Thermodynamic Properties of Strong Electrolytes in Aqueous Solutions

A generalized analytic correlation is presented for activity coefficient. osmotic coefficient, enthalpy, and heat capacity of single and multicomponent strong aqueous solutions. A good correlation for each salt to an ionic strength of six is obtained by assigning a single parameter "B" value to each salt. These B values are well approximated by assigning two parameters for each ion. Values presented for the common ions at 25°C allow the estimation of activity and osmotic coefficients of many unmeasured salt solutions.

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SCOPE

Engineers and scientists frequently require reasonably accurate values of thermodynamic properties of aqueous solutions. The problem is particularly acute when no values have been measured for a particular electrolyte solution.

Compilations of data by Robinson and Stokes (1968), Harned and Owen (1958), and Wu and Hamer (1969) are most useful as are the recent graphical correlations for activity coefficients of Meissner et al. (1972). Recently Pitzer (1972) has addressed himself to this complex problem. None of these, however, except Meissner's allow systematic estimation of properties for salts that have never been measured.

CONCLUSIONS AND SIGNIFICANCE

The activity coefficients of strong aqueous electrolytes are well correlated by the single parameter Equation (4) to an ionic strength of about six. Equations derived from this for other thermodynamic properties are given by Equations (5) through (13).

Individual "B" values are found to be well represented by Equation (14) which involves two parameters per ion. This implies that for strong electrolytes only physical interactions are involved.

Equations (15) to (30) are presented for multi-ion solutions which are somewhat more rigorous than those of Meissner et al. (1972). (See footnote on page 317.) Equation (29) for trace quantities, although more complex than Meissner's does give a slightly better average fit.

Suggested expressions for the effect of temperature, for high concentration, and for systems involving ion association are presented.

The equations and tables presented provide scientists and engineers with methods not previously available to estimate with reasonable accuracy the activity coefficient and osmotic coefficient of aqueous solutions.

Activity coefficients of strong electrolyte aqueous solutions have recently been graphically correlated by Meissner et al. (1972) using data from Robinson and Stokes (1965), Harned and Owen (1958), and Wu and Hamer (1969). Use of a reference material has been suggested by Akerlof and Thomas (1934). Inspection of the curves of Figure 22-8 in Pitzer and Brewer's revision (1961) of Lewis and Randall's *Thermodynamics* led this author to believe that the curves are linear in I and approach constant values at large I. Pitzer (1972) has recently given an improved analysis of the Debye-Hückel model and showed that there is an ionic strength dependence of the effect of short range forces in binary interactions. This suggests that the β in Guggenheim's equation

$$\ln \gamma_{\pm} = \frac{-A_{\gamma} I^{1/2}}{1 + I^{1/2}} + \beta m \qquad (1)$$

for 1-1 salts is a function of $I^{1/2}$ even at small I. Bromley (1972) has shown that β (taken as a constant) may be approximated as the sum of individual ion β values although the constant is only applicable to about 0.1 molal.

Inspection of Meissner's curves at high concentration indicates that, to a first approximation at high ionic strength, $(1/(Z_+Z_-))$ log $\gamma_{\pm}$ is linear with ionic strength and that a single parameter per salt provides a fair approximation to the activity coefficient variation over the entire range of ionic strength. Meissner also showed that the functional dependence is essentially temperature independent, although the parameter (equivalent to B) may be temperature dependent.

SUGGESTED EQUATION

After numerous trials the following equation was found to provide a good fit to most of the data on strongly ionized salts.

$$\log \gamma_{\pm} = \frac{-A_\gamma |Z_+Z_-| I^{1/2}}{1 + \rho I^{1/2}} + \frac{(B_0 - B)I}{(1 + aI)^n} + BI + CI^2 \tag{2}$$

A few determinations quickly indicated that the best integer value of n was 2. With the data prepared by Robinson and Stokes (1968) and Wu and Hamer (1969), a determination of ρ was made for each salt valence type at 25°C. Except for 3-1 (for example, $LiCl_3$), 4-1, and 1-3 valence types, which gave ρ values of 1.4, 1.6, and 1.4 respectively, all other types, including 1-1, 2-1, 1-2, 2-2, 3-2, and 1-4, gave $\rho = 1.0 \pm 0.2$. The fit of all types with $\rho = 1.0$ was reasonably satisfactory and the advantage of a common value of ρ equal to that widely accepted justified its use. The value of ρ was also found to be temperature independent by using the data on sodium chloride from 0 to 100°C.

The value of a is near unity but appears to decrease systematically with increase in valence number such that the product $a|Z_+Z_-| \approx 1.5$. Individual values of this product ranged from 0.8 to 3. Fortunately the data fit is not sensitive to the value of a.

The values of ρ and a were also determined independently using data on heats of mixing and heat capacity for a number of salts including sea water treated as a single salt solution. The values of $\rho = 1.0$ and $a|Z_+Z_-| = a[(\Sigma m_i Z_i^2)/(\Sigma m_i)] = 1.5$ were satisfactory to within the accuracy of the data, even to 200°C in the cases tested.

The value of C was found to bear no consistent relation to either B value, and individual values of C formed a nearly normal probability distribution about $C = 0$. Accordingly, to an ionic strength of six, C was assigned the value zero.

