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EMPIRICAL CONSIDERATIONS OF ENTROPY II. THE ENTROPIES OF INORGANIC COMPLEX IONS

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February 3, 1953

Berkeley, California

EMPIRICAL CONSIDERATIONS OF ENTROPY

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James W. Cobble
Radiation Laboratory and
Department of Chemistry and Chemical Engineering
University of California, Berkeley, California

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ABSTRACT

A method is proposed by which the partial molal entropies of aqueous complex ions can be correlated in a simple manner as a function of the ratio of their charge to interatomic distance. The agreement obtained between the observed values and those calculated by this method has been shown to be within the accuracy of the experimental data. It is also demonstrated that when the complexing agent is water alone (i.e., no complexing) the proposed equation reduces to an expression similar to that previously obtained by Powell and Latimer for simple monatomic ions.

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

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INTRODUCTION

With the success of Powell and Latimer¹ in correlating the entropies of simple ions, and the recent treatments of Powell and Connick² and Cobble³ in correlations for the oxy-anions, it seemed desirable to search for a similar method of treating aqueous complex ions, if, indeed, any such correlation existed. Although there are a large number of complex species which have been identified, there are few which have been characterized by accurate determinations of stability constants, and still fewer for which heat or temperature coefficient data are available so that entropy values can be calculated. In addition, many of the reported values are subject to large errors inherent in the conditions required for their study (i.e., high ionic strength), and frequently large discrepancies exist between values reported by different observers. We have, however, observed a correlation which is believed to be generally applicable to positively and negatively charged complex ions alike. A treatment for neutral

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

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

²Powell, R. E. and Connick, R. E., Private communication.

³Cobble, J. W., J. Chem. Phys., in press.

non-dissociated complex ions is also presented.

THE PROPOSED METHOD

Since the previous entropy treatments of aqueous ions have involved functions of the charge to radius ratio,³ it was of interest to try a similar function for the complex ions. By "complex" ions, we mean in this communication those ions in which "simple" ions have associated to form a "complex." Thus, sulfate ion would not normally be thought of a union of aqueous S^{+6} and O^{-2} ions, although substances such as $Fe(CN)_6^{-4}$ and $FeBr^+$ are easily formed in this manner. Further, partial complexing of these ions to give species such as SO_3^{-4} , SO_2^{-6} , etc., has not been observed. Our definition is occasionally troublesome in the case of a few very stable ions (such as $PtCl_6^{-2}$). In general, however, the distinction is clear, and for the majority of ions little ambiguity exists in assigning them to either the oxy-anion or complex ion class. It is also clear that one would expect the oxy-anions to differ from "complex ions" since their immersion in water will not disturb the structure of the solvent as much as non-oxygenated species of the same Z/r_{12} ratio. It will be seen, however, that the hydroxy complexes ($M(OH)^{+n}$) fit well into the treatment proposed for the "complex" ions, but did not agree with the method proposed for the oxy-anions. This is probably related to the supposition that the bond distances are greater in the $M(OH)^{+n}$ ionic complexes than in partially covalent oxy-ions. In any event, our original classification which is, in reality, based upon ease of dissociation, is as probably useful as any other.

In Figure 1 the partial molal entropy⁴ has been plotted against the ratio of the charge to interatomic distance ($r_{12} = r_1 + r_2$) for the ion, since this function had been found to be useful with the oxy-anions.³ The interatomic distances were computed from the sum of the appropriate ionic⁵ and covalent⁶ radii. In cases where the magnetic evidence was not available to make such a classification, the decision has been based upon chemical reasoning. The distinction will cause

⁴Values obtained mostly from Latimer, W. L., "Oxidation-Potentials," 2nd Ed., Prentice-Hall, New York, 1952; data for the aluminum fluoride complexes are from Latimer, private communication (in press); AgCl_2^- from Jonte, J. H. and Martin, D. S., J. Am. Chem. Soc. 74, 2053 (1952); SnCl^+ , SnCl_2^0 , SnCl_3^- from Vanderzee, C. E. and Rhodes, D. E., J. Am. Chem. Soc. 74, 3552 (1952); SnBr^+ , SnBr_2^0 , SnBr_3^- from Vanderzee, C. E., J. Am. Chem. Soc. 74, 480 (1952); $\text{V}(\text{OH})^{+2}$ calculated from the ΔS value given by Furman, S. C. and Garner, C.S., J. Am. Chem. Soc. 72, 1785 (1950), and assuming that S^0 of V^{+3} , aq., is -66 e.u. (calc. from reference 1); FeF^{+2} calculated from Uri, N., Chem. Rev. 50, 375 (1952).

