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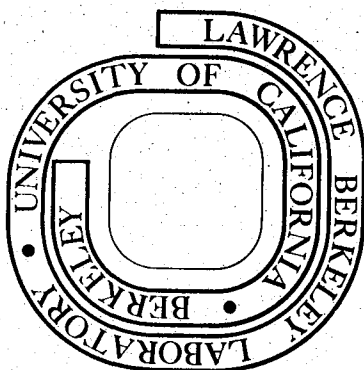
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THERMODYNAMICS OF ELECTROLYTES. X. ENTHALPY AND  
THE EFFECT OF TEMPERATURE ON THE ACTIVITY COEFFICIENTS

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(Abstract)

Heat of dilution and of solution data are fitted to the form of equation corresponding to that used successfully for activity and osmotic coefficients over a wide range of concentration. The resulting parameters give the change with temperature of the activity and osmotic coefficients. Results are reported for 84 electrolytes of 1-1, 2-1, 3-1, and 2-2 valence types.

(Key Words)

Enthalpy, Heat of Dilution, Heat of Solution,  
Activity Coefficient, Electrolyte, Thermodynamics



## Introduction

While the thermodynamic relationship between the partial molal enthalpy and the temperature derivative of the activity coefficient is well known, it is convenient to use the same basic equation for both. Then the temperature derivative of each parameter in the equation for the activity coefficient is just the corresponding parameter for the enthalpy equation. We have derived the detailed equations in connection with our analysis<sup>1</sup> of the properties of aqueous NaCl to 300°C. For most solutes we have only heat of dilution data at or near 25°C. In the present paper these data for 84 electrolytes are fitted to the enthalpy equation corresponding to the equations used in papers II<sup>2</sup> and III<sup>3</sup> of this series for the osmotic and activity coefficients for 237 solutes. The parameters given below allow the convenient calculation of properties at other temperatures not too different from 25°C.

It was shown in paper IV<sup>4</sup> that this system of equations was convenient and effective for mixed electrolytes and that the important parameters were those for pure electrolytes. Thus the results of this paper will allow calculations of mixed electrolyte properties at temperatures other than 25°C.

## Equations

The derivation of equations for enthalpy change with molality has been given in paper VII.<sup>1</sup> For our present purposes, including various valence types, an additional term (not used for NaCl) is sometimes needed and certain

rearrangements are convenient. Hence the derivations are given briefly below.

The total excess Gibbs energy is

$$G^{ex} = n_w v m R T (1 - \phi + \ln \gamma_{\pm}) \quad (1)$$

where  $n_w$  is the number of kg of solvent,  $m$  is the molality,  $R$  is the gas constant,  $T$  designates the temperature in °K,  $\phi$  is the osmotic coefficient, and  $\gamma_{\pm}$  is the activity coefficient.

From papers II,<sup>2</sup> and III<sup>3</sup> of this series the equations for  $\phi$  and  $\ln \gamma_{\pm}$  of a pure electrolyte are

$$\phi - 1 = -|z_M z_X| A_{\phi} \frac{I^{1/2}}{1 + bI^{1/2}} + m \frac{2v_M v_X}{v} [\beta_{MX}^{(0)} + \beta_{MX}^{(1)} \exp(-\alpha_1 I^{1/2}) + \beta_{MX}^{(2)} \exp(-\alpha_2 I^{1/2})] + m^2 \frac{2(v_M v_X)^{3/2}}{v} C_{MX}^{\phi} \quad (2)$$

Here  $z_M$  and  $z_X$  are the charges (in electronic units) on ions  $M$  and  $X$  while  $v_M$  and  $v_X$  are the numbers of these ions in the formula; also  $v = v_M + v_X$ . The term in  $\beta^{(2)}$  is used only for 2-2 and higher valence types. Where the term in  $\beta^{(2)}$  is omitted, the subscript to  $\alpha$  is also omitted.