Although individual B_0 and B values scatter rather badly, the best relation between B_0 and B was found at 25° to depend on $|Z_+Z_-|$ as follows:

$$\frac{B_0 - B}{|Z_+Z_-|} = 0.06 + 0.6\,B \tag{3}$$

This relationship was tested for the effect of temperature, using the data on sodium chloride, and was also found to be temperature independent in the range 0 to 100°C. The term involving $B_0 - B$ in Equation (2), which represents a transition between the Debye-Hückel term and the linear term, contributes at most a few percent to the activity coefficient. Most of the above tests were made using activity coefficients, but numerous individual tests were made using osmotic coefficient data, enthalpies of solution, and heat capacities; reasonable agreement was obtained in all cases. The final single empirical constant equation for activity coefficient thus becomes

$$\log \gamma_{\pm} = \frac{-A_\gamma |Z_+Z_-| I^{1/2}}{1 + \rho I^{1/2}} + \frac{(0.06 + 0.6\,B)\,|Z_+Z_-|\,I}{\left(1 + \frac{1.5}{|Z_+Z_-|} I\right)^2} + BI \tag{4}$$

A complete set of B values at 25°C with ρ set equal to 1.0 determined by the method of least squares to an ionic strength of six is given in Table 1. Because of the exponential nature of the function extrapolated values (above $I = 6$) are apt to introduce a large error in γ. Equation (4) is satisfactory for all strong salts (nearly completely ionized). Examples for which it is not satisfactory include bivalent metal sulfates, sulfuric acid, and the zinc and cadmium halides, all of which are incompletely ionized (Davies, 1962). The average maximum error in γ per salt with data to $I = 6$ is 5.1% excluding the above mentioned salts. Even some of this error can be attributed to salts which show limited ion association such as silver and lead nitrates. If this were allowed for, it is expected that such B values would be appreciably more positive and self consistent.

NEW FINDINGS

At 25°C, Equation (4) may be written

$$\log \gamma_{\pm}^{\frac{1}{Z_1 Z_2}} = \frac{-0.511\,I^{1/2}}{1 + I^{1/2}} + \frac{(0.06 + 0.6\,B)I}{\left(1 + \frac{1.5}{|Z_+Z_-|} I\right)^2} + \frac{BI}{|Z_+Z_-|} \tag{4a}$$

Values of B are found in Table 1 or calculated from the values in Table 2. Values from Table 2 should be used only when not available in Table 1.

OTHER THERMODYNAMIC PROPERTIES

Starting with Equation (4), it is possible to write equations for a number of other thermodynamic properties using rigorous thermodynamics. The resulting equations are

$$1 - \phi = 2.303\,A_\gamma |Z_+Z_-| \frac{I^{1/2}}{3} \sigma(\rho I^{1/2}) - 2.303(0.06 + 0.6\,B)|Z_+Z_-| \frac{I}{2} \psi(aI) - 2.303\,B \frac{I}{2} \tag{5}$$

Here as above $\rho = 1.0$ and $a = 1.5/|Z_+Z_-|$

$$\sigma(\rho I^{1/2}) = \frac{3}{(\rho I^{1/2})^3}\left[1 + \rho I^{1/2} - \frac{1}{1 + \rho I^{1/2}} - 2\ln(1 + \rho I^{1/2})\right] \tag{6}$$

$$\psi(aI) = \frac{2}{aI}\left[\frac{1 + 2aI}{(1 + aI)^2} - \frac{\ln(1 + aI)}{aI}\right] \tag{7}$$

$$\phi L = \frac{\nu}{2} A_H |Z_+Z_-| I^{1/2}\left[\frac{1}{1 + \rho I^{1/2}} - \frac{\sigma(\rho I^{1/2})}{3}\right] - 2.303\nu RT^2 I\left\{\left[\frac{1}{(1 + aI)^2} - \frac{\psi(aI)}{2}\right](0.6\,|Z_+Z_-|) + \frac{1}{2}\right\}\frac{dB}{dT} \tag{8}$$

$$\bar{L}_2 = \frac{\nu}{2} \frac{A_H |Z_+Z_-| I^{1/2}}{1 + \rho I^{1/2}} - 2.303\nu RT^2 I\left[\frac{0.6\,|Z_+Z_-|}{(1 + aI)^2} + 1\right]\frac{dB}{dT} \tag{9}$$

$$\frac{\overline{L}_1}{m} = \frac{-\nu}{2}\,\frac{A_H\,|Z_+Z_-|\,I^{1/2}}{3(1000/M_1)}\,\sigma(\rho I^{1/2}) + \frac{2.303\nu RT^2\,I}{(1000/M_1)}\left[\frac{\psi(aI)\;0.6\,|Z_+Z_-|}{2} + \frac{1}{2}\right]\frac{dB}{dT} \quad (10)$$

$$\phi C_p - \overline{C}_{p2}{}^0 = \frac{\nu}{2}A_j\,|Z_+Z_-|\,I^{1/2}\left[\frac{1}{1+\rho I^{1/2}} - \frac{\sigma(\rho I^{1/2})}{3}\right] - 2.303\nu RT^2\,I\left\{\left[\frac{1}{(1+aI)^2} - \frac{\psi(aI)}{2}\right](0.6\,|Z_+Z_-) + \frac{1}{2}\right\}\left(\frac{2}{T}\,\frac{dB}{dT} + \frac{d^2B}{dT^2}\right) \quad (11)$$

