

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY, LAFAYETTE, INDIANA]

## The Thermodynamic Properties of High Temperature Aqueous Solutions. IV. Entropies of the Ions up to 200° and the Correspondence Principle<sup>1</sup>

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A general treatment has been developed which describes the entropies of ions in solution in terms of various ionic and solvent parameters. By using the entropies themselves at some reference temperature to define these parameters, it is possible to derive a principle of entropy correspondence for ions between different temperatures. If the standard state is chosen properly by fixing the entropy of H<sup>+</sup>(aq) at each temperature, then the ionic entropies at one temperature are linearly related to their corresponding entropies at 25°. A generalized treatment of nonaqueous solvents also follows directly from the theory. Various equilibria and thermochemical data from the literature have been used to calculate the partial molal entropies for over forty solutes, and a consistent set of ionic entropies is given for higher temperatures. These experimental entropies are in good agreement with the correspondence principle, and preliminary constants are given to allow the prediction of entropies up to 200° for the common types of ions.

### Introduction

The need for accurate thermodynamic data for solutes in aqueous solutions at elevated temperatures such as those which already exist at 25° is obvious. The correlation and prediction of properties of aqueous systems relating to solution theory, chemical processing, geochemistry, and hydrothermal and inorganic synthesis is hampered by the sparsity of partial molal free energies, entropies, and heat capacities as a function of temperature. During the past decade a few measurements of heat capacities,<sup>3-6</sup> cell potentials over wide temperature ranges,<sup>7,8</sup> and some accurate equilibria data<sup>9-11</sup> have provided detailed thermodynamic characterizations of selected systems, but the various systems were not interrelated in any obvious manner.

The prospect of merely repeating thermodynamic measurements on all of the ions at even reasonably spaced temperature intervals up to the critical point does not provide much promise of hastening our understanding of this area. Consequently, it appears that any successful attempts to predict or systematize the thermodynamic functions of ions at higher temperatures would be both timely and useful. Such a systematization is the purpose of this communication. First, an attempt is made to develop a general correspondence principle for ionic entropies over wide ranges of temperatures. Secondly, data from the literature have been used to generate consistent sets of experimental ionic entropies up to 200° and to test the proposed theory. Finally, general equations are derived for predicting as yet unknown entropies of ionic species up to 200° and beyond.

High temperature ionic entropies can be used to derive partial molal ionic heat capacities for almost any

species desired. The use of these heat capacities for predicting a wide variety of thermochemical properties at higher temperatures will be the subject of the communications immediately following the present paper.<sup>12</sup>

### Nature of the Problem

Any *a priori* attempt to predict thermochemical properties of ionic aqueous species above room temperature immediately comes to face with the fact that purely theoretical methods to treat this problem at 25° have not been very successful. Most of these attempts usually start in one way or the other from the simple (or modified) electrostatic Born<sup>13</sup> equation for the free energy of hydration of an ion of charge  $Z$  and radius  $r$ , in a medium of dielectric constant  $D^*$ .

$$\Delta F_e = -\frac{(Ze)^2N}{2r} \left(1 - \frac{1}{D^*}\right) \quad (1)$$

Unfortunately, such an equation does not accurately predict ionic hydration energies, largely because there is no good operational definition of either the ionic radius,  $r$ , or the microscopic dielectric constant,  $D^*$ , in the ionic atmosphere. Hydration energy data are consistent with the  $Z^2/r$  functional dependence,<sup>14</sup> and good estimations of hydration energies can be made on a semiempirical basis for many simple ions. However, a few per cent error in a hydration energy may amount to a few kilocalories for many ions, and such a hydration energy approach would not seem to offer much hope of making *accurate* predictions of free energies for aqueous ions at higher temperatures.

Much more success has been had in relating the partial molal ionic entropies to various structural parameters such as charge, size, mass, and geometry.<sup>15-18</sup> Although none of these empirical entropy correlations appear to be on a very sound theoretical basis,<sup>19</sup> they nevertheless are capable of predicting entropies for a

(1) Supported by a grant from the National Science Foundation.

(2) From the Ph.D. Thesis of C. M. Criss, Purdue University, 1961.

(3) M. Eigen and E. Wicke, *Z. Elektrochem.*, **55**, 354 (1951).

(4) E. Wicke, M. Eigen, and Th. Ackermann, *Z. physik. Chem. (Frankfurt)*, **1**, 340 (1954).

(5) Th. Ackermann, *Discussions Faraday Soc.*, **24**, 180 (1957); *Z. Elektrochem.*, **62**, 441 (1958).

(6) C. M. Criss and J. W. Cobble, *J. Am. Chem. Soc.*, **83**, 3223 (1961).

(7) R. S. Greeley, W. T. Smith, Jr., R. W. Stoughton, and M. H. Lietzke, *J. Phys. Chem.*, **64**, 652 (1960).

(8) M. B. Towns, R. S. Greeley, and M. H. Lietzke, *ibid.*, **64**, 1861 (1960).

(9) R. W. Stoughton and M. H. Lietzke, *ibid.*, **64**, 133 (1960).

(10) References of the dissociation constant of water up to 308° are summarized in H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 3rd Ed., Reinhold Publishing Corp., New York, N. Y., 1958, pp. 634-649.

(11) M. H. Lietzke, R. W. Stoughton, and T. F. Young, *J. Phys. Chem.*, **65**, 2247 (1961).

(12) (a) C. M. Criss and J. W. Cobble, *J. Am. Chem. Soc.*, **86**, 5390 (1964), paper V of this sequence; (b) J. W. Cobble, *ibid.*, **86**, 5394 (1964), paper VI of this sequence.

(13) M. Born, *Z. Physik*, **1**, 45 (1920).

(14) W. M. Latimer, *J. Chem. Phys.*, **23**, 90 (1955).

(15) R. E. Powell and W. M. Latimer, *ibid.*, **19**, 1139 (1951).

(16) J. W. Cobble, *ibid.*, **21**, 1443, 1446, 1451 (1953).