$$\begin{aligned} \ln \gamma_{\pm} = & -|z_M z_X| A_{\phi} \left( \frac{I^{1/2}}{1 + bI^{1/2}} + \frac{2}{b} \ln(1 + bI^{1/2}) \right) + \\ & m \frac{2v_M v_X}{v} \left( 2\beta_{MX}^{(0)} + \frac{2\beta_{MX}^{(1)}}{\alpha_1^2 I} [1 - (1 + \alpha_1 I^{1/2}) \right. \\ & \left. \frac{\alpha_1^2 I}{2}] \exp(-\alpha_1 I^{1/2}) \right] + \frac{2\beta_{MX}^{(2)}}{\alpha_2^2 I} [1 - (1 + \alpha_2 I^{1/2}) \\ & \left. \frac{\alpha_2^2 I}{2}] \exp(-\alpha_2 I^{1/2}) \right] + \frac{3m^2}{2} \left( \frac{2(v_M v_X)^{3/2}}{v} \right) C_{MX}^{\phi}. \quad (3) \end{aligned}$$

I is the ionic strength,

$$I = \frac{1}{2} \sum_i m_i z_i^2,$$

and  $A_\phi$  is the Debye-Hückel coefficient for the osmotic function given as

$$A_\phi = \frac{1}{3} \left( \frac{2\pi N_0 \rho_w}{1000} \right)^{1/2} \left( \frac{e^2}{DkT} \right)^{3/2} = \frac{A_Y}{3} \quad (4)$$

where  $N_0$  is Avagadro's number,  $\rho_w$  is the density of the solvent and D the static dielectric constant of pure water, k is Boltzmann's constant, and e is the absolute electronic charge. Since the values of  $\nu_M$ ,  $\nu_X$ , and  $\nu$  for any symmetrical electrolyte are 1,1 and 2 the factor  $(2\nu_M\nu_X/2)$  is then unity.

The leading term in equations (2) and (3) arises from the long-range electrostatic interactions; the coefficients  $\beta_{MX}^{(0)}$ ,  $\beta_{MX}^{(1)}$ , and  $\beta_{MX}^{(2)}$  account for various types of short-range interactions between pairs of ions (M-X, M-M, and X-X), and for indirect forces arising from the solvent; the third coefficient  $C_{MX}^\phi$  is for triple ion interactions and is important only at high concentrations. The parameter b was given the value 1.2 for all electrolytes,  $\alpha_1$  is 2.0 for all except 2-2 solutes (where it is 1.4), and  $\alpha_2$  is 12.0; b,  $\alpha_1$ , and  $\alpha_2$  are taken as temperature independent. The quantities  $\beta_{MX}^{(0)}$ ,  $\beta_{MX}^{(1)}$ ,  $\beta_{MX}^{(2)}$ , and  $C_{MX}^\phi$  are adjusted for a given salt at fixed temperature by a least-square fit of osmotic and/or activity coefficient data.



Equations (2) and (3) are consistent with the standard states adopted for this study which are the pure solvent at the same temperature and pressure as the solution and for the solute the limiting state in which  $\gamma_{\pm}$  approaches unity as the concentration becomes infinitely dilute, this to apply at every temperature.

The relative enthalpy,  $L$ , of an electrolyte solution is defined to be

$$L = H - H^{\circ} \quad (5)$$

where  $H$  is the total enthalpy of the solution and  $H^{\circ}$  that of the components of the solution in their standard states.

The quantity  $L$  is related to  $G^{\text{ex}}$  by the equation

$$L = -T^2 \left( \frac{\partial(G^{\text{ex}}/T)}{\partial T} \right)_{P,m} \quad (6)$$

Equations (1) and (6) yield for  $L$ ,

$$L = \nu m R T^2 \left[ \left( \frac{\partial \phi}{\partial T} \right)_{P,m} - \left( \frac{\partial \ln \gamma_{\pm}}{\partial T} \right)_{P,m} \right] \quad (7)$$

The apparent relative molal enthalpy,  $\phi_L$ , is defined as

$$\phi_L = \frac{L - n_1 \bar{L}_1^{\circ}}{n_2} = \frac{L}{n_2} \quad (8)$$

Taking the appropriate derivatives of equations (2) and (3) as prescribed by equations (7) and (8), one obtains for  $\phi_L$  the result

$$\phi_L = v |z_M z_X| (A_H/3b) \ln(1+bI^{1/2}) - 2v_M v_X RT^2 [m B_{MX}^L + m^2 (v_M z_M) C_{MX}^L] \quad (9)$$