$$\overline{C}_{p2} - \overline{C}_{p2}{}^0 = \frac{\nu}{2}\,\frac{A_j\,|Z_+Z_-|\,I^{1/2}}{1+\rho I^{1/2}} - 2.303\nu RT^2\,I\left[\frac{0.6\,|Z_+Z_-|}{(1+aI)^2} + 1\right]\left(\frac{2}{T}\,\frac{dB}{dT} + \frac{d^2B}{dT^2}\right) \quad (12)$$

$$\frac{C_{p1} - C_{p1}{}^0}{m} = \frac{-\nu}{2}\,\frac{A_j\,|Z_+Z_-|\,I^{1/2}\,\sigma(\rho I^{1/2})}{3(1000/M_1)} + \frac{2.303\nu RT^2\,I}{1000/M_1}\left[\left(\frac{\psi(aI)}{2}\right)(0.6\,|Z_+Z_-) + \frac{1}{2}\right]\left(\frac{2}{T}\,\frac{dB}{dT} + \frac{d^2B}{dT^2}\right) \quad (13)$$

TABLE 1. B VALUES AT 25°C DETERMINED BY THE METHOD OF LEAST SQUARES ON LOG γ TO $I = 6.0$ (OR LESS IF LIMITED DATA)

Data on γ contained in Wu & Hamer (1969), Robinson & Stokes (1965), Latimer (1952) and Pitzer (1972). σ is the standard deviation in log γ.