(17) R. E. Connick and R. E. Powell, *ibid.*, **21**, 2206 (1953); see also R. E. Powell, *J. Phys. Chem.*, **58**, 528 (1954).

(18) K. J. Laidler and C. Pegis, *Proc. Roy. Soc. (London)*, **A241**, 80 (1957); see also K. J. Laidler, *Can. J. Chem.*, **34**, 1107 (1956); and A. M. Couture and K. J. Laidler, *ibid.*, **35**, 202 (1957).

(19) G. N. Lewis and M. Randall, "Thermodynamics," revised by K. S. Pitzer and L. Brewer, 2nd Ed., McGraw-Hill Book Co., Inc., New York, N. Y., 1961, p. 523.

wide variety of ions at 25° accurately enough so that the error introduced in a corresponding free energy calculation is small. Consequently, ionic entropies appeared to offer one reasonable entry into the problem of predicting thermochemical properties in solutions at higher temperatures.

A perusal of the experimental entropy data at higher temperatures indicated that the entropies of ions can be expressed as functions of mass, charge, and ionic size at higher temperatures similar to the observed correlations at 25°. Indeed, the functional dependences seem to be the same. This situation immediately suggested that there might exist a series of corresponding states for ionic entropies at various temperatures. If so, the necessity of knowing complete functional dependences for this (or any other) thermodynamic function is avoided, and the entropy function itself can be used to operationally define the state of an ion in solution.<sup>20</sup>

### The Correspondence Principle

Assume that the entropy of an ion (with no internal degrees of freedom) at some temperature  $t$  is given by some function of the charge  $Z$ , the dielectric constant  $D$ , mass  $m$ , radius  $r$ , and any other required variable.

$$S^\circ_{(t)} = f(Z, r, D, m, t, \dots) \quad (2)$$

Some of these functions will be to a large extent independent of the nature of the ion and depend only upon the choice of standard state, solvent, and temperature; eq. 2 can then be factored and written as

$$S^\circ_{(t)} = g(t, \text{solvent}) + f(\text{ion}) + [g(t, \text{solvent}) \times f(\text{ion})] \quad (3)$$

The third (cross) term in eq. 3 allows for the possibility that some of the variables may be interdependent. It will be assumed that eq. 3 can be expanded about a reference entropy,  $S^\circ_{(t_1)}$ , at a temperature  $t_1$ , such that

$$S^\circ_{(t_2)} = a_{(t_2)} + b_{(t_2)}S^\circ_{(t_1)} + c_{(t_2)}(S^\circ_{(t_1)})^2 + d_{(t_2)}(S^\circ_{(t_1)})^3 + \dots \quad (4)$$

In principle, eq. 2 and 4 could be simplified by initially subtracting some of the well-known functional parameters so that only that part of the entropy which reflected solvent interactions was considered. Such terms as  $\frac{3}{2}R \ln M$ ,<sup>15</sup> or in the case of ions with internal degrees of freedom,  $R \ln \sigma$ <sup>21</sup> (where  $\sigma$  is the symmetry number) are possible examples. However, in the final treatment to be presented, such a procedure does not have any appreciable effect in either increasing the accuracy of or simplifying the final equations and will not be used.<sup>22</sup> Experimentally, it appears that the first two terms of eq. 4 are adequate to express the entropy data in water which are known up to 200°, and perhaps even higher.

(20) Latimer had suggested using ionic entropy to define the effective ionic radius of an ion in order to make more reliable estimations of the hydration energy (ref. 14).

(21) E. L. King, *J. Phys. Chem.*, **63**, 1070 (1959).

(22) The main reason for this result is simply that the differences in the entropies due to the mass and symmetry terms, when spread out among all the various ions, are small. Further, the correspondence relation (eq. 4) essentially involves further differences between entropies which again reduces the effect. It is of interest to note that, experimentally, one is hard pressed to find data which could be used to prove experimentally the dependence of ionic solution entropies upon mass.

### Experimental Ionic Entropies

In attempting to test the general correspondence relationship (eq. 4), it was necessary to obtain a set of experimental ionic entropies over as wide a range of ion types and temperature as possible. In a comprehensive survey of various types of chemical and thermochemical information in the literature, there exist data which can be interpreted sufficiently accurately to calculate the partial molal entropies at infinite dilution for some forty aqueous solutes above 25°. Many of these are known up to 100°, about fifteen are known or easily estimated up to 150°, and a few systems up to 200° and beyond. Much of the solubility and equilibrium data could not be used reliably because of lack of information on hydrolysis and/or complex ion formation at higher temperatures. The composition and identity of solutes in high temperature solutions (or alternatively, information on activity coefficients) is one of the critical areas to be studied in this field.

The most accurate and useful thermodynamic functions which have been directly determined experimentally above room temperature are the partial molal heat capacities,  $\overline{C}_{p_2}^\circ$ , as a function of temperature. Unfortunately, only a few systems have been studied up to 100°, and there are no values of  $\overline{C}_{p_2}^\circ$  above 130°. However, reliable estimates can be made for this function up to 150° for a few selected solutes. While more data on  $\overline{C}_{p_2}^\circ$  exist for a wide variety of species at a single temperature, 25°, such heat capacities cannot usually be used over higher temperature ranges since this function may vary considerably with temperature.<sup>3-6,23</sup> Consequently, much of the entropy data above 100° must still be inferred from determinations of various equilibrium constants or cell potentials as a function of temperature.