where

$$B_{MX}^L = (\partial B_{MX}/\partial T)_{I,P} \quad (10)$$

$$B_{MX} = \beta_{MX}^{(0)} + (2\beta_{MX}^{(1)}/\alpha_1^2 I) [1 - (1 + \alpha_1 I^{1/2}) \exp(-\alpha_1 I^{1/2})] + (2\beta_{MX}^{(2)}/\alpha_2^2 I) [1 - (1 + \alpha_2 I^{1/2}) \exp(-\alpha_2 I^{1/2})] \quad (11)$$

$$C_{MX}^L = (\partial C_{MX}^\phi/\partial T)_{P/2} |z_M z_X|^{1/2}. \quad (12)$$

The quantity  $A_H$  is the Debye-Hückel coefficient for enthalpy

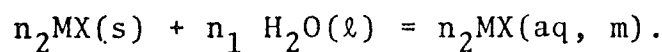
$$A_H = 6RT^2 (\partial A_\phi/\partial T)_P = -9A_\phi RT^2 [T^{-1} + (\partial \ln D/\partial T)_P + \alpha_w/3] \quad (13)$$

where  $\alpha_w = (\partial \ln V/\partial T)_P$  is the coefficient of thermal expansion of water. At 25°C,  $A_H/RT = 1.1773$ .

A common type of enthalpy measurement is the heat of dilution. If this is reported for the dilution of solution containing one mole of solute from  $m_1$  to  $m_2$ , it is related as follows to the apparent molal enthalpy

$$\Delta \bar{H}_D(m_1 \rightarrow m_2) = \phi_{L_2} - \phi_{L_1}. \quad (14)$$

The integral heat of solution of a salt MX is taken as the heat effect for the reaction



The enthalpy change for this reaction is given as

$$\Delta H_S = n_1 \bar{H}_1 + n_2 \bar{H}_2 - n_1 \bar{H}_1^\circ - n_2 \bar{H}_2^\circ(s) \quad (15)$$

which is found on rearrangement to be

$$\Delta H_S/n_2 = \Delta \bar{H}_S^\circ + \phi_L. \quad (16)$$

where  $\bar{H}_S^\circ$  is the heat of solution per mole of salt at infinite dilution. The value of  $\Delta \bar{H}_S^\circ$  at a given temperature may be found by fitting the experimental values of  $\Delta \bar{H}_S$  to equations (9) and (16) treating  $\Delta \bar{H}_S^\circ$  as an adjustable parameter.

The temperature derivative of the activity coefficient is given, of course, by the derivative of equation (3). This yields

$$\begin{aligned} \frac{\partial \ln \gamma_{\pm}}{\partial T} = & |z_M z_X| \left( \frac{A_H}{6RT^2} \right) \left( \frac{I^{1/2}}{1+bI^{1/2}} + \frac{2}{b} \ln(1+bI^{1/2}) \right) + \\ & m \frac{2v_M v_X}{v} \left\{ 2 \left( \frac{\partial \beta^{(0)}}{\partial T} \right) + \frac{2}{\alpha_1^2 I} \left( \frac{\partial \beta^{(1)}}{\partial T} \right) [1 - (1+\alpha_1 I^{1/2} - \frac{\alpha_1^2 I}{2}) \times \right. \\ & \left. \exp(-\alpha_1 I^{1/2})] + \frac{2}{\alpha_2^2 I} \left( \frac{\partial \beta^{(2)}}{\partial T} \right) [1 - (1+\alpha_2 I^{1/2} - \frac{\alpha_2^2 I}{2}) \times \right. \\ & \left. \exp(-\alpha_2 I^{1/2})] \right\} + \frac{3m^2}{2} \left( \frac{2(v_M v_X)^{3/2}}{v} \right) \left( \frac{\partial C_{MX}^\phi}{\partial T} \right) \quad (17) \end{aligned}$$

The corresponding equation for the derivative of the osmotic coefficient is also readily obtained from equations (7), (8), and (17) or by a separate derivation from equation (2).

Data for Apparent Molal Enthalpy

The data for heat of dilution for 1-1 aqueous electrolytes were reviewed as of 1964 by Parker<sup>5</sup> who also considered heat capacity and heat of solution data. For the solutions considered by Parker, most of our results do not differ significantly, but we did base our calculations on the original data. Our contribution is in the compactness of the results and their direct usefulness in calculating activity coefficients at temperatures other than 25°C.