Salt	B, kg mol^{-1}	σ
1-1 salts		
$AgNO_3$	−0.0828	0.027
CsAc	0.1272	0.010
CsBr	−0.0039	0.015
CsCl	0.0025	0.017
CsF	0.0906	0.004
CsI	−0.0188	0.007
$CsNO_3$	−0.1173	0.004
CsOH	0.1299	0.003
HBr	0.1734	0.004
HCl	0.1433	0.003
$HClO_4$	0.1639	0.019
HI	0.2054	0.004
HNO_3	0.0776	0.019
KAc	0.1188	0.009
KBr	0.0296	0.003
$KBrO_3$	−0.0884	0.003
KCl	0.0240	0.0005
$KClO_3$	−0.0739	0.003
$KClO_4$	−0.1637	0.000
KCNS	0.0137	0.007
KF	0.0565	0.006
KH_2AsO_4	−0.0798	0.003
$K_2H_2PO_4$	−0.1124	0.008
KH Adipate	0.0286	0.001
KH Malonate	−0.0227	0.006
KH Succinate	−0.0035	0.007
KI	0.0428	0.008
KNO_3	−0.0862	0.013
KOH	0.1131	0.011
KTol	−0.0559	0.012
LiAc	0.0722	0.005
LiBr	0.1527	0.017
LiCl	0.1283	0.009
$LiClO_3$	0.1442	0.004
$LiClO_4$	0.1702	0.006
LiI	0.1815	0.007
$LiNO_3$	0.0938	0.014
LiOH	−0.0097	0.022
LiTol	0.0230	0.007
NaAc	0.1048	0.009
NaBr	0.0749	0.0009
$NaBrO_3$	−0.0278	0.002
Na Butyrate	0.1474	0.023
Na Caprate	−0.4786	0.074
Na Caprate	0.0480	0.097
Na Caprylate	−0.1419	0.060
NaCl	0.0574	0.002
$NaClO_3$	0.0127	0.005
$NaClO_4$	0.0330	0.007
NaCNS	0.0758	0.011
NaF	0.0041	0.0006
Na Formate	0.0519	0.008
NaH_2AsO_4	−0.0291	0.006
NaH_2PO_4	−0.0460	0.033
NaH Adipate	0.0461	0.001
NaH Malonate	−0.0011	0.002
NaH Succinate	0.0131	0.005
Na Heptylate	−0.0467	0.086
NaI	0.0994	0.002
$NaNO_3$	−0.0128	0.002
NaOH	0.0747	0.010
Na Pelargonate	−0.3040	0.080
Na Propionate	0.1325	0.008
NaTol	−0.0200	0.011
Na Valerate	0.1222	0.057
NH_4Br	−0.0066	0.013
NH_4Cl	0.0200	0.005
NH_4ClO_4	−0.0640	0.011
NH_4I	0.0210	0.004
NH_4NO_3	−0.0358	0.011
RbAc	0.1239	0.008
RbBr	0.0111	0.004
RbCl	0.0157	0.005
RbF	0.0650	0.006
RbI	0.0108	0.005
$RbNO_3$	−0.0869	0.023
TlAc	−0.0224	0.014
TlCl	0.0372	0.002
$TlClO_4$	−0.1288	0.0005
$TlNO_3$	−0.2340	0.003
1-2 salts $I = 3$m		
Cs_2SO_4	−0.0012	0.004
H_2SO_4	0.0606	0.175
K_2CO_3	0.0372	0.015
K_2CrO_4	−0.0003	0.003
K_2HAsO_4	0.0296	0.015
K_2HPO_4	−0.0096	0.006
K_2SO_4	−0.0320	0.005
Li_2SO_4	0.0207	0.003
Na_2CO_3	0.0089	0.006
Na_2CrO_4	0.0096	0.006
Na_2 Fumarate	0.0366	0.013
Na_2HAsO_4	0.0022	0.016
Na_2HPO_4	−0.0265	0.011
Na_2 Maleate	−0.0029	0.033
Na_2SO_4	−0.0204	0.008
$Na_2S_2O_3$	−0.0005	0.005
$(NH_4)_2SO_4$	−0.0287	0.024
Rb_2SO_4	−0.0091	0.005
1-3 salts $I = 6$m		
K_3AsO_4	0.0551	0.033
$K_3Fe(CN)_6$	0.0195	0.003
K_3PO_4	0.0344	0.031
Na_3AsO_4	0.0159	0.033
Na_3PO_4	0.0043	0.037
1-4 salts $I = 10$m		
$K_4Fe(CN)_6$	0.0085	0.009
$K_4Mo(CN)_8$	0.0110	0.018
2-1 salts $I = 3$m		
$BaAc_2$	0.0357	0.015
$BaBr_2$	0.0852	0.004
$BaCl_2$	0.0638	0.007
$Ba(ClO_4)_2$	0.0936	0.012
BaI_2	0.1254	0.003
$Ba(NO_3)_2$	−0.0545	0.001
$Ba(OH)_2$	−0.0240	0.003
$CaBr_2$	0.1179	0.009
$CaCl_2$	0.0948	0.005
$Ca(ClO_4)_2$	0.1457	0.003
CaI_2	0.1440	0.007
$Ca(NO_3)_2$	0.0410	0.007
$CdBr_2$	−0.1701	0.237
$CdCl_2$	−0.1448	0.180
CdI_2	−0.2497	0.383
$Cd(NO_3)_2$	0.0719	0.017
$CoBr_2$	0.1361	0.012
$CoCl_2$	0.1016	0.004
CoI_2	0.1683	0.013
$Co(NO_3)_2$	0.0912	0.002
$CuCl_2$	0.0654	0.017
$Cu(NO_3)_2$	0.0797	0.005
$FeCl_2$	0.0961	0.004
$MgAc_2$	0.0339	0.015
$MgBr_2$	0.1419	0.012
$MgCl_2$	0.1129	0.010
$Mg(ClO_4)_2$	0.1760	0.009
MgI_2	0.1695	0.014
$Mg(NO_3)_2$	0.1014	0.004
$MnCl_2$	0.0869	0.005
$NiCl_2$	0.1039	0.007
$Pb(ClO_4)_2$	0.0987	0.003
$Pb(NO_3)_2$	−0.0606	0.034
$SrBr_2$	0.1038	0.005
$SrCl_2$	0.0847	0.002
$Sr(ClO_4)_2$	0.1254	0.008
SrI_2	0.1339	0.005
$Sr(NO_3)_2$	0.0138	0.012
UO_2Cl_2	0.1157	0.015
$UO_2(ClO_4)_2$	0.2267	0.022
$UO_2(NO_3)_2$	0.1296	0.010
$ZnBr_2$	0.0911	0.057
$ZnCl_2$	0.0364	0.043
$Zn(ClO_4)$	0.1755	0.019
ZnI_2	0.1341	0.060
$Zn(NO_3)_2$	0.1002	0.006
2-2 salts $I = 4$m		
$BeSO_4$	−0.0301	0.110
$CdSO_4$	−0.0371	0.064
$CuSO_4$	−0.0364	0.066
$MgSO_4$	−0.0153	0.051
$NiSO_4$	−0.0296	0.052
$ZnSO_4$	−0.0240	0.046
3-1 salts $I = 6$m		
$AlCl_3$	0.1089	0.018
$CeCl_3$	0.0815	0.010
$Co(EN)_3Cl_3$	−0.0251	0.016
$CrCl_3$	0.1026	0.015
$Cr(NO_3)_3$	0.0919	0.010
$EuCl_3$	0.0867	0.009
$Ga(ClO_4)_3$	0.1607	0.019
$LaCl_3$	0.0818	0.011
$LaNO_3$	0.0868	0.034
$NdCl_3$	0.0815	0.011
$PrCl_3$	0.0805	0.009
$ScCl_3$	0.0969	0.016
$SmCl_3$	0.0848	0.010
YCl_3	0.0882	0.014
3-2 salts $I = 15$m		
$Al_2(SO_4)_3$	−0.0044	0.041
$Cr_2(SO_4)_3$	0.0122	0.014
4-1 salts $I = 10$m		
$ThCl_4$	0.1132	0.056
$Th(NO_3)_4$	0.0894	0.079

From a knowledge of these thermodynamic properties it is possible to calculate the activity of water, the boiling point elevation, heats of mixing, and their variation with temperature over a short range (Harned and Owen, 1958).

UNIT MASS BASIS

In the event it is desired to express the above equation on a unit mass basis instead of a molal basis, replace

$$\nu\,|Z_+Z_-| \quad \text{by} \quad \frac{\Sigma m_i Z_i^2}{\Sigma m_i M_i}$$

for the salt in question, and

$$\nu \quad \text{by} \quad \frac{\Sigma m_i}{\Sigma m_i M_i}$$

CORRELATION OF *B* VALUES

The author (1972) has previously shown that B values could be approximated as the sum of values for individual ions. Although additive terms gave a fair approximation for the alkali halides (and alkaline earth halides), it became quite apparent that the addition of a product term would markedly improve the correlation.

Accordingly

$$B = B_{\text{cation}} + B_{\text{anion}} + \delta_{\text{cation}}\delta_{\text{anion}} \qquad (14)$$

(for example, for $CaCl_2$:

$$B_{CaCl_2} = B_{Ca^{++}} + B_{Cl^-} + \delta_{Ca^{++}}\delta_{Cl^-}$$

was found to give a good approximation to the B values which range from about -0.48 to $+0.23$.