It should be pointed out that while equilibrium data do not usually give a very good picture of the detailed variation of  $\overline{C}_{p_2}^\circ$  with temperature, satisfactory estimates can usually be obtained for the average value of the heat capacity over a given, extended temperature interval,  $\overline{C}_{p_2}^\circ \int_{t_1}^{t_2}$ . In fact, a single free energy, accurately known at a higher temperature, will also allow the calculation of an average heat capacity, if  $\Delta F$  and  $\Delta S$  are also known accurately at a lower temperature.

$$\Delta F^\circ_{(t_2)} \cong \Delta F^\circ_{(t_1)} + \Delta C_{p_2}^\circ \int_{t_1}^{t_2} \Delta T - \Delta S^\circ_{(t_1)} \Delta T - T_2 C_{p_2}^\circ \int_{t_1}^{t_2} \ln \frac{T_1}{T_2} \quad (5)$$

A summary of entropies (including both simple and complex ions) up to 200° from hundreds of separate calculations is given in Table I. In a few cases, activity coefficient estimations were required above 100° to obtain better estimates of  $\Delta F^\circ_{(t)}$ . While this introduces somewhat more error into the free energy and entropy functions, such estimates were only used when it could be demonstrated that the resulting entropies were not unduly sensitive to the choice of  $\gamma$ . For the details of the calculations, the reader is referred elsewhere.<sup>24</sup> For convenience, it is desirable to con-

(23) Th. Ackermann and F. Schreiner, *Z. Elektrochem.*, **62**, 1143 (1958).

(24) C. M. Criss, Ph.D. Thesis, Purdue University, 1961. Additional or revised data reported since the original calculations were made are given in Table I.

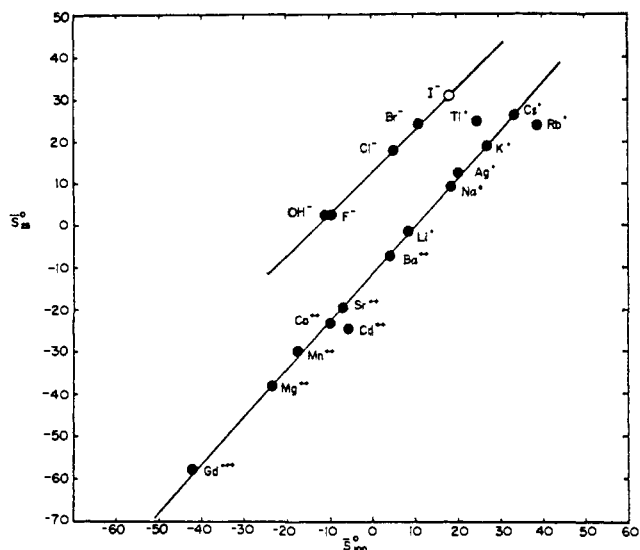


Fig. 1.—Correspondence diagram illustrating the linear relationship between the absolute entropies of simple ions at 25 and 100°.  $I^-$  has been assigned in order to use data on  $Cs^+$ ,  $Ti^+$ , and  $Cd^{+2}$ ;  $Pb^{+2}$  has been omitted since the hydrolysis state of this ion is so uncertain (data are from Table I).

struct a set of *ionic* entropies at each temperature, and this has been done by fixing the entropy of  $H^+(aq)$  at each temperature. This division, which in effect sets a standard state at each temperature, was not made completely arbitrary and will be discussed further in a later section.

### Discussion

**A. Simple Ions.**—The proposed correspondence principle (eq. 4) can best be tested by the data on cations from Table I. It soon became obvious that if the entropy of  $H^+(aq)$  was fixed by trial and error at a certain value at each temperature, only the first two terms of eq. 4 were required to relate the entropies at 60, 100, and 150° accurately and within the experimental errors. Consequently, experimentally, a linear relationship exists between the entropies of all of the known cations at 25° to the entropies at other temperatures up to 150°. This relationship is demonstrated over a wide range of entropy values at 100° in Fig. 1; similar correspondence diagrams can be constructed at 60 and 150°. The same situation exists for the simple anions although the constants of eq. 4 are different from the cations. The demonstration is not nearly so dramatic for simple anions because there are so few examples.

The difference in behavior of monatomic anions and cations may be due to the fact that the hydration shells are constructed differently for these two species. The effect is quite dramatic when the heat capacities are compared for a series of ions, wherein a "saturation" effect is seen in the anions. This comparison is made in Table II; it can be seen that the contribution to the heat capacity of a solute is essentially independent of the size of the anion. This simply means that the rate of change of entropy with temperature will be different for anions than that for cations. Consequently, the entropies of anions as a class will not be simply related to the entropies of cations as a class at higher temperatures. (A similar phenomena exists for complex ions.) It should also be noted that while the charge effect on  $\bar{S}_2^0$  and  $\bar{C}_{p_2}^0$  is the same (i.e.,  $(d\bar{S}_2^0/dt)$  and  $(d\bar{C}_{p_2}^0/dt)$

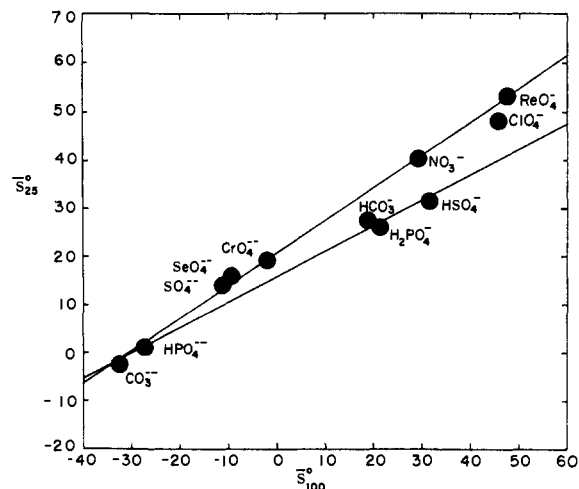


Fig. 2.—Correspondence diagrams illustrating the linear relationship between the absolute entropies of complex oxygenated anions at 25 and 100° (data are from Table I).

have the same sign) the radius or size effect is just the opposite for  $\bar{C}_{p_2}^0$  and  $\bar{S}_2^0$ .

It is important to note that the choice of standard states given in Table I corresponds to an ionic entropy of  $-5.0 \text{ cal. mole}^{-1} \text{ deg.}^{-1}$  for the hydrogen ion at 25°. This falls within the range of values ( $-2.1$  to  $-6.3$ ) suggested by others for the "absolute" ionic entropy of  $H^+(aq)$ .<sup>14, 18, 25-27</sup> Consequently, for consistency, the values of ionic entropy in use here will be assumed to be on the "absolute" scale. The consequences of this assignment with regard to the ionic partial molal heat capacities will be discussed elsewhere.<sup>12</sup> However, it was observed that other assignments of the entropy of  $H^+$  at the various temperatures different from the ones given in Table I do not lead to a simple linear correspondence relationship.