In addition to the 1-1 electrolytes considered by Parker, we made a reasonable effort to consider most available data for higher valence electrolytes (but we do not pretend to have made an exhaustive search of the literature).

In some cases there are heat of solution results for various concentrations and these yield, in effect, also heat of dilution data. The treatment of these heat of solution data yield also the  $\Delta\bar{H}_S^\circ$  of solution at zero molality.

Values of the temperature derivatives of  $\beta^{(0)}$ ,  $\beta^{(1)}$ , and  $\beta^{(2)}$  and/or  $C^\phi$  where applicable, are listed in Tables I through III. Listed in the last column of each table are the references and in next to last column are the maximum molalities to which the enthalpy equations were fit. Though the goodness of fit for individual salts varied depending on the concentration range and the quality of the data, in general the overall fit for all 1-1 inorganic electrolytes is 4.3 cal/mole with individual variations from 0.5 to 12 cal/mole with deviations from any given data point usually less than 1.5%. The overall fit to the tetraalkylammonium halides is 17 cal/mole with fits

to individual salts ranging from 0.5 to 40 cal/mole and deviations from data points generally less than 1%. For the 2-1 inorganic electrolytes the overall fit is 4.0 cal/mole with individual fits from 0.5 to 10 cal/mole with electrons from data points less than 1%.

Though virial coefficients beyond  $(\partial C^\phi / \partial T)_p$  could be added to the equations, the improvement in fit is slight while only complicating the equations. Generally, the three- or four-parameter equation (the latter for 2-2 electrolytes) fits the data within experimental error up to practical concentrations (ionic strength = 6). Consequently the use of additional virial coefficients was deemed unnecessary.

### Discussion

Although  $\beta^{(0)}$ ,  $\beta^{(1)}$ , and  $\beta^{(2)}$  relate primarily to the short-range forces between pairs of ions, they include also effects related to the difference of molality from concentration and various changes in the solvent caused by the solute. Similarly the temperature derivatives of these quantities relate primarily to temperature changes in the appropriate integral over the interionic potential of mean force but include temperature changes in these other effects. Thus, in discussion of the results it is difficult to draw unambiguous conclusions.

The most important conclusion is that these temperature derivatives are small. Thus for 1-1 electrolytes where  $\beta^{(0)}$  and  $\beta^{(1)}$  are commonly of the magnitude of one tenth or a few tenths, their derivatives are of the order  $10^{-3}$ . Hence a

temperature change of a few degrees or even ten or twenty degrees causes little change in these parameters. Beyond that range one must also consider the effect of the second derivative or of the heat capacity of the solution.

In paper II<sup>2</sup> a general correlation was noted between  $\beta^{(1)}$  and  $\beta^{(0)}$ ; their derivatives still show some correlation but the departure from a single curve is considerably larger. One might also expect a correlation of the derivative with the function itself and this is shown in figure 1 for  $\partial\beta^{(0)}/\partial T$  and  $\beta^{(0)}$  for alkali halides. A general trend with negative slope is noted; this implies that the  $\beta^{(0)}$  values come closer together as the temperature rises. In other words the effect of individual solute differences decreases which seems reasonable. But for intermediate values of  $\beta^{(0)}$  near 0.11, the range in  $\partial\beta^{(0)}/\partial T$  is considerable with fluorides having low values and iodides high values. Presumably this is related to details of the solvation of these ions, but we have no detailed explanation.

In the case of the 2-2 electrolytes, where there is a tendency toward electrostatic ion-pairing and the additional term in  $\beta^{(2)}$  is required to fit the osmotic coefficient, the corresponding equation fits the heat of dilution data quite well. There are some heat of dilution data for 3-2 and 4-2 valence type electrolytes<sup>45,46</sup> and preliminary calculations indicate that with appropriate values of  $\alpha_1$  and  $\alpha_2$  the same form of equation will fit these data. We hope to present results for these higher valence-type electrolytes in a future paper.

