complex aqueous ions. Such a correlation would be generally useful in predicting the properties of as yet undetermined species, as well as indicating upon what types of ions further study might be fruitful. One might also hope that such an empirical treatment could provide some additional basis for a better understanding of the theory of ionic interactions in aqueous media. To this end, it has been found possible to correlate the entropies of aqueous complex ions similar to the methods of Latimer et al.,^{1, 2} and this communication describes the method and results obtained for the oxygenated anions and related species.

*This work was performed under the auspices of the AEC.

¹R. E. Powell and W. M. Latimer, J. Chem. Phys. 19, 1139 (1951).

²L. V. Coulter and W. M. Latimer, J. Am. Chem. Soc. 62, 2557 (1940).

Powell and Connick³ have also recently developed a theory for the oxygenated anions based upon different reasoning, but which, except in the case of large molecules, leads to quite similar results. The comparison of these two theories will be the subject of a future communication.

THE GENERAL METHOD

The equation proposed for the entropy of the oxygenated anions is of the form:

$$\bar{S}^{\circ} - 3/2 R \ln M = a - b \left(\frac{Z}{\rho} \right) \quad (1)$$

where \bar{S}° is the partial molal entropy (based upon $\bar{S}^{\circ}_{(H^+)} \equiv 0$), a and b are general constants for all of the oxy-anions, M is the ionic mass, Z the absolute integral charge, and ρ the effective ionic radius (in angstroms). The necessity for the linear dependence of the entropy on the charge Z has been previously discussed,¹ and is in apparent disagreement with the Born⁴ electrostatic model. Attempts to fit the data to any other power of Z than unity were not successful. We have also observed that in the particular method we have chosen of assigning the effective radii to the ions, the data seem to agree better with a $1/\rho$ rather than a $1/\rho^2$ dependence. This is in disagreement with the model for simple ions¹ where it was observed that an inverse square-power of the radii rather than the inverse first power seemed to fit the data better. The differences may arise from the lesser amount of ion interaction of the oxygenated species with surrounding water dipoles. The effect of hydrogen bonding between

³R. E. Powell and R. E. Connick, private. ~~These private~~ communication.

⁴M. Born, Z. Physik. 1, 45 (1920).

the peripheral oxygen atoms of the ion and the solvent will, of course, be greater although the net interaction must surely be smaller.

THE EFFECTIVE IONIC RADII

The key to the problem was in the assignment of an effective ionic radius to the ion. Powell and Latimer¹ used the Pauling⁵ ionic crystal radii for the simple ions plus an added one (for anions) and two (for cations) angstroms for the effects of hydration. No such well-defined set of radii are available for oxygenated ions. Further, one cannot simply add up either the appropriate covalent or ionic radii of the ion since the observed crystal interatomic distances usually lie somewhere between these two values. It is also clear that the effective ionic radius will be different for the linear ions than that for tetrahedral ions, and in general will be expected to depend in some manner on the structure of the ion. Finally, the effective radii will not be equal to the distance from the center of the central atom to the periphery of the outer oxygen atom, since this radius would not allow for penetration of the ion by water molecules. Indeed, this distance could not be easily and accurately calculated, since the oxygen diameter will be some function of its formal charge, and the crystal data in general would only give the interatomic distances. After trying various schemes, it was decided to fit the data using the interatomic distance between the central atom and the peripheral oxygen atom, although it was obvious that this distance would be

⁵L. Pauling, The Nature of the Chemical Bond, Cornell University Press, Ithaca, New York, (1939).

somewhat too small for the effective radius of some ions. These data are readily available in Wyckoff,⁶ although the values observed for the distance, r_{12} , usually vary from 0.1 - 0.2 Å depending upon the cationic species involved in the crystal. We have found it convenient, therefore, to use the values of r_{12} calculated by the method of Pauling.⁷ In practically all of the cases these calculated r_{12} values fall between the various observed values, except in cases where there is not enough data on various cationic forms to obtain a good average value for r_{12} (see Table 1). Further, experimental r_{12} values are not always available, and may never be for some ions. The method must be used with reservation for the estimation of interatomic distances between non-oxygen bonds.

THE EMPIRICAL EQUATION AND STRUCTURAL FACTORS

The equation for the oxy-anions has been found by inspection to

⁶R. W. G. Wyckoff, Crystal Structures, Interscience, New York, Vols I and II (1951).