⁵Ionic Radii from compilation of Wyckoff, R. W. G., "Crystal Structures," Interscience, New York, 1951, Vol. I; this compilation is more complete for ionic radii than reference (6).

⁶Covalent radii from Pauling, L., "Nature of the Chemical Bond," Cornell University Press, Ithaca, New York, 1938; for the radii of molecules, we have used the radius of NH_4^+ for NH_3 (1.48 Å) and ~1.1 Å for NO; the value of 1.40 Å for OH^- and 1.92 Å for CN^- are from Wells, A. F., "Structural Inorganic Chemistry," Clarendon Press, Oxford, 1945.

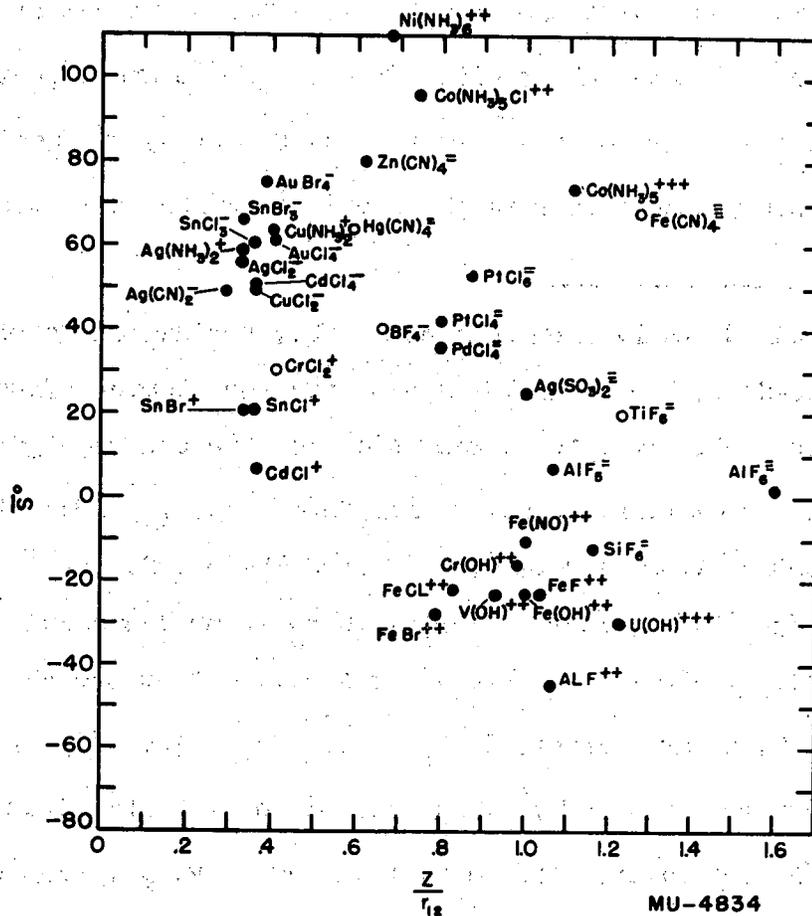
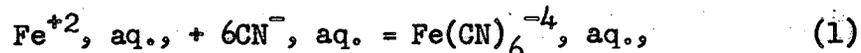


Figure 1. Illustration of the absence of correlation of the aqueous entropies of complex ions with the charge to radius ratio.

little ambiguity in the r_{12} values except in those cases where the complexing agent is molecular (NH_3 , SO_3^{-2} , CN^- , and NO). It can be seen that the method illustrated in Figure 1 is of little use in classifying or comparing the species, since there is no obvious separation into groups dependent upon such variables as radii, charge, number of ions making up the complex, or structure. For example, AlF^{+2} and $\text{Co}(\text{NH}_3)_5^{+3}$ have about the same Z/r_{12} values, yet they differ in entropy by 120 entropy units; $\text{Zn}(\text{CN})_4^{-2}$ and SiF_6^{-2} have the same charge, but differ by 92 e.u.; $\text{Co}(\text{NH}_3)_5^{+3}$ and $\text{Fe}(\text{CN})_6^{-4}$ have the same entropy but no other obvious similarities, etc.