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Table 1. Parameters for 1-1 Electrolytes

	$\frac{\partial\beta(0)}{\partial T}$ $\times 10^4$	$\frac{\partial\beta(1)}{\partial T}$ $\times 10^4$	$\frac{\partial C^\phi}{\partial T}$ $\times 10^5$	Max. m	Ref.
HCl	-3.08 <sub>1</sub>	1.41 <sub>9</sub>	6.21 <sub>3</sub>	4.5	6,7
HClO <sub>4</sub>	4.90 <sub>5</sub>	19.3 <sub>1</sub>	-11.7 <sub>7</sub>	6.	8
LiCl	-1.68 <sub>5</sub>	5.36 <sub>6</sub>	- 4.52 <sub>0</sub>	6.4	9,10
LiBr	-1.81 <sub>9</sub>	6.63 <sub>6</sub>	- 2.81 <sub>3</sub>	6.	11,12
LiClO <sub>4</sub>	0.38 <sub>6</sub>	7.00 <sub>9</sub>	- 7.71 <sub>2</sub>	4.	13
NaF	5.36 <sub>1</sub>	8.70	-	0.7	9
NaCl	7.15 <sub>9</sub>	7.00 <sub>5</sub>	-10.5 <sub>4</sub>	6.	1
NaBr	7.69 <sub>2</sub>	10.7 <sub>9</sub>	- 9.30	9.	14-16
NaI	8.35 <sub>5</sub>	8.28	- 8.35	6.	9
NaOH	7.00	1.34	-18.9 <sub>4</sub>	4.2	17
NaClO <sub>3</sub>	10.35	19.0 <sub>7</sub>	- 9.29	6.4	18
NaClO <sub>4</sub>	12.96	22.9 <sub>7</sub>	-16.2 <sub>3</sub>	6.	8,20
NaBrO <sub>3</sub>	5.59	34.3 <sub>7</sub>	-	0.1	18
NaIO <sub>3</sub>	20.6 <sub>6</sub>	60.5 <sub>7</sub>	-	0.1	18
NaCNS	7.80	20.0	-	0.1	19
NaNO <sub>3</sub>	12.66	20.6 <sub>0</sub>	-23.1 <sub>6</sub>	2.2	18
KF	2.14	5.44	- 5.9 <sub>5</sub>	5.9	21
KCl	5.79 <sub>4</sub>	10.71	- 5.09 <sub>5</sub>	4.5	22,23
KBr	7.39	17.4 <sub>0</sub>	- 7.00 <sub>4</sub>	5.2	14,15
KI	9.91 <sub>4</sub>	11.86	- 9.44	7.	14
KClO <sub>3</sub>	19.8 <sub>7</sub>	31.8	-	0.1	24
KClO <sub>4</sub>	0.6 <sub>0</sub>	100.7	-	0.1	24
KCNS	6.87	37.0	0.43	3.1	19

Table 1 (continued)

	$\frac{\partial\beta^{(0)}}{\partial T}$	$\frac{\partial\beta^{(1)}}{\partial T}$	$\frac{\partial C^\phi}{\partial T}$	Max. m	Ref.
	$\times 10^4$	$\times 10^4$	$\times 10^5$		
KNO <sub>3</sub>	2.06	64.5	39.7	2.4	25
KH <sub>2</sub> PO <sub>4</sub>	6.04 <sub>5</sub>	28.6	-10.1 <sub>1</sub>	1.8	26
RbF	-0.76	14.7	-	1.0	9,25
RbCl	5.52 <sub>2</sub>	15.0 <sub>6</sub>	-	0.8	9
RbBr	6.78 <sub>0</sub>	20.3 <sub>5</sub>	-	1.0	9
RbI	8.57 <sub>8</sub>	23.8 <sub>3</sub>	-	0.7	9
CsF	0.95	5.9 <sub>7</sub>	-	1.1	9
CsCl	4.5 <sub>4</sub>	23.8	-	0.1	
CsBr	7.80	28.4 <sub>4</sub>	-	1.0	9
CsI	9.75	34.7 <sub>7</sub>	-	0.7	9
NH <sub>4</sub> Cl	0.77 <sub>9</sub>	12.5 <sub>8</sub>	2.1 <sub>0</sub>	4.	27
NH <sub>4</sub> H <sub>2</sub> PO <sub>4</sub>	1.51	22.8	-2.8 <sub>4</sub>	3.4	26
Me <sub>4</sub> NF	-0.82	16.0	-9.2 <sub>7</sub>	3.	28
Et <sub>4</sub> NF	-16.4	43.4	-	0.5	28
Pr <sub>4</sub> NF	-39.1	41.6	-	0.8	28
Bu <sub>4</sub> NF	-117.8	105.3	43.5	1.9	28
MeH <sub>3</sub> NCl	1.1 <sub>3</sub>	10.8	-	0.5	27
Me <sub>2</sub> H <sub>2</sub> NCl	0.2 <sub>3</sub>	18.2	-	0.5	27
Me <sub>3</sub> HNC1	0.2 <sub>2</sub>	35.3	-	0.5	27
Me <sub>4</sub> NCl	5.93	49.0	-7.66	8.1	27,29
Et <sub>4</sub> NCl	2.0 <sub>0</sub>	61.4	-13.1	5.3	29
Pr <sub>4</sub> NCl	-32.2	85.1	11.3	4.4	29
Bu <sub>4</sub> NCl	-122.8	163.6	258.5	2.5	29