**B. Oxygenated Complex Ions.**—It would be surprising to find that the correspondence principle could be accurately applied to complex ions since these species have internal degrees of freedom, and their internal contributions to the entropies and heat capacities would be expected to vary from ion to ion. However, good correlations exist on the entropies of these species<sup>16-18</sup> at 25° which tends to suggest that in solution such variations are minor. While data at higher temperatures for complex ions are sparse, those which are available suggest that the linear correspondence principle might be a useful approximation. Entropy diagrams at 100° are summarized in Fig. 2. The data for  $IO_3^-$  have not been included<sup>28</sup> because it does not appear that the entropy of the iodate is correct at 25° from separate considerations.<sup>16, 17</sup> At present, there are only two entropies of  $XO_n^{-m}$  species available at 150°,  $ReO_4^-$  and  $SO_4^{2-}$ . These two data can hardly be used as a proof of the validity of the correspondence principle, but can be used to fix the important first two constants in eq. 4.

**C. Other Complex Ions.**—Between 25, 60, and 100°, there are sufficient data to demonstrate a linear en-

(25) R. W. Gurney, "Ionic Processes in Solution," McGraw-Hill Book Co., Inc., New York, N. Y., 1953.

(26) J. C. Goodrich, F. M. Goyan, E. E. Morse, R. G. Preston, and M. B. Young, *J. Am. Chem. Soc.*, **72**, 4411 (1950).

(27) J. M. Sherfey, private communication.

(28) Thermodynamically, this does not prevent the calculated partial molal entropy of the iodate ion from being used as an intermediate in the calculations of the entropies of other species at other temperatures in Table I.