It thus appeared that little, if any, correlation existed until the observation was made that the entropies of highly complexed species ($\text{Co}(\text{NH}_3)_5\text{Cl}^{+2}$, AuBr_4^- , $\text{Zn}(\text{CN})_4^{-2}$) appear to be uniformly more positive than the entropies for lesser complexed ions (FeBr^{+2} , AlF^{+2}). This situation indicates, of course, less interaction of a restrictive nature between the highly complexed ion and the solvent molecules, than with the lesser complexed ions, and suggests that this fact should be considered in the thermodynamic entropies under consideration.

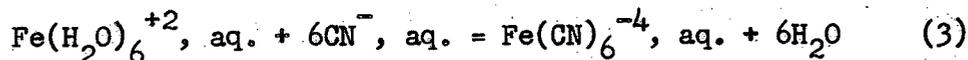
Therefore, we have defined a quasi-thermodynamic function, the "corrected" partial molal entropy, \bar{S}^1 , which arises from the following considerations. In the complexing of a simple ion:



the entropy change for the process is measurable, and the entropy of the complex ferrocyanide is given by:

$$\begin{aligned} \bar{S}^0 \text{ complex} &= \Delta S + 6\bar{S}^0(\text{CN}^-, \text{aq.}) + \\ &\bar{S}^0(\text{Fe}^{+2}, \text{aq.}) \end{aligned} \quad (2)$$

\bar{S}^0 represents the "normal," partial, molal entropies for ionic species commonly in use. One can, however, also treat equation (1) as a replacement of the water in a fully coordinated aquated ferrous ion by cyanide ions, thus:



for which:

$$\Delta S = \bar{S}'(\text{Fe}(\text{CN})_6^{-4}, \text{aq.}) + 6\bar{S}^0(\text{H}_2\text{O}) - 6\bar{S}^0(\text{CN}^-, \text{aq.}) - \bar{S}^0\text{Fe}^{+2}, \text{aq.} \quad (4)$$

and

$$\bar{S}' \text{ complex} = \Delta S + 6\bar{S}^0(\text{CN}^-, \text{aq.}) + \bar{S}^0(\text{Fe}^{+2}, \text{aq.}) - 6\bar{S}^0(\text{H}_2\text{O}), \quad (5)$$

where \bar{S}' refers to the "corrected" entropy.

ΔS is the same in both cases, being an experimental observation, and the corrected entropy, \bar{S}' , is related to the "normal" entropy, \bar{S}^0 , by the relation:

$$\bar{S}' = \bar{S}^0 - n\bar{S}^0(\text{H}_2\text{O}) \quad (6)$$

where n represents the number of water molecules replaced from the normal coordinated aquated ion by the complexing agent.^{7,8} In general, whether the complex ion can be formed by simple replacement or not is immaterial, as long as one is consistent in using the same (and correct) "n" value for a particular ion.

In Figure 2, the corrected entropy values, \bar{S}' , have been plotted as before against the same Z/r_{12} values, and it can be seen that there is a

⁷This value of "n" is similar to the "characteristic" and "maximum" coordination numbers of Bjerrum, J., Chem. Rev. 46, 381 (1950).

⁸Since this paper was submitted, Professor Latimer has also independently, although earlier, used this same method in treating the entropies of hydration in the aluminum fluoride complexes (c.f., J. Am. Chem. Soc., to be published).