⁷L. Pauling, J. Phys. Chem. 56, 361 (1952); covalent radii from reference 5 except for the case of the first row elements, where we have used the values recommended by Schomaker and Stevenson (J. Am. Chem. Soc. 63, 37 (1941)). Where covalent radii were not available, the metallic radii were used. For the special case of hydroxyl ion, the value of 1.40 Å observed in solid hydroxides has been used (A. F. Wells, "Structural Inorganic Chemistry," Clarendon Press, Oxford, 1945); this is not exactly equivalent to the interatomic distance, but this latter quantity becomes difficult to define in aqueous solution, for this species.

Table 1
 Comparison of Some Observed
 and Calculated Interatomic Distances

Ion	Observed (Å) (a)	Calculated (Pauling's method) ⁷
ClO_4^-	1.48 - 1.56	1.48
MnO_4^-	1.52 - 1.86	1.81
ReO_4^-	1.80 - 2.02	1.97
SeO_4^{-2}	1.61	1.66
CrO_4^{-2}	1.60 - 1.98	1.86
PO_4^{-3}	1.56	1.56
SiO_4^{-4}	1.62	1.63
CO_3^{-2}	1.26	1.24
NO_3^-	1.21 - 1.26	1.21
BrO_3^-	1.54 - 1.78	1.67
NO_2^-	1.13 - 1.23	1.23
CNS^-	1.42	1.37
SO_3^{-2}	1.39	1.34

(a) Some of these values for the ions containing heavier elements may be in error by 0.1 Å or more.

be:

$$\bar{S}^{\circ} - 3/2 R \ln M = 66 - 81 \left(\frac{Z}{\rho} \right) \quad (2)$$

where ρ is related to the interatomic crystal distance, r_{12} , by a suitable structural constant, f :

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

It is to be expected for reasons already discussed that f will be a function of the ion structure, and this has been found to be the case. It was also found that within the limits of experimental error all of the ions of one structural class (except in one case to be discussed) have the same structural factor. If this were not so, of course, the method proposed here would be of little value. The exception occurs in the tetrahedral class, where we find that the -3 ions require a somewhat different factor than the -1 or -2 ions. This need is probably not due to the failure of equation (1) since a linear dependence on Z was observed for the simple, highly charged ions.¹ We have also observed the linear Z dependence in the case of the highly charged non-oxygenated complex ions, which will be discussed in the second paper of this sequence.

The structural parameters, their average deviation, and the ions from which they were determined are given in Table 2. The "f" values were obtained by dividing the calculated value of r_{12} by the value of ρ necessary to fit the mass-corrected entropy to equation (2).

It may seem that the desirability of basing a structural factor in some cases only on the data of a few ions is questionable. This practice has been used, however, since the method suggests a structural

Table 2

Structural Classes and Factors

Ion Class	f		Ions (b)
	(a)	(c)	
Tetrahedral, -1, -2	0.74 ± 0.04		ClO_4^- , MnO_4^- , ReO_4^- (c), CrO_4^{2-} , SO_4^{2-} , SeO_4^{2-}
Tetrahedral, -3	0.83 ± 0.02		PO_4^{3-} , AsO_4^{3-}
Tetrahedral, -4	(0.9)	(d)	--
Pyramidal	0.74 ± 0.01		SO_3^{2-} , SeO_3^{2-} , ClO_3^- , BrO_3^-
Plane-triangular	0.68 ± 0.03		CO_3^{2-} , NO_3^-
Triatomic V-shaped	0.87 ± 0.11		NO_2^- , ClO_2^-
Triatomic linear	0.96 ± 0.02		BeO_2^{2-} (BO_2^- , AlO_2^-) (e)
Complex shape	0.77 ± 0.02		$\text{N}_2\text{O}_2^{2-}$, $\text{Cr}_2\text{O}_7^{2-}$, $\text{C}_2\text{O}_4^{2-}$ (f)
Linear related species	0.69 ± 0.01		CNO^- , N_3^-
Diatomic	1.34 ± 0.01		ClO^- , OH^-
Monohydrogen acid ions	0.91 ± 0.05		HCO_3^- , HSO_4^- , HSeO_3^- , HPO_4^{2-} , HASO_4^{2-} , HSO_3^-
Dihydrogen acid ions	1.13 ± 0.02		H_2BO_3^- , H_2PO_4^- , $(\text{H}_2\text{PO}_3^-)$
Trihydrogen acid ions	(1.34)	(f)	--
Tetrahydrogen acid ions	(1.55)	(g)	--

(a) Deviations correspond to average deviations of all the ions in that class.