The individual ion values for B and δ are given in Table 2. Since an arbitrary choice of one B and δ value may be made, the B_{Na^+} was set equal to 0.0 and δ_{OH^-} was set equal to -1.0 (a zero value choice for δ resulted in computer difficulties). In the determination, experimental B values were given weighting factors ranging from 10 for NaCl, KCl, and $CaCl_2$ to 0.5 for a few salts obtained from Latimer (1952). All values in Table 1 were used except those for sulfuric acid, the bivalent metal sulfates, and the zinc and cadmium halides for which Equation (4) is a poor approximation because of strong ion association. The values were calculated on a CDC 6400 computer using an iterative procedure to minimize the standard deviation of B values. As the procedure did not converge to a unique set a better set of values might be found.

TABLE 2. INDIVIDUAL ION VALUES OF B AND δ IN AQUEOUS SOLUTIONS AT 25°C

$B = B_+ + B_- + \delta_+\delta_-$

The units of B are kg mol^{-1}.

Cation	B_+	δ_+	Anion	B_-	δ_-
H^+	0.0875	0.103	F^-	0.0295	−0.93
Li^+	0.0691	0.138	Cl^-	0.0643	−0.067
Na^+	0.0000*	0.028	Br^-	0.0741	0.064
K^+	−0.0452	−0.079	I^-	0.0890	0.196
Rb^+	−0.0537	−0.100	ClO_3^-	0.005	0.45
Cs^+	−0.0710	−0.138	ClO_4^-	0.002	0.79
NH_4^+	−0.042	−0.02	BrO_3^-	−0.032	0.14
Tl^+	−0.135	−0.02	IO_3^-	(−0.04)	(0)
Ag^+	−0.058	(0)	NO_3^-	−0.025	0.27
Be^{++}	(0.1)	(0.2)	$H_2PO_4^-$	−0.052	0.20
Mg^{++}	0.0570	0.157	$H_2AsO_4^-$	−0.030	0.05
Ca^{++}	0.0374	0.119	CNS^-	0.071	0.16
Sr^{++}	0.0245	0.110	OH^-	0.076	−1.00*
Ba^{++}	0.0022	0.098	Formate (C_1)	0.072	(−0.7)
Mn^{++}	0.037	(0.21)	Acetate (C_2)	0.104	−0.73
Fe^{++}	0.046	(0.21)	Propionate (C_3)	0.152	(−0.7)
Co^{++}	0.0490	0.210	Butyrate (C_4)	0.167	(−0.7)
Ni^{++}	0.054	(0.21)	Valerate (C_5)	0.142	(−0.7)
Cu^{++}	0.022	0.30	Caproate (C_6)	0.068	(−0.7)
Zn^{++}	0.101	0.09	Heptylate (C_7)	−0.027	(−0.7)
Cd^{++}	0.072	(0.09)	Caprylate (C_8)	−0.122	(−0.7)
Pb^{++}	−0.104	0.25	Pelargonate (C_9)	−0.284	(−0.7)
UO_2^{++}	0.079	0.19	Caprate (C_{10})	−0.459	(−0.7)
Cr^{+++}	0.066	0.15	H Malonate (C_3)	+0.005	−0.22
Al^{+++}	0.052	0.12	H Succinate (C_4)	+0.021	−0.27
Sc^{+++}	0.046	(0.2)	H Adipate (C_5)	+0.053	−0.26
Y^{+++}	0.037	(0.2)	Toluate	−0.022	−0.16
La^{+++}	0.036	0.27	CrO_4^{--}	0.019	−0.33
Ce^{+++}	0.035	(0.27)	SO_4^{--}	0.000	−0.40
Pr^{+++}	0.034	(0.27)	$S_2O_3^{--}$	0.019	(−0.7)
Nd^{+++}	0.035	(0.27)	HPO_4^{--}	−0.010	−0.57
Sm^{+++}	0.039	(0.27)	$HAsO_4^{--}$	0.021	−0.67
Eu^{+++}	0.041	(0.27)	CO_3^{--}	0.028	−0.67
Ga^{+++}	0.000	(0.2)	Fumarate (Trans C_4)	0.056	(−0.7)
†$Co(en)_3^{+++}$	−0.089	(0)	Maleate (Cis C_4)	0.017	(−0.7)
Th^{++++}	0.062	0.19	PO_4^{---}	0.024	−0.70
			AsO_4^{---}	0.038	−0.78
			$Fe(CN)_6^{---}$	0.065	(0)
			$Fe(CN)_6^{---}$	0.054	(0)
			$Mo(CN)_8^{---}$	0.056	(0)

* For convenience the value of B_{Na^+} was set equal to zero and the δ_{OH^-} set equal to -1.0.
† $Co(en)_3^{+++}$ denotes tris-(ethylenediamine) cobalt III.
Values in parentheses are estimated.

It may be noted that the individual ion B values for the alkali metals, the alkaline earths, the transition metals, and the rare earths, as well as those for the halides and the aliphatic monobasic anions, all appear quite systematic and appear simply related to the entropies of the aqueous ions within each group.

The individual δ values for the anions appear roughly parallel to the proton affinities for these ions. Thus, hydroxide, fluoride, acetate, and the anions of weak acids have negative δ values whereas those of strong acids tend to have positive values.