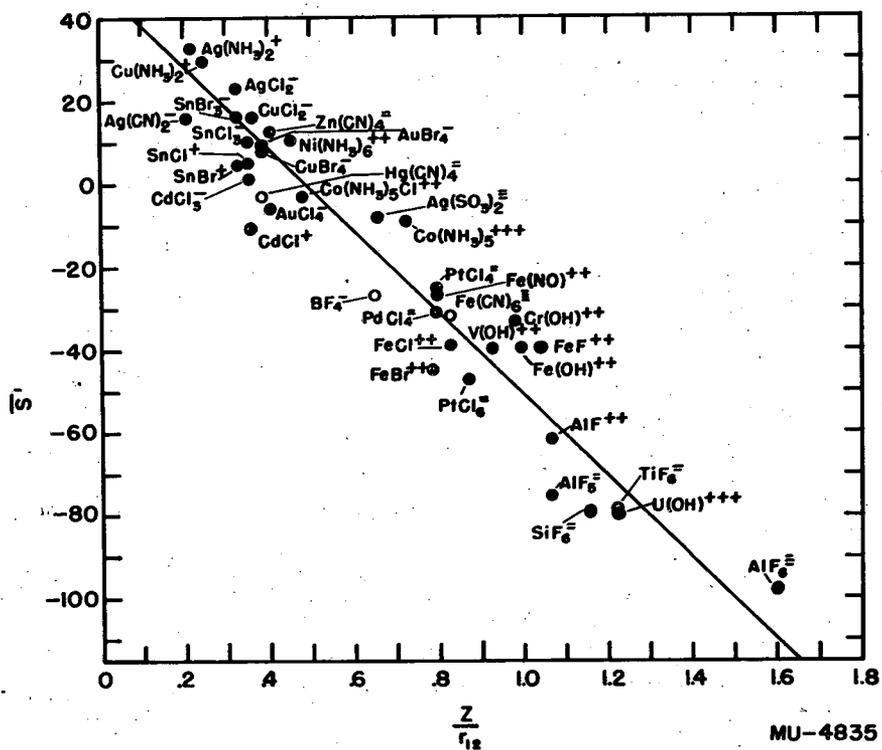


Figure 2. Correlation of the hydration corrected entropies of complex ions with the charge to radius ratio.

linear relationship between \bar{S}^{\dagger} and Z/r_{12} which is, by inspection:

$$\bar{S}^{\dagger} = 49 - 99 (Z/r_{12}) \quad (7)$$

This equation strictly holds only for complex ions which contain monatomic ions as ligands, and not molecules. To fit the molecularly complexed species, it was necessary to introduce a structural factor, f , so that $r_{12} = \frac{r_1 + r_2}{f}$. This procedure was necessary in the case of the oxy-anions³ and would be expected to be necessary in comparing the complexes involving complicated groups (NO, NH₃, etc.) with monatomic ions (e.g., halides, etc.). The need for the structural factor for the former is undoubtedly related to the fact that these complexes have a more "open" structure. The center of gravity of the complexing molecule as a whole cannot approach the central ion as closely as a monatomic ion can because the charge distribution of the former is not uniform. Thus the calculated interatomic distance does not represent the effective radius of the ion, being too small. At present, neither the abundance nor accuracy of the data require but a single structural factor ($f = 0.65$) for all of the known molecularly complexed ions for which data are available: (NO, NH₃, CN⁻, SO₃⁻²). This approximation may have to be revised at some future date. It was not necessary to use the factor for hydroxy complexes (M(OH)⁺ⁿ) because, apparently, of the small size of the hydrogen atom.

The average deviation of the data given in Figure 2 is about eight entropy units. It should be noted that the experimental determinations of the entropies of complex ions are subject to much larger errors than are the entropies of the simple ions or oxy-anions. Many of the entropy values have been obtained from equilibrium studies at different

temperatures in high ionic strength media. In an excellent review article, Young⁹ has pointed out the various difficulties in obtaining true thermodynamic constants from such studies, since the values at infinite dilution are required to calculate the \bar{S}° (and hence, \bar{S}^1) values. Further, while the stability constants determined by cells with liquid junctions are usually more accurate and reproducible, the potentials may also suffer from unknown junction potentials as well as high ionic strength corrections. Thus, the ΔS data for cadmium chloride obtained by King¹⁰ in solubility studies were for 3 molar chloride solutions, but absolute entropies were calculated using standard state partial molal entropies for the Cd^{+2} and Cl^{-} ions. These entropy values reported seem rather low in Figure 1, and we would assume that when the proper corrections can be made, the cadmium chloride values will correspond more closely to those predicted by equation (7).

Further, we have no accurate means by which to evaluate the true interatomic distances for aqueous complex species, and most certainly the r_{12} value for SnCl_3^{-} , for example, is not the same as that in SnCl^{+} , although this had to be assumed in calculating (Z/r_{12}) . In general, however, the radii are probably more accurate than the experimental errors and not greatly affected by solvation. Considering these difficulties, it is believed that the average deviation corresponds rather well to what one expects from the accuracy of most

⁹Young, T. F., "Annual Reviews of Physical Chemistry," Vol. III, Annual Reviews, Inc., Stanford, California, p. 275.