TABLE I  
 EXPERIMENTAL IONIC ENTROPIES IN WATER AT ELEVATED TEMPERATURES<sup>a</sup>

Ion	Source	$\bar{S}_2^{\circ(60)}$		$\bar{S}_2^{\circ(100)}$		$\bar{S}_2^{\circ(160)}$		$\bar{S}^{\circ(200)}$		
		Exptl.	Adopted	Exptl.	Adopted	Exptl.	Adopted			
H <sup>+</sup>	Assigned	...	-2.5	...	2.0	...	6.5			
Li <sup>+</sup>	LiBr ( $\bar{C}_{p_2}^{\circ}$ )	2.3 ± 1	2.3	8.3 ± 1	8.3	14.2 ± 1.3	14.2			
Na <sup>+</sup>	NaCl ( $\bar{C}_{p_2}^{\circ}$ )	13.3 ± 0.4	13.3	18.8 ± 0.4	18.8	23.7 ± 0.9	23.7			
K <sup>+</sup>	KCl (soly.)	22.1 ± 1.5	22.1	27.1 ± 1.2	27.1	Assigned	32.0			
Rb <sup>+</sup>	Rb <sub>2</sub> PtCl <sub>6</sub> (soly.)	29.8 ± 2.1	29.8	39.0 ± 4	39.0					
Cs <sup>+</sup>	CsI ( $\bar{C}_{p_2}^{\circ}$ ) <sup>b</sup>	29.5 ± 0.5	29.5	33.7 ± 0.5	33.7					
Tl <sup>+</sup>	TlI (soly.)	24.9 ± 2.5	24.9	24.9 ± 5.2	24.9					
Ag <sup>+</sup>	AgCl (soly.)	15.7 ± 1.2	15.7	20.6 ± 2.3	20.6	30.3 ± 1.4	30.3			
Mg <sup>+2</sup>	MgCl <sub>2</sub> ( $\bar{C}_{p_2}^{\circ}$ )	-32.6 ± 1.0	-32.6	-23.4 ± 1.0	-23.4	-14.1 ± 1.9	-14.1			
Ca <sup>+2</sup>	CaCl <sub>2</sub> ( $\bar{C}_{p_2}^{\circ}$ )	-18.3 ± 0.4	-18.3	-9.9 ± 0.9	-9.9	-1.9 ± 1.9	-1.9			
	Ca(OH) <sub>2</sub> (eq.)	-14.8 ± 2.0		-0.4						
Sr <sup>+2</sup>	SrCl <sub>2</sub> ( $\bar{C}_{p_2}^{\circ}$ )	-14.8 ± 1.5	-14.8	-6.9 ± 1.5	-6.9	0.5 ± 1.9	0.5			
Ba <sup>+2</sup>	BaCl <sub>2</sub> ( $\bar{C}_{p_2}^{\circ}$ )	-3.0 ± 0.3	-3.0	4.4 ± 0.5	4.4	10.9 ± 2	10.9			
Cd <sup>+2</sup>	CdI <sub>2</sub> (soly.)			-5.7 ± 4.6	-5.7					
Mn <sup>+2</sup>	Mn(IO <sub>3</sub> ) <sub>2</sub> (soly.)	-25.8 ± 2	-25.8	-17.5 ± 3	-17.5					
Pb <sup>+2</sup>	PbCl <sub>2</sub> (soly.)	6.4 ± 4.5	2.1	23.3 ± 4	18.6					
	PbI <sub>2</sub> (soly.)	-2.2 ± 3.6		13.8 ± 4						
Gd <sup>+3</sup>	GdCl <sub>3</sub> ( $\bar{C}_{p_2}^{\circ}$ ) <sup>c</sup>	-52 ± 1	-52	-42.2 ± 1	-42.2					
F <sup>-</sup>	NaF (soly.)	-2.6 ± 1.8	-2.3	-10.1 ± 3.2	-9.4	-18.6 ± 1	-18.6			
	KF ( $\bar{C}_{p_2}^{\circ}$ ) <sup>d</sup>	-2.3 ± 0.4		-9.4 ± 0.4						
Cl <sup>-</sup>	HCl ( $\bar{C}_{p_2}^{\circ}$ )	12.4 ± 0.3	12.6	5.0 ± 0.7	5.2	-3.9 ± 1.3	-3.2			
	HCl (e.m.f.)	12.86		4.91						
Br <sup>-</sup>	HBr (e.m.f.) <sup>e</sup>	18.7		10.8		-2.4		2.5		HCl(aq) = -0.8 ± 2
	AgBr (soly.)	21.5 ± 1.2		17.8 ± 2.4		2.7 ± 1.3		2.7		HBr(aq) = 4.9
	NaBr ( $\bar{C}_{p_2}^{\circ}$ )	18.7 ± 0.6		11.2 ± 0.7						
I <sup>-</sup>	Assigned (see Cs <sup>+</sup> )		25.1		18.3					
OH <sup>-</sup>	NaOH ( $\bar{C}_{p_2}^{\circ}$ )	-3.2 ± 0.4	-3.2	-11.2 ± 0.7	-11.2	-20.8 ± 1.3	-19.7			
	H <sub>2</sub> O ( <i>K</i> <sub>ion</sub> )	-4.9 ± 3.0		-13.3 ± 3						
ReO <sub>4</sub> <sup>-</sup>	NaReO <sub>4</sub> ( $\bar{C}_{p_2}^{\circ}$ ) <sup>f</sup>	51.0 ± 0.4	51.0	47.7 ± 0.4	47.7	44.6 ± 1 <sup>g</sup>	44.6			
	HReO <sub>4</sub> ( $\bar{C}_{p_2}^{\circ}$ ) <sup>f</sup>	50.9 ± 0.4		46.3 ± 1						
	KReO <sub>4</sub> (soly.)	51.4 ± 1.8		50.0 ± 1.6						
ClO <sub>4</sub> <sup>-</sup>	KClO <sub>4</sub> (soly.)	50.6 ± 4.8	50.6	45.9 ± 4.3	45.9					
IO <sub>3</sub> <sup>-</sup>	Ba(IO <sub>3</sub> ) <sub>2</sub> (soly.)	33.6 ± 2	33.6	31.9 ± 2	31.9					
NO <sub>3</sub> <sup>-</sup>	NaNO <sub>3</sub> ( $\bar{C}_{p_2}^{\circ}$ )	35.2 ± 0.6	35.2	28.9 ± 0.9	28.9					
HSO <sub>3</sub> <sup>-</sup>	CO <sub>2</sub> (aq) (e.m.f.) <sup>h</sup>	23.0	23.0							
	( <i>K</i> <sub>eq</sub> ) <sup>k</sup>			18.5	18.5	15.2	15.2	H <sup>+</sup> + HCO <sub>3</sub> <sup>-</sup> = 23.6 ± 4		
HSO <sub>4</sub> <sup>-</sup>	HSO <sub>4</sub> <sup>-</sup> ( <i>K</i> <sub>ion</sub> ) <sup>h</sup>	30.9		29.0		27.7				
		32.4	32.4	31.5	31.5	31.7	31.7			
H <sub>2</sub> PO <sub>4</sub> <sup>-</sup>	H <sub>2</sub> PO <sub>4</sub> <sup>-</sup> , HPO <sub>4</sub> <sup>-2</sup> (e.m.f.) <sup>g</sup>	20.7	20.7							
	NaH <sub>2</sub> PO <sub>4</sub> ( $\bar{C}_{p_2}^{\circ}$ ) <sup>i</sup>			21.1	21.1					
SO <sub>4</sub> <sup>-2</sup>	Ag <sub>2</sub> SO <sub>4</sub> (eq.)	5.5		-8.8		-34.4		Ag <sub>2</sub> SO <sub>4</sub> (aq) = 19.7		
	CaSO <sub>4</sub> ·0.5H <sub>2</sub> O (soly.)	3.2 ± 1.8		-15.8 ± 4.3		-16.7 ± 2				
	CaSO <sub>4</sub> ·2H <sub>2</sub> O (soly.)	-2.9 ± 1.5	1.9	-10.8 ± 1.3	-11.2		-25.3			
	CaSO <sub>4</sub> (soly.)			-0.1 ± 5.4		-24.9 ± 5		CaSO <sub>4</sub> (aq) = -32.5 <sup>l</sup>		
		6.4 ± 4 <sup>i</sup>		-11.2 ± 4 <sup>i</sup>		-26.2 ± 2 <sup>i</sup>				
	BaSO <sub>4</sub> (soly.)	2.0 ± 2.2		-13.5 ± 4.5						
SeO <sub>4</sub> <sup>-2</sup>	Ag <sub>2</sub> SeO <sub>4</sub> (soly.)	-4.8 ± 3.0	-4.8	-9.3 ± 3	-9.3					
PtCl <sub>6</sub> <sup>-2</sup>	K <sub>2</sub> PtCl <sub>6</sub> (soly.)	58.0 ± 3.2	52.4	48.2 ± 4.6	51.0					
	Cs <sub>2</sub> PtCl <sub>6</sub> (soly.)	46.7 ± 4		53.8 ± 4						
CrO <sub>4</sub> <sup>-2</sup>	Ag <sub>2</sub> CrO <sub>4</sub> (soly.)			-1.9 ± 4.5	-1.9					
CO <sub>3</sub> <sup>-2</sup>	HCO <sub>3</sub> <sup>-</sup> (e.m.f.) <sup>h</sup>	-17.5	-17.5							
	( <i>K</i> <sub>eq</sub> ) <sup>k</sup>			-32.5	-32.5	-49.6	-49.6	H <sup>+</sup> + CO <sub>3</sub> <sup>-2</sup> = -53.8 ± 6		
HPO <sub>4</sub> <sup>-2</sup>	HPO <sub>4</sub> <sup>-2</sup> , H <sub>2</sub> PO <sub>4</sub> <sup>-</sup> (e.m.f.) <sup>g</sup>	-11.9	-11.9							
	Na <sub>2</sub> HPO <sub>4</sub> ( $\bar{C}_{p_2}^{\circ}$ ) <sup>i</sup>			-27.6	-27.6					