The variation of the δ values for the cations is considerably less than for the anions and except for the heavy alkali metals (and NH_4^+ and Tl^+) which have near zero to small negative δ values, most have values within $+0.2 \pm 0.1$. All values in parentheses are estimated.

The average error in calculated B values is 0.0092 for 114 salts (this does not include 29 individual and 19 double-valued salts). If the six worst values, five of which have very limited data, are omitted from this average, that is, TlCl, $TlNO_3$, $KClO_4$, NH_4Br, NH_4NO_3, and $Ba(NO_3)_2$, the average error is reduced to 0.006. Thus using this correlation, one might expect an error in activity coefficient roughly linear with ionic strength and up to about 10% at $I = 6.0$. The error in individual cases may of course be considerably larger, although except for the compounds listed above only NaOH and $Mg(NO_3)_2$ show errors larger than 0.023 in B.

CAUTION

The individual ion values are meant to apply to strong salts only and do not allow for strong specific ion-ion chemical association such as in acetic acid or cadmium iodide. Such ion association produces at low concentration a marked reduction in apparent B to strongly negative values. This is usually followed by a rise of B with concentration. The correlation does not appear to do well for thalium and ammonium compounds and is somewhat erratic with nitrates. At least part of the difficulty is caused by the incomplete ionization of some of these.

EFFECT OF VALENCE TYPE

Meissner has postulated that a plot of $(1/Z_+Z_-) \log \gamma$ $(= \log \Gamma)$ versus I results in only one parameter per salt. This concept is tested in Figure 1 along with Equation (4) using the accurate data available for NaCl, KCl, HCl, and $CaCl_2$. A few other salts are included for comparison. A Hewlett-Packard 9810A calculator and plotter were used to prepare this graph.

It will be noted that the curves for NaCl and $CaCl_2$ distinctly cross and that the shape of the curves for the higher valence salts, such as $LaCl_3$ and $Cr_2(SO_4)_3$, is distinctly different from that of the 1-1 salts. This effect was pointed out by Meissner.

Thus, although a single set of curves for $\log \Gamma$ versus I is a first approximation, it is only that and, as Meissner points out, experimental data should be used wherever possible, provided they are reliable.

The curves in Figure 1 represent Equation (4) applied to the experimental data to $I = 6$ with the value of B (Table 1) determined by the method of least squares.

MULTICOMPONENT SALT SOLUTIONS

If there are appropriate data available, and if only the properties of the water and the salt mixture are desired, probably the simplest procedure is to treat the salt mixture as a single complex salt with a characteristic (temperature dependent) "B" value. This approach appears to be quite successful for the data on sea water. For enthalpy and heat capacity it is somewhat easier to use the equations on a unit mass basis in this case.

If values of B are known for all the individual salts present it may be shown, using Equations (16) through (24), that the "B" for the complex solution, treating all the ions as from a single complex salt of ν ions is given by

$$"B" = \frac{4\Sigma_M\Sigma_X B_{MX}\overline{Z}_{MX}^2\nu_M\nu_X}{\nu \Sigma \nu_i Z_i^2} \qquad (15)$$

In this case all ν values may be replaced by the corresponding m values. $\overline{Z}_{MX}$ is the arithmetic average charge number of M and X.

Although the equations of Meissner (1972) appear to give a reasonable approximation for multicomponent solutions, they appear to be rigorous in giving a single value to each ion activity coefficient only in the case where all the negative ions have one charge ($Z_2 = Z_4 = Z_6 = \cdots = Z_-$) and all the positive ions have the same or another charge ($Z_1 = Z_3 = Z_5 = \cdots = Z_+$).*

Accordingly a single ion activity coefficient equation was written, similar to the equations for single ion activities given by Pitzer and Brewer (1961). For cation 1, a function F was defined as follows:

$$\log \gamma_1 = \frac{-A_\gamma Z_1^2 I^{1/2}}{1 + I^{1/2}} + F_1 \qquad (16)$$

At the total ionic strength of the solution, define γ_{12}^0 as the activity coefficient of the salt 12 if alone in the solution at the same total ionic strength I. Also let B_{12} be defined by the following equation

$$\log \gamma_{12}^0 = \frac{-A_\gamma |Z_1Z_2| I^{1/2}}{1 + I^{1/2}} + B_{12} I \approx \frac{-A_\gamma |Z_1Z_2| I^{1/2}}{1 + I^{1/2}} + \frac{(0.06 + 0.6B) |Z_1Z_2| I}{\left(1 + \frac{1.5}{|Z_1Z_2|} I\right)^2} + BI \qquad (17)$$

---

* Proof of lack of rigor in Meissner & Kusik multicomponent equation:

By definition, the mean activity coefficient of a completely ionized salt, 12, in any solution is related to those of the individual ions by

$$\log \gamma_{12} = \log \left(\gamma_1^{\frac{\nu_1}{\nu_1+\nu_2}} \gamma_2^{\frac{\nu_2}{\nu_1+\nu_2}} \right) = \frac{Z_2}{Z_1 + Z_2} \log \nu_1 + \frac{Z_1}{Z_1 + Z_2} \log \nu_2 \qquad (a)$$

Meissner and Kusik (1972) write

$$\log \gamma_{12} = Z_1Z_2F_1 + Z_1Z_2F_2 \qquad (b)$$

(F_1 & F_2 are as defined by Meissner and Kusik (1972) Equations 4 & 5 respectively of their paper).