Table 1 (continued)

	$\frac{\partial\beta(0)}{\partial T}$	$\frac{\partial\beta(1)}{\partial T}$	$\frac{\partial C^\phi}{\partial T}$	Max. m	Ref.
	$\times 10^4$	$\times 10^4$	$\times 10^5$		
Me <sub>4</sub> NBr	6.3 <sub>5</sub>	62.2	- 5.32	5.5	30
Et <sub>4</sub> NBr	4.1 <sub>3</sub>	72.4	-12.3 <sub>5</sub>	4.6	29
Pr <sub>4</sub> NBr	-22.3	90.1	- 2.1 <sub>2</sub>	4.4	29
Bu <sub>4</sub> NBr	-123.0	181.2	328.5	2.1	29
Me <sub>4</sub> NI	- 7.0 <sub>6</sub>	100.9	-	0.3	29,31
Et <sub>4</sub> NI	- 1.9 <sub>7</sub>	92.0	-36.3	2.	29,31
Pr <sub>4</sub> NI	-23.4	107.0	-	0.5	29,31

Table II. Parameters for 2-1 Electrolytes

	$\frac{4}{3} \frac{\partial \beta^{(0)}}{\partial T}$	$\frac{4}{3} \frac{\partial \beta^{(1)}}{\partial T}$	$\frac{2^{5/2}}{3} \frac{\partial C^\phi}{\partial T}$	Max m	Ref.
	$\times 10^3$	$\times 10^3$	$\times 10^4$		
MgCl <sub>2</sub>	-0.57 <sub>2</sub>	4.8 <sub>7</sub>	-	0.1	32
MgBr <sub>2</sub>	-0.07 <sub>5</sub>	5.1 <sub>5</sub>	-	0.1	32
Mg(CLO <sub>4</sub> ) <sub>2</sub>	0.69 <sub>7</sub>	6.0 <sub>0</sub>	-6.6 <sub>5</sub>	3.2	33
Mg(NO <sub>3</sub> ) <sub>2</sub>	0.68 <sub>7</sub>	5.9 <sub>9</sub>	-	0.1	34
CaCl <sub>2</sub>	-0.23 <sub>0</sub>	5.2 <sub>0</sub>	-	0.1	32
CaBr <sub>2</sub>	-0.69 <sub>7</sub>	8.0 <sub>5</sub>	-	0.6	32
Ca(NO <sub>3</sub> ) <sub>2</sub>	0.70 <sub>6</sub>	12.2 <sub>5</sub>	-	0.1	34, 35
SrCl <sub>2</sub>	0.95 <sub>6</sub>	3.7 <sub>9</sub>	-	0.1	32
SrBr <sub>2</sub>	-0.43 <sub>7</sub>	8.7 <sub>1</sub>	-	0.1	32
Sr(NO <sub>3</sub> ) <sub>2</sub>	0.23 <sub>6</sub>	16.6 <sub>3</sub>	-	0.2	34, 36
Sr(CLO <sub>4</sub> ) <sub>2</sub>	1.52 <sub>4</sub>	7.1 <sub>9</sub>	-5.8 <sub>6</sub>	3.	33
BaCl <sub>2</sub>	0.85 <sub>4</sub>	4.3 <sub>1</sub>	-2.9	1.8	32, 37
BaBr <sub>2</sub>	-0.45 <sub>1</sub>	9.0 <sub>4</sub>	-	0.1	32
Ba(NO <sub>3</sub> ) <sub>2</sub>	-3.88	38.8	-	0.1	34
CuCl <sub>2</sub>	-3.62	11.3	-	0.6	19
Li <sub>2</sub> SO <sub>4</sub>	3.29	-3.4 <sub>5</sub>	-	0.1	34
Na <sub>2</sub> SO <sub>4</sub>	3.06	7.3 <sub>6</sub>	-	0.4	34, 38, 39
K <sub>2</sub> SO <sub>4</sub>	1.92	8.9 <sub>3</sub>	-	0.1	34
Rb <sub>2</sub> SO <sub>4</sub>	1.25	11.5 <sub>2</sub>	-	0.1	34
Cs <sub>2</sub> SO <sub>4</sub>	-1.19	19.3 <sub>1</sub>	-	0.1	34