(b) Entropy data from Latimer, W. M., "Oxidation Potentials," Prentice-Hall (1952) N. Y., except as indicated.

(c) J. W. Cobble, W. T. Smith, Jr., and G. D. Oliver, 1952, to be published.

(d) Estimated from di- and trivalent tetrahedral ions.

(e) Values in parenthesis are from estimated values in reference (b).

(f) For $\text{M}_2\text{O}_4^{2-}$ ions, $r_{12} = r_{\text{M-O}} + 1/2 r_{\text{M-M}}$.

(g) Estimated from the mono- and dihydrogen acid ions.

dependence, and we wish to keep it as flexible as possible. Some values may have to be revised slightly as new data become available, and yet the agreement obtained using the calculated values of r_{12} , the factors in Table 2, and equation (2) is good, as is shown in Figure 1. The average deviation is about 3 e.u. for some 30 experimental values, and some 12 estimates taken from Latimer.⁹ Considering that an error in r_{12} (or ρ) of $\pm 0.05 \text{ \AA}$ can cause in some cases an error of up to 15 e.u., this agreement is as good as one could expect.

It is interesting that placing a proton on the ions reduces the need for further structural differentiation, since the hydrogenated ions now fall in groupings dependent upon only the total number of hydrogen atoms in the ion. We have used the same r_{12} values as calculated for the completely dissociated ions, ignoring the effect of the hydrogen atom on r_{12} . This is usually in agreement with the crystal structure data.

It is believed that one of the entropies of the two triatomic shaped ions is incorrect, since a much larger deviation in f is observed for this class. It is further believed that nitrite ion is the one in error since the independent method proposed by Powell and Connick also indicates this discrepancy. Until other data for this class are available, however, we have no recourse but to average the values for both species.

There are a few isolated cases where the data cannot be made to fit on the curve in Figure 1. These are IO_3^- , HSeO_4^- , and HCrO_4^- . In view of the fact that Crouthamel *et al.*⁸ have found IO_4^- to exist

⁸Crouthamel, Hayes, and Martin, J. Am. Chem. Soc. 72, 82 (1951).

in aqueous solution at room temperatures largely as the hydrated species, $H_4IO_6^-$, it is clear that IO_3^- cannot be considered as a failure of the method. Indeed, this is a case where the theory might seem to be useful in interpreting the data. Hall and Alexander⁹ have also reported that O^{18} will exchange ^{between} aqueous IO_3^- and the solvent, suggesting that some hydration equilibrium does exist for this ion. No such exchange was observed for ClO_3^- where the entropy seems to be normal. Further, the Raman spectra of the aqueous solution also indicate the formula for the iodate species in aqueous solution is not simple.¹⁰ The data for $HSeO_4^-$ and $HCrO_4^-$, if correct, indicate a similar situation in that the formula written simply does not correspond to the species present. The oxygen exchange data are in agreement with the hypothesis that hydration equilibria exist for these ions also.

THE ENTROPY OF IONIZATION

Powell and Latimer¹ have also proposed that the entropy of neutral species in water can be represented by the equation:

$$\bar{S}^{\circ} = S_{int.} + 3/2 R \ln M + 10 - 0.22 V_m \quad (3)$$

If one examines the weak acids, in general, it is found that they can be represented fairly well by the equation:

$$\bar{S}^{\circ} - 3/2 R \ln M \approx 30 \pm 5 \quad (4)$$

Combining equation (4) with (2) it can then be shown that for the first

⁹N. F. Hall and O. R. Alexander, J. Am. Chem. Soc. 62, 3455 (1940).

¹⁰J. H. Hibben, "The Raman Effect and its Chemical Applications," Reinhold Pub. Co., New York, 1939, p. 381.

ionization of a weak electrolyte, the entropy change is given by:

$$\Delta S_{\text{ioniz.}} = 36 - \frac{81}{r_{12}} \quad (5)$$

We have taken an average value of f for the various species. Equation (5) is an extension of Pitzer's rule¹¹ in which the entropy of ionization of a weak electrolyte is about 22 e.u. Equation (5) predicts values between 17 and 25 e.u. for r_{12} values between 1.6 - 1.4 Å. The agreement of the experimental data with equation (5) is fair, although the equation $\Delta S_{\text{ioniz.}} = 20 - \frac{59}{r_{12}}$ fits the data better to an average deviation of 2-3 entropy units. The real interest in equation (5) is that it predicts the correct trend, so that low values of ionization (H_2SeO_3 , $\Delta S = -15$) and high values (H_3BO_3 , $\Delta S = -31$) are now somewhat easier to understand.