¹⁰King, E. L., J. Am. Chem. Soc. 71, 322 (1949).

of the data.⁴

There are four ions which cannot be treated by the proposed method, and were omitted from Figure 2: AlF_2^+ , AlF_4^- , HgBr_4^{-2} , and $\text{Au}(\text{CN})_2^-$. In the case of the latter, the value reported¹¹ for the potential leads to a value for the dissociation constant of 10^{-39} , which seems remarkably low ($\text{Cu}(\text{CN})_2^{-1}$: 1×10^{-16} ; $\text{Ag}(\text{CN})_2^{-1}$: 1.8×10^{-19}). If it is assumed that the heat of formation is correct ($\Delta H_f^\circ = 58.4$ kcal mole⁻¹)¹², then the predicted value of the entropy of 64 e.u. (exp. value calc.: 29.5 e.u.) leads to a much lower value of K ($\sim 10^{-30}$). This value is still small but seems corrected in the right direction.

The data of Sherill¹³ on the halide complexing of mercury do not, in the case of the chloride complexes, agree with the more recent values of Johnson, Quarfort and Sillen.¹⁴ If the data for the HgBr_4^{-2} are also incorrect, then the entropy value calculated for this species by Latimer⁴ is also incorrect, as indeed, equation (7) predicts (exp. 84 e.u.; calc.: 39 e.u.).

In the case of the two aluminum fluorides, no apparent explanation seems very satisfactory in view of the fact that the entropies of AlF_6^{-3} , AlF_5^{-2} , AlF^{+2} , BF_4^- , SiF_6^{-2} , TiF_6^{-2} , and FeF^{+2} seem to fit the proposed treatment. Unless these species are dimerized or further

¹¹G. Bodländer, Ber. 36, 3933 (1903).

¹²National Bureau of Standards, "Selected Values of Chemical Thermodynamic Properties," 1948.

¹³Sherill, M. S., Z. physik. Chem. 43, 735 (1903); 47, 103 (1904).

¹⁴Johnson, Quarfort, and Sillen, Acta. Chem. Scand. 1, 46, 473 (1947).

hydrated, we are unable to account at present for this apparent discrepancy: AlF_4^- , obs.: 5 e.u., calc.: 62; AlF_2^+ , obs.: -23 e.u., calc.: 28.

It is of interest to note that the oxy-cations UO_2^{+2} , UO_2^+ are also in agreement with the present treatment (not shown in Figures 1, 2), while they did not seem to fit well in the treatment of the oxy-anions.³ This may be accidental, and much more data will be required to see if this class in actuality represents a complex ion of the type under discussion.¹⁵

We have also included in Figure 2 some estimates made by Latimer⁴ which are based on only partially complete thermodynamic data.

NEUTRAL SPECIES

The same general method can be extended to neutral species and seems to reasonably correlate the few data which are available. Table I contains the calculated and observed entropies for five neutral halide complex ions. The calculated values are from the equation obtained by inspection:

$$\bar{S}' = 132 - 354\left(\frac{1}{r_{12}}\right). \quad (8)$$

The mean deviation of the calculated and observed values is ~7 e.u., although if the CdCl_2^0 data are not used for reasons already given, then a revised equation can be used with a much smaller average deviation. Much more data on these species will have to be collected before the general validity of equation (8) can be established.

¹⁵ See also: Connick, R. E., and Hugus, Z. Z., J. Am. Chem. Soc. 74, 6012, (1952).

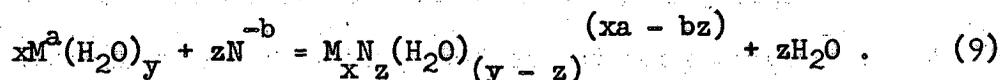
TABLE I

Neutral Aqueous Complex Ions

Species	r_{12} (Å)	\bar{S}° obs.	\bar{S}° calc.	\bar{S}' calc.
SnBr_2°	2.98	47	46	13
CdCl_2°	2.79	17	38	5
AgCl°	2.77	37	21	4
SnCl_2°	2.82	39	40	7
AlF_3°	1.88	-6	-6	-56

GENERAL EQUATIONS FOR COMPLEX ION FORMATION

The general equation for the complexing of a simple ion by ionic ligands can be written:



Recalling that Powell and Latimer¹ have proposed for the simple ions the expression:

$$\bar{S}^{\circ} = 3/2R \ln M + 37 - 270 Z/r_e^2, \quad (10)$$

for which we can substitute without any loss of generality and little in accuracy:

$$\bar{S}^{\circ} = 49 - 270 Z/r_e^2, \quad (11)$$

where $r_e = r_N + 1.00 M^{\circ}$ for anions, and $r_M + 2.00 \text{ Å}$ for cations.