<sup>a</sup> Data are from ref. 24 except as indicated; ionic entropies in units of cal. mole<sup>-1</sup> deg.<sup>-1</sup>; heat capacities for pure substances are mostly from K. K. Kelley, U. S. Bureau of Mines Bulletin 476, U. S. Government Printing Office, Washington, D. C., 1949. <sup>b</sup> R. E. Mitchell and J. W. Cobble, *J. Am. Chem. Soc.*, **86**, 5401 (1964), paper VII of this sequence. <sup>c</sup> E. C. Jekel, C. M. Criss, and J. W. Cobble, *ibid.*, **86**, 5404 (1964), paper VIII of this sequence. <sup>d</sup> Th. Ackermann, private communication. <sup>e</sup> Ref. 8. <sup>f</sup> J. C. Ahluwalia and J. W. Cobble, *J. Am. Chem. Soc.*, **86**, 5377 (1964), paper II of this sequence. <sup>g</sup> Calculated from the  $\Delta C_p$  compilation of Harned and Owen, ref. 10, pp. 667, 690, and 758. The average value of  $\bar{C}_{p_2}^{\circ}$  for undissociated H<sub>2</sub>PO<sub>4</sub>(aq) between 25 and 60° was taken as 26 cal. mole<sup>-1</sup> deg.<sup>-1</sup> by extrapolation from the high concentration  $\bar{C}_{p_2}^{\circ}$  data of E. P. Egan, Jr., B. B. Luff, and Z. T. Wakefield, *J. Phys. Chem.*, **62**, 1091 (1958). <sup>h</sup> There are two sets of equilibrium constant calculations on the HSO<sub>4</sub><sup>-</sup> ion (ref. 11); the larger values are derived from the same data by another method of calculation given by M. H. Lietzke and R. W. Stoughton, *J. Phys. Chem.*, **63**, 1190 (1959). The absolute entropy of HSO<sub>4</sub><sup>-</sup>(aq) has been changed (footnote c) at 25° from 35.3 to 31.6 cal. mole<sup>-1</sup> deg.<sup>-1</sup>. <sup>i</sup> The  $\bar{C}_{p_2}^{\circ}$  of NaReO<sub>4</sub>(aq) between 100 and 150° was estimated from the 0 to 100° data.<sup>j</sup> This can be done with some confidence since  $\bar{C}_{p_2}^{\circ}$  is changing only slowly with temperature between 60 and 100°. <sup>k</sup> Unpublished data of R. E. Mitchell and J. W. Cobble; see R. E. Mitchell, Ph.D. Thesis, Purdue University, 1963. <sup>l</sup> Data on CO<sub>3</sub><sup>-2</sup> and HCO<sub>3</sub><sup>-</sup> at 100° and above are from the measurements of B. N. Ryzenko, *Geokhimiya*, No. 2, 137 (1963); required solubility data on CO<sub>2</sub>(aq) are from W. Wiebe and V. L. Gaddy, *J. Am. Chem. Soc.*, **61**, 315 (1939), and S. D. Malinin, *Geokhimiya* (Engl. Transl.), No. 3, 292 (1959). <sup>m</sup> W. L. Marshall, R. Slusher, and E. V. Jones, *J. Chem. Eng. Data*, **9**, 187 (1964).

entropy relationship for acid oxy anions of the class XO<sub>n</sub>(OH)<sub>1-m</sub>. These data appear (Fig. 2) to form a correspondence diagram roughly parallel to the XO<sub>n-m</sub> class of ions, but displaced towards more negative

entropies. At higher temperatures there exist data for only one species, HSO<sub>4</sub><sup>-</sup>. Heat capacity measurements on this important class of species are currently being carried out in these laboratories.

TABLE II  
SOME PARTIAL MOLAL IONIC ENTROPIES AND HEAT CAPACITIES AT 25°

Ion	$\bar{S}_2^\circ = \bar{C}_{p_2}^\circ \equiv 0$ for $H^+(aq)$		Crystal radius, Å. <sup>b</sup>
	$\bar{S}_2^\circ$ , cal. mole <sup>-1</sup> deg. <sup>-1</sup>	$\bar{C}_{p_2}^\circ$ , cal. mole <sup>-1</sup> deg. <sup>-1</sup>	
H <sup>+</sup>	0.0	0.0	...
Li <sup>+</sup>	3	14	0.60
Na <sup>+</sup>	14	8	0.95
K <sup>+</sup>	25	2	1.33
Cs <sup>+</sup>	32	-6	1.69
Mg <sup>+2</sup>	-28	4	0.65
Ba <sup>+2</sup>	3	-13	1.35
F <sup>-</sup>	-2	-28	1.36
Cl <sup>-</sup>	13	-30	1.81
Br <sup>-</sup>	19	-31	1.95
I <sup>-</sup>	26	-31	2.16

<sup>a</sup>  $\bar{C}_{p_2}^\circ$  data are from the compilation given in ref. 19, p. 652, except for cesium where the data are obviously in error. A value of  $\bar{C}_{p_2}^\circ$  for CsI(aq) of -36.6 cal. mole<sup>-1</sup> deg.<sup>-1</sup> has been used by Mitchell and Cobble, footnote b, Table I.  $\bar{C}_{p_2}^\circ$  for F<sup>-</sup>(aq) is from heat capacity data on KF(aq) (Th. Ackermann, private communication). Data on Ba<sup>+2</sup>(aq) are from  $\bar{C}_{p_2}^\circ$  of BaCl<sub>2</sub>(aq).<sup>8</sup> Entropy values are from W. M. Latimer, "Oxidation-Reduction Potentials," 2nd Ed., Prentice-Hall, New York, N. Y., 1952. <sup>b</sup> Ionic crystal radii are from L. Pauling, "Nature of the Chemical Bond," Cornell University Press, 3rd Ed., Ithaca, N. Y., 1960, p. 514.

present treatment anticipates the existence of such corresponding states, with respect to changing temperature, dielectric constant (solvent), pressure, and density, or any other important variable of the system.