It can also be shown that the entropies of successive ionizations will also depend upon $1/r_{12}$ in general agreement with the few experimental observations available. These results should be generally useful in estimating entropies of various ionic and hydrated species, especially where the entropy for one member of the pair is available.

CONCLUSION

The method given here may not necessarily be unique in systematizing the aqueous entropy data, but for methods involving the charge to radius ratio (Z/ρ) it seems to work very well. For example, one can also use an equation of the type proposed by Powell and Latimer¹ for

¹¹K. S. Pitzer, J. Am. Chem. Soc. 59, 2365 (1937).

the simple ions in which 1.00 Å is added to the interatomic distance in a $Z/(r + 1.00)^2$ term, but the fit is not as good, nor can the acid ions be treated simply in this manner. Another method which gives fair results is to use the "thermodynamic" radii of Kapustinskii and Yatsimuskii¹² obtained from lattice energy calculations. The fit becomes poorer for highly charged species, which is what one might expect from their treatment of the crystal energies.

There seems to be no a priori reason why oxygenated cationic species should not take on the same structural factors as their negative counterparts, but the data are not available to test this hypothesis.

It should also be interesting to test the large amount of entropy of activation data available from kinetic studies to see whether the observed values for the transition states are in agreement with those calculated by the method presented here.

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¹²A. F. Kapustinskii and K. B. Yatsimuskii, Zhur. Obsheei Khim. 19, 2191 (1949).

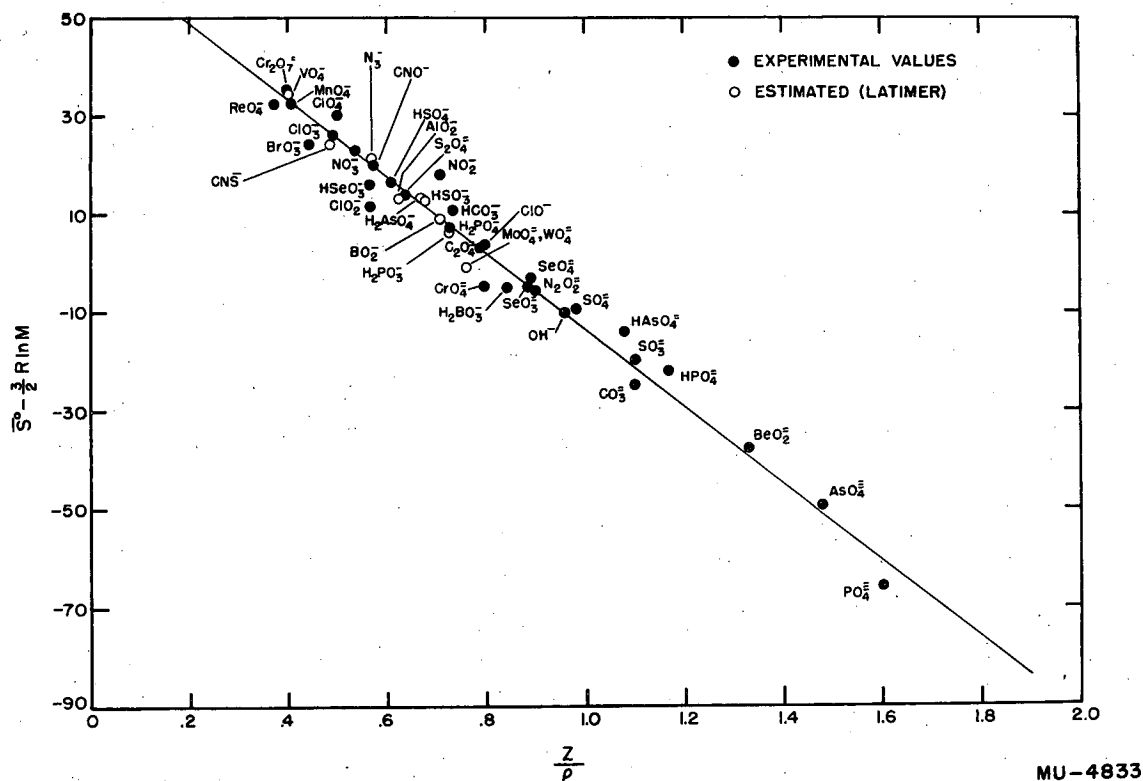


Figure 1. Correlation of the mass corrected aqueous entropies with the charge to effective radius ratio.