Equating Equations (a) and (b) and writing similar equations for a solution also containing ions 3 and 4, one has equations for the salts 12, 14, 32, and 34. If one attempts to solve for F values in terms of individual ion γ values, the following identity results:

$$(F_1 - F_3)(Z_4 - Z_2) = (F_4 - F_2)(Z_3 - Z_1)$$

This must be true if equation (b) is to be true. Clearly this can only be true when

$$Z_4 - Z_2 = 0 = Z_3 - Z_1$$

since F values are finite and usually different. Hence it follows that $Z_2 = Z_4$ and $Z_1 = Z_3$ is a necessary condition for Equation (b) to be true.

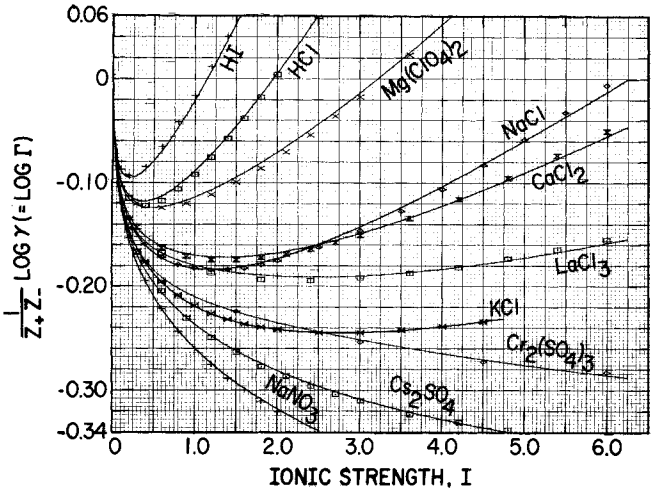

Fig. 1. The effect of valence type on $\frac{1}{Z_+Z_-}\log\gamma = \log\Gamma$. Smooth curves are from Equation (4) with B determined by least squares to $I = 6$. Data are from references cited in Table 1.

It will be assumed that since the following equations for F may be shown to be correct for $\dot{B}$ = constant, they will be reasonably accurate if $\dot{B}$ is a slowly varying function of I. Some evidence for this is that Harned's Rule (1958) is found to hold reasonably well even at high concentrations in many mixed (multivalent) electrolyte systems at constant ionic strength. The expressions do ignore interactions between like charged species which Pitzer (1972) has shown to be rather important in some univalent salt mixtures. They also ignore higher order interactions. Then

$$F_1 = \dot{B}_{12}\overline{Z}_{12}^2 m_2 + \dot{B}_{14}\overline{Z}_{14}^2 m_4 + \dot{B}_{16}\overline{Z}_{16}^2 m_6 + \cdots \quad (18)$$

where

$$\overline{Z}_{12} = \frac{Z_1 + Z_2}{2} \quad (19)$$

(The absolute magnitude of all charge numbers, Z, is used without regard to sign.)

$$F_2 = \dot{B}_{12}\overline{Z}_{12}^2 m_1 + \dot{B}_{32}\overline{Z}_{32}^2 m_3 + \dot{B}_{52}\overline{Z}_{52}^2 m_5 + \cdots \quad (20)$$

and in the multicomponent solution

$$\log\gamma_{12} = \frac{-A_\gamma |Z_1Z_2| I^{1/2}}{1 + I^{1/2}} + \frac{\nu_1 F_1}{\nu} + \frac{\nu_2 F_2}{\nu} \quad (21)$$

$$= \frac{-A_\gamma |Z_1Z_2| I^{1/2}}{1 + I^{1/2}} + \frac{|Z_1Z_2|}{Z_1 + Z_2}\left[\frac{F_1}{Z_1} + \frac{F_2}{Z_2}\right] \quad (22)$$

For a complex salt of ν ions in the solution

$$\log\gamma_\pm = \frac{-A_\gamma\left(\frac{\Sigma\nu_i Z_i^2}{\nu}\right) I^{1/2}}{1 + I^{1/2}} + \frac{1}{\nu}\Sigma\nu_i F_i \quad (23)$$

where

$$\nu = \Sigma\nu_i\,. \quad (24)$$

Although numerous other ions may be present, the i ions refer only to those in the solution which arise from the salt whose activity coefficient is desired. The values of $\dot{B}$ can be eliminated and the F values expressed in terms of γ^0 values. Equations (18) and (20) for F_1 and F_2 may then be written

$$F_1 = Y_{21}\log\gamma_{12}^0 + Y_{41}\log\gamma_{14}^0 + Y_{61}\log\gamma_{16}^0 + \cdots + \frac{A_\gamma I^{1/2}}{1 + I^{1/2}}[Z_1Z_2Y_{21} + Z_1Z_4Y_{41} + Z_1Z_6Y_{61} \cdots] \quad (25)$$

and

$$F_2 = X_{12}\log\gamma_{12}^0 + X_{32}\log\gamma_{32}^0 + \cdots + \frac{A_\gamma I^{1/2}}{1 + I^{1/2}}[Z_1Z_2X_{12} + Z_3Z_2X_{32} + \cdots] \quad (26)$$

where

$$Y_{21} = \frac{\overline{Z}_{12}^2 m_2}{I} = \left(\frac{Z_1 + Z_2}{2}\right)^2\frac{m_2}{I} \quad (27)$$

$$X_{12} = \frac{\overline{Z}_{12}^2 m_1}{I} \quad (28)$$

The equation for trace concentration may be written (in Meissner's nomenclature)