### Summary

Although information on some of the various classes of ions in aqueous solutions are somewhat sparse, the data are nevertheless convincing that the linear entropy relationships between ions at various temperatures are real and perhaps universal. It is perhaps worthwhile to summarize a correspondence principle as follows. *A standard state can be chosen at every temperature such that the partial molal entropies of one class of ions at that temperature are linearly related to the corresponding entropies at some reference temperature.*<sup>32</sup>

$$\bar{S}^\circ_{(t_2)} = a_{(t_2)} + b_{(t_2)}\bar{S}^\circ_{(t_1)} \quad (7)$$

The surprising feature of this correspondence principle is not the qualitative features of eq. 7, but the accuracy of its application (to within  $\pm 0.5$  cal. mole<sup>-1</sup> deg.<sup>-1</sup> for simple ions up to 150°).

The constants for eq. 7 defined by the data of Table I are summarized in Table III; also included are estimated values obtained by extrapolations to higher temperatures.

TABLE III

SUMMARY OF ENTROPY CONSTANTS FOR EQ. 7 (IN CAL. MOLE<sup>-1</sup> DEG.<sup>-1</sup>)

t, °C.	Simple cations		Simple anions and OH <sup>-</sup>		Oxy anions, XO <sub>n</sub> <sup>-m</sup>		Acid oxy anions, XO <sub>n</sub> (OH) <sub>1-m</sub>		Std. state (entropy of H <sup>+</sup> (aq) <sup>29</sup> )
	a <sub>(t)</sub>	b <sub>(t)</sub>	a <sub>(t)</sub>	b <sub>(t)</sub>	a <sub>(t)</sub>	b <sub>(t)</sub>	a <sub>(t)</sub>	b <sub>(t)</sub>	
25	0	1.000	0	1.000	0	1.000	0	1.000	-5.0
60	3.9	0.955	-5.1	0.969	-14.0	1.217	-13.5	1.380	-2.5
100	10.3	0.876	-13.0	1.000	-31.0	1.476	-30.3	1.894	2.0
150	16.2	0.792	-21.3	0.989	-46.4	1.687	(-50.0) <sup>b</sup>	(2.381) <sup>b</sup>	6.5
200	(23.3) <sup>b</sup>	(0.711) <sup>b</sup>	(30.2) <sup>b</sup>	(0.981) <sup>b</sup>	(-67.0) <sup>b</sup>	(2.020) <sup>b</sup>	(-70.0) <sup>b</sup>	(2.960) <sup>b</sup>	(11.1) <sup>b</sup>

<sup>a</sup> The entropy of H<sup>+</sup>(aq) is assigned. <sup>b</sup> These constants were estimated by extrapolation of corresponding values of a<sub>(t)</sub> and b<sub>(t)</sub> from lower temperatures and are subject to greater error.

Unfortunately, data on other complex ions are at present lacking, with the exception of PtCl<sub>6</sub><sup>-2</sup>(aq). Since the interrelationship of this complex ion to other species is not known at present, general conclusions cannot be given on the high temperature behavior of other ions of this type. There is some evidence that the entropies of oxy cations (e.g., UO<sub>2</sub><sup>+2</sup>) lie near the correspondence diagrams for simple cations.<sup>29</sup>

### Nonaqueous Solvents

It is interesting to examine the consequences of expanding the general correspondence equation (eq. 3) about a reference dielectric constant *D*, at constant temperature.

$$\bar{S}^\circ_{(D_1)} = a_{(D_1)} + b_{(D_1)}\bar{S}^\circ_{(D_2)} + c_{(D_1)}(\bar{S}^\circ_{(D_2)})^2 + \dots \quad (6)$$

One might thus expect to find simple relationships existing between the entropies of ions in water to those in other nonaqueous solvents. Two such cases are known at present. Latimer and Jolly<sup>30</sup> and Jakuszewski and Taniowska-Osinska<sup>31</sup> have found empirically simple linear entropy relationships for ions in liquid ammonia and methanol, respectively. The

(29) From calculations on the hydrolysis of UO<sub>2</sub><sup>+2</sup>, see ref. 12b.

(30) W. M. Latimer and W. L. Jolly, *J. Am. Chem. Soc.*, **75**, 4147 (1953).

(31) B. Jakuszewski and S. Taniowska-Osinska, *Lod. Towarz. Nauk Wydzial III, Acta Chim.*, **7**, 32 (1961).

The constants summarized in Table IV should be considered preliminary in the sense that more accurate data, particularly at the higher temperatures, will lead to revisions from time to time.<sup>33</sup>

### Entropies at Temperatures above 150°

If the correspondence principle has general validity, as is proposed by this research, then one can expect it to hold at temperatures all the way up to the critical point, and beyond, in steam systems. At present there are not sufficient data above 150° to make a rigorous test. However, if it is assumed that the linear relationship given by eq. 7 is valid, then it is possible that some type of extrapolation of the constants a<sub>(t)</sub> and b<sub>(t)</sub> with temperature could lead to estimations of the ionic entropies above 150°. It turns out that a plot of these constants against temperature is nearly linear up to 150° except around 60°. This behavior at 60° is to be

(32) It can be seen that such a principle does not follow from the thermodynamic definition of the partial molal heat capacity

$$\bar{S}^\circ_{(t_2)} = \bar{S}^\circ_{(t_1)} + \int_{t_1}^{t_2} \bar{C}_{p_2}^\circ d \ln T$$

unless b<sub>(t)</sub> in eq. 7 is unity, which is generally not the case (see Table III).

(33) It can be noted here that there is disagreement on the heat capacity of H<sup>+</sup>(aq) at 100° and above from two separate sets of measurements on the heat capacity of HCl(aq); see footnote f, Table I.

expected since much of the  $\overline{C}_{p_1}^\circ$  data on ionic solutes pass through a maximum near this temperature. By this empirical extrapolation, entropy constants have been estimated up to 200° (Table III). The validity of such extrapolations can be tested in a limited way by comparison of the predicted and experimental entropies for the few solutes known at 200° (Table IV).

The agreement between the predicted and observed values of  $\overline{S}_2^\circ$  at 200° is quite satisfactory and suggests that the general validity of the correspondence principle holds up to at least 200°.