Combining equation (11) with (7) we obtain for the reaction in equation (9):

$$\Delta S = 49 + 16.7 z - 49(z+x) - \frac{99(xa-bz)}{r_{12}} + 270 \left[\frac{bz}{(r_2+1)^2} + \frac{xa}{(r_1+2)^2} \right] \quad (12)$$

$xa \neq bz$

Differentiation of this expression with respect to any one of the five variables (x, a, y, z, b) results in still complicated expressions which contain more than one term and frequently four variables. It thus appears that any "rules" or generalizations for entropy changes on complexing, in order to be accurately in agreement with equation (12) are not simply formulated, since the sign of the differential will depend upon the relative magnitudes of the various terms. This expression should be useful in comparing ΔS values of one cationic sequence and a particular anion complexing agent, with another series of the same cationic sequence and a different anion. In these cases, it might be hoped that the expression would be applicable even in non-ideal situations of high ionic strength.

One generalization is evident, however, from our replacement model: The entropies of complex ions of the same cation-anion pair which have the same charge will differ by the difference in their number of ligands times the entropy of water, the more highly complexed species having the larger entropy; thus, $\bar{S}^{\circ}_{\text{SnBr}_3^-} - \bar{S}^{\circ}_{\text{SnBr}^+} = 2S^{\circ}_{(\text{H}_2\text{O})} = 33 \text{ e.u.}$, (obs. 45);

$$\Delta S(\text{SnCl}_3^- - \text{SnCl}^+) = 33 \text{ e.u.}, \text{ (obs. 39);}$$

$$\Delta S(\text{AlF}_5^{-2} - \text{AlF}^{+2}) = 67 \text{ e.u.}, \text{ (obs. 52).}$$

If the general hypothesis of hydration which has been outlined here is valid, then it ought to be possible to calculate the entropies of the monatomic, aqueous ions by our same general method. For these ions, $\bar{S}^{\circ} \equiv \bar{S}$ by equation (6) since $n = 0$. Thus the general expression (7) becomes:

$$\bar{S}^{\circ} = 49 - 99 \left(\frac{z}{r_{12}} \right) \quad (13)$$

which we can compare to the modified Powell and Latimer equation (11) for monatomic ions. These two equations are strictly compatible only if $270 \frac{Z}{r_e^2} \approx 99 \left(\frac{Z}{r_{12}} \right)$. Identifying $r_{\text{eff.}}$ with r_{12} gives $r_e \approx 2.7 \text{ \AA}$; since $r_e = r_1 + 2 \text{ \AA}$ for the cations, then $r_1 \approx 0.7 \text{ \AA}$ for which these two expressions are exactly equivalent. However, equation (11) is somewhat insensitive to changes in r , and since most of the simple ions have radii lying between $0.55 \text{ (Al}^{+3})$ and $1.70 \text{ (Cs}^+) \text{ \AA}$, equation (13) effectively (though not as accurately) also reproduces the entropies for most of the monatomic ions. This fact is illustrated in Table 2. The agreement is obviously poor for extreme r_1 values.

Table 2

Calculated Values of \bar{S}° for Some Monatomic Cations

Species	\bar{S}° (obs.)	\bar{S}° (calc.) (a)
Cs ⁺	32	20
Na ⁺	14	15
Ag ⁺	18	14
Sr ⁺⁺	-9	-15
Gd ⁺⁺⁺	-43	-49
Al ⁺⁺⁺	-70	-75
Pu ⁺⁺⁺⁺	-87	-83

(a) Calc. from equation (13) using ionic radii of reference 5, and $r_2 = 2.0 \text{ \AA}$.

The general usefulness of the method will perhaps be greatest in obtaining bond strengths for complex species from equilibrium measurements at single temperatures. Thus, it is now possible to estimate

heats of formation for many complex ions for which only free energy data at one temperature are now available. It is also possible that the method may be useful in aiding the extrapolation of thermodynamic functions to infinite dilution.

Although the heats of formation will be in error by only a few kilocalories due to an error of 5-10 e.u. in the estimation of ΔS values, the need for much more accurate entropy determinations (and redeterminations), properly corrected to standard state conditions is obvious from the scatter of the data in Figure 2 and lack of agreement in the literature between various observers for some species.

ACKNOWLEDGMENT

The author would like to thank Professor W. M. Latimer for his values on the entropies for the fluoride complexes of aluminum prior to publication, and for helpful discussions of the problem.