Table III. Parameters for Higher Valence Electrolytes

	$\frac{\partial\beta(0)}{\partial T}$	$\frac{\partial\beta(1)}{\partial T}$	$\frac{\partial\beta(2)}{\partial T}$	$\frac{\partial C^\phi}{\partial T}$	Max m	Ref.
	$\times 10^3$	$\times 10^2$	$\times 10$	$\times 10^3$		
LaCl <sub>3</sub> <sup>a</sup>	0.25 <sub>3</sub>	0.79 <sub>8</sub>	-	-0.37 <sub>1</sub>	3.6	40
La(ClO <sub>4</sub> ) <sub>3</sub> <sup>a</sup>	0.15 <sub>2</sub>	1.50 <sub>3</sub>	-	-0.67 <sub>2</sub>	2.1	40
La(NO <sub>3</sub> ) <sub>3</sub> <sup>a</sup>	0.17 <sub>3</sub>	1.09 <sub>5</sub>	-	-0.45 <sub>1</sub>	2.2	40
Na <sub>3</sub> Fe(CN) <sub>6</sub>	3.05	1.52	-	-	0.1	41
K <sub>3</sub> Fe(CN) <sub>6</sub>	-0.87	3.15	-	-	0.1	42,43
K <sub>4</sub> Fe(CN) <sub>6</sub>	4.74	3.92	-	-	0.2	42,43
MgSO <sub>4</sub>	-	2.09 <sup>b</sup>	-3.06	-	0.05	34
CaSO <sub>4</sub>	-	5.46 <sup>b</sup>	-5.16	-	0.02	25,34
CuSO <sub>4</sub>	-4.4	2.3 <sub>8</sub> <sup>b</sup>	-4.7 <sub>3</sub>	4.8 <sub>0</sub>	1.0	44
ZnSO <sub>4</sub>	-3.6 <sub>6</sub>	2.3 <sub>3</sub> <sup>b</sup>	-3.3 <sub>3</sub>	3.9 <sub>7</sub>	1.0	44
CdSO <sub>4</sub>	-2.7 <sub>9</sub>	1.7 <sub>1</sub> <sup>b</sup>	-5.2 <sub>2</sub>	2.6 <sub>1</sub>	1.0	44

<sup>a</sup> Parameters for other rare earths are given in reference 40.

<sup>b</sup> The parameter  $\alpha_1$  is 1.4 for these cases; it is 2.0 in all other cases;  $\alpha_2 = 12.0$ .

Table IV. Heats of Solution

	$\Delta\bar{H}_s^\circ/\text{cal}$
HCl	-17874
LiCl	- 8843
LiBr	-11716
NaCl	918
NaBr	- 147
NaI	- 1862
NaClO <sub>4</sub>	3333
NaCNS	1636
KF	-4237
KClO <sub>3</sub>	9865
KCNS	5860
KH <sub>2</sub> PO <sub>4</sub>	4637
NH <sub>4</sub> Cl	3513
NH <sub>4</sub> H <sub>2</sub> PO <sub>4</sub>	3807
Me <sub>4</sub> NI	9970
Et <sub>4</sub> NI	6730
Pr <sub>4</sub> NI	2750
Sr(NO <sub>3</sub> ) <sub>2</sub>	4178
BaCl <sub>2</sub>	- 3163
CuCl <sub>2</sub>	-12133
Na <sub>2</sub> SO <sub>4</sub>	- 564