It is to be noted that once the extrapolation method has been decided upon, values for the constants  $a_{(t)}$  and  $b_{(t)}$  above 150° are fixed and are not arbitrarily defined. Consequently, the test given in Table IV is rigorous for the species listed, although necessarily limited.

TABLE IV  
COMPARISON OF PREDICTED AND OBSERVED ENTROPIES AT 200°

Ions	$\overline{S}_2^\circ$ (obsd), <sup>a</sup> cal. mole <sup>-1</sup> deg. <sup>-1</sup>	$\overline{S}_2^\circ$ (calcd), <sup>b</sup> cal. mole <sup>-1</sup> deg. <sup>-1</sup>
H <sup>+</sup> , CO <sub>3</sub> <sup>-2</sup>	-54 ± 6	-61
H <sup>+</sup> , Cl <sup>-</sup>	-1 ± 2	-1.3
H <sup>+</sup> , Br <sup>-</sup>	5 ± 2	4.7
H <sup>+</sup> , OH <sup>-</sup>	-16 ± 4	-16.7
2Ag <sup>+</sup> , SO <sub>4</sub> <sup>-2</sup>	20 ± 4	21.7
H <sup>+</sup> , HCO <sub>3</sub> <sup>-</sup>	24 ± 4	23.1
Ca <sup>+2</sup> , SO <sub>4</sub> <sup>-2</sup>	-32	-31.7

<sup>a</sup> From Table I; some data are available in the literature on the solubility of AgCl up to 200°. However, at the present time it is almost impossible to account quantitatively for the hydrolysis of Ag<sup>+</sup> at these high temperatures under the conditions of the experiments. <sup>b</sup> Calculated from eq. 7 using the constants given in Table III.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY, LAFAYETTE, INDIANA]

## The Thermodynamic Properties of High Temperature Aqueous Solutions. V. The Calculation of Ionic Heat Capacities up to 200°. Entropies and Heat Capacities above 200°<sup>1</sup>

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Equations are given for calculating heat capacities at 25° and at elevated temperatures from the correspondence principle for entropies previously developed.

### Introduction

Probably the most useful function for predicting the thermodynamic properties of electrolyte solutions at higher temperatures is the partial molal heat capacity,  $\overline{C}_{p_1}^\circ$ , as a function of temperature. Consider the situation when it is desirable to know the free energy of a reaction at some elevated temperature,  $t_2$ , when it is known at  $t_1$

$$\Delta F^\circ_{(t_2)} = \Delta F^\circ_{(t_1)} + \left[ \overline{\Delta C_p}^\circ \right]_{t_1}^{t_2} \times \left[ \Delta T - \Delta S^\circ_{(t_1)} \Delta T - T_2 \overline{\Delta C_p}^\circ \right]_{t_1}^{t_2} \ln \frac{T_2}{T_1} \quad (1)$$

or combining terms

$$\Delta(\Delta F^\circ) = -\Delta S^\circ_{(t_1)} \Delta T + \left[ \overline{\Delta C_p}^\circ \right]_{t_1}^{t_2} \times \left[ \Delta T - T_2 \ln \frac{T_2}{T_1} \right] \quad (2)$$

where  $\left[ \overline{\Delta C_p}^\circ \right]_{t_1}^{t_2}$  is the average value of  $\Delta C_p^\circ$  between  $t_1$  and  $t_2$ .

The knowledge of  $\Delta F^\circ$  and  $\Delta S^\circ$  at one temperature and a value of the average heat capacity change between the two temperatures are sufficient to calculate  $\Delta F^\circ_{(t_2)}$ .<sup>3</sup> However, there are so few data at present on  $\overline{C}_{p_2}^\circ$  as a function of temperature that the method cannot be used for any significant number of electro-

lytes. Furthermore, although a greater number of  $\overline{C}_{p_1}^\circ$  values are known at just one temperature, 25°, such data cannot be reliably used at other temperatures since in general  $\overline{C}_{p_2}^\circ$  varies considerably with temperature.

In a previous communication, a correspondence principle for entropies for higher temperature solutions was developed.<sup>4</sup> It immediately follows that whenever the entropy of an ion is known or can be accurately predicted at two temperatures, the average value of the heat capacity  $\left[ \overline{C}_{p_2}^\circ \right]_{t_1}^{t_2}$  between those temperatures can be calculated. The purpose of this communication is to extend the entropy correspondence principle to the calculation and prediction of  $\overline{C}_{p_2}^\circ$  and  $\overline{C}_{p_1}^\circ$  for electrolytes over extended temperature ranges.

### The Correspondence Principle and Heat Capacity Equations

The linear correspondence of entropy for ions between 25° and  $t_2$  can be written as<sup>4</sup>

$$S^\circ_{(t_2)} = a_{(t_2)} + b_{(t_2)} S^\circ_{25}(\text{abs.}) \quad (3)$$

$S^\circ_{25}(\text{abs.})$  refers to the ionic entropies on the "absolute" scale;  $S^\circ_{25}(\text{abs.}) = S^\circ_{25}(\text{conventional}) - 5.0Z$ , where  $Z$  is the ionic charge.<sup>5</sup> The average value of the partial molal heat capacity between 25° and  $t_2$  is

$$\left[ \overline{C}_{p_2}^\circ \right]_{25}^{t_2} = \frac{S^\circ_{(t_2)} - S^\circ_{(25)}}{\ln T_2 / 298.2} \quad (4)$$

(4) C. M. Criss and J. W. Cobble, *J. Am. Chem. Soc.*, **86**, 5385 (1964).

(5) Hereafter, entropies will be considered as being on an "absolute" scale unless specifically noted otherwise.

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(2) Partly from the Ph.D. Thesis of Cecil M. Criss, Purdue University, 1961.

(3) Strictly speaking,  $\overline{\Delta C_p}^\circ$  in the linear temperature term will be somewhat different from the value of the function in the  $\ln T$  term. In practice, this difference is not significant between 25 and 200°, and in 50° steps at temperatures above 200°.