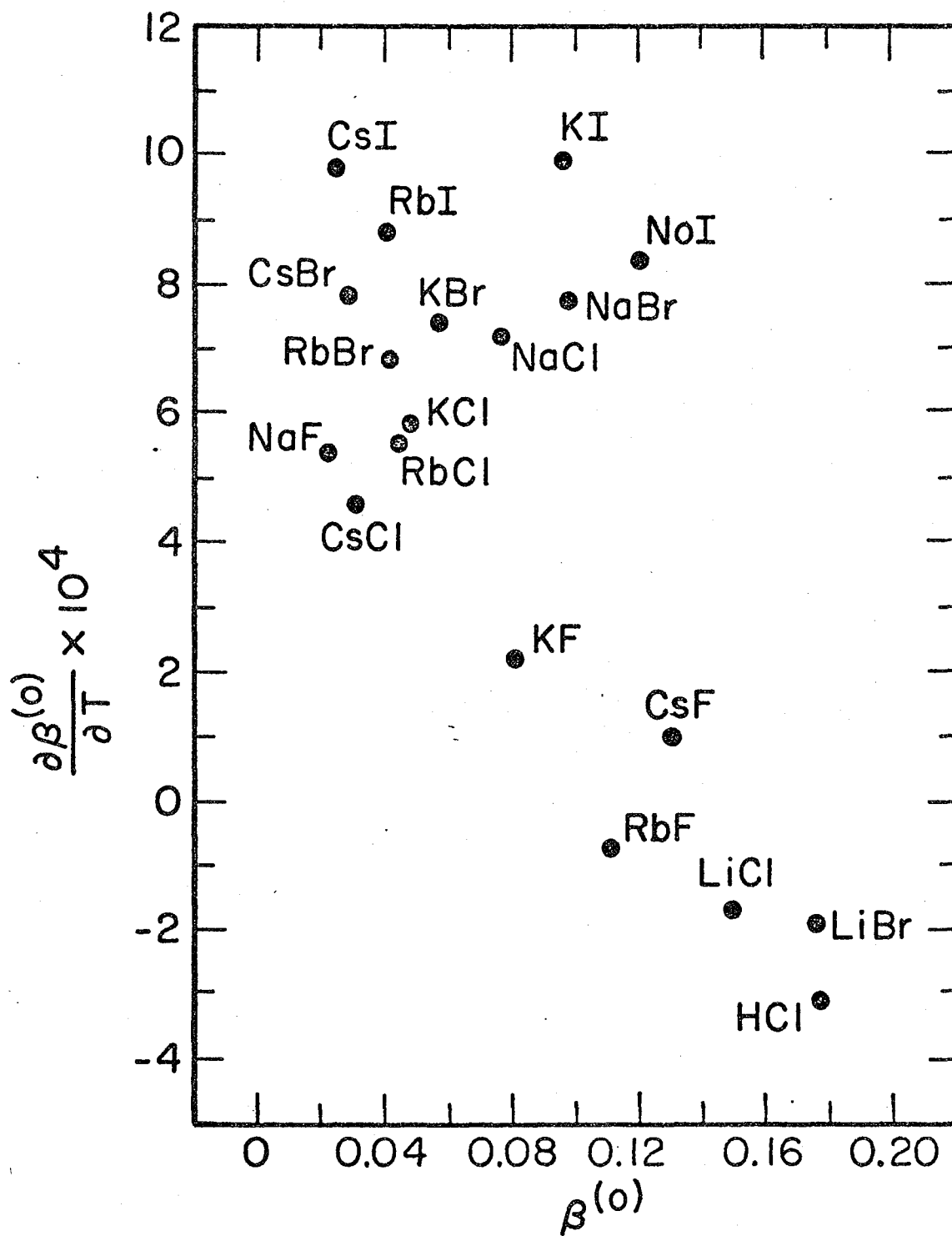


Figure 1. The temperature derivative of the ion interaction coefficient,  $\beta^{(0)}$ , for the alkali halides.

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