$$\Gamma_{32}^{tr} = \Gamma_{12}^{tr} = \left\{\left[\Gamma_{12}^0\right]^{\frac{Z_1+Z_2}{Z_2+Z_3}}\left[\Gamma_{32}^0\right]^{\frac{Z_3+Z_2}{Z_1+Z_2}}\right\}^{1/2} \times \left\{(10)^{\frac{A_\gamma I^{1/2}}{1+I^{1/2}}\left[\frac{Z_1+Z_2}{2(Z_2+Z_3)} + \frac{Z_3+Z_2}{2(Z_1+Z_2)} - 1\right]}\right\} \quad (29)$$

as compared with Meissner's simpler equation

$$\Gamma_{32}^{tr} = \Gamma_{12}^{tr} = (\Gamma_{12}^0 \cdot \Gamma_{32}^0)^{1/2} \quad (30)$$

where

$$\Gamma_{32} = \gamma_{32}^{\frac{1}{Z_3Z_2}} \quad (31)$$

Note that when $Z_1 = Z_3$, Equations (29) and (30) are identical.

The results are compared in Table 3. For the multivalent salts, $Z_3 > Z_1$, Equation (29) appears to be somewhat more accurate; otherwise the results are rather comparable and seem to indicate that neglected like ion-ion interactions are important in some cases.

EFFECT OF TEMPERATURE

After some of the data on heat capacity including some given by Bromley et al. (1970) and by Likke (1972) was studied, it was concluded that either of the following equations will provide a satisfactory expression for the variation of B with temperature although each requires enough data to determine the necessary constants:

$$B = B^* \ln\left(\frac{T - 243}{T}\right) + \frac{B_1}{T} + B_2 + B_3 \ln T \quad (31)$$

or

$$B = \frac{B^*}{T - 230} + \frac{B_1}{T} + B_2 + B_3 \ln T \quad (32)$$

where T is the absolute temperature in degrees Kelvin. The four constants B^*, B_1, B_2, and B_3 would be slightly different depending on the equation used. The last three terms have been used by numerous authors. It may be noted that B_1 and B_2 offer no contribution to the heat capacity and the term in B_3 corresponds to a constant heat capacity.

Fortunately if only one good activity coefficient is known at ionic strength I at a given temperature, the B of Equation (4) may be determined. At an ionic strength of 10, the equation given by Meissner, Kusik, and Tester

TABLE 3. COMPARISON OF γ^{trace} VALUES FROM EQUATION (29) WITH THOSE OF MEISSNER 1972 (EQUATION 30 THIS PAPER)
Cl^- is common anion

12	32	I	$\gamma_{12}°$	$\gamma_{32}°$	Exp	γ_{12}^{tr} Calc. Eq. (29)	Calc. Meisner	Exp	γ_{32}^{tr} Calc. Eq. (29)	Calc. Meisner
HCl	$CaCl_2$	0.3	0.588	0.326	0.578	0.57	0.58	0.334	0.32	0.34
NaCl	$MgCl_2$	3	0.714	0.569	0.77	0.77	0.73	0.636	0.59	0.54
NaCl	$CaCl_2$	6	0.965	0.79	0.935	0.97	0.93	—	0.94	0.86
NaCl	$SrCl_2$	3	0.714	0.465	0.714	0.70	0.70	0.536	0.51	0.49
HCl	$AlCl_3$	3	1.318	0.33	0.85	0.88	0.95	0.45	0.69	0.87
HCl	$AlCl_3$	12	7.25	3.37	3.96	3.09	3.30	—	—	—
HCl	$LaCl_3$	1	0.809	0.282	0.655	0.72	0.73	0.256	0.37	0.38
HCl	$ThCl_4$	3	1.318	0.14	0.895	0.80	0.90	—	0.406	0.65

(1972) may be used

$$\log (\Gamma_t)_{I=10} = [1 - 0.0050(t - 25)] \log(\Gamma_{25°C})_{I=10} \quad (33)$$

They also give a method for other ionic strengths.

Similarly, to calculate other thermodynamic properties, one value of that property must be known at the temperature in question with the exception of heat capacity where a value of $\overline{C_P}^0_{salt}$, the partial or apparent molal heat capacity at infinite dilution, must be known, estimated, or calculated.

VALUES AT HIGH IONIC STRENGTHS (ABOVE 6)

As a first approximation, Equation (4) may be used, although because of the exponential nature of the function the error will increase rapidly as I increases. The error may be reduced by fitting over the entire range of data or by use of an accurate value at high ionic strength to determine B. The error may also be reduced and accuracy improved by suitable choice of added terms. For strong salts, simply adding $CI^{3/2} + DI^2$ to Equation (4) gives a reasonable fit, and it appears that D and C are related by $D \sim -0.15C$ although this relation has been tested on only a few salts.

Meissner and Tester's (1972) graphical correlation may also be used to an ionic strength of 20.

ION ASSOCIATION

Although strong ion association occurs only in a few salts such as the bivalent metal sulfates and the cadmium halides, it is nonetheless appreciable in many of the so-called "strong" salts such as silver nitrate, potassium nitrate, and lithium hydroxide (Davies, 1962).

If it is assumed that only one association product is important, for example, $ZnSO_4$, $CdCl^+$, etc., then in the limit of low concentration it may be shown that the following term should be added to the expression for $\log \gamma$:

$$-\frac{2m(\nu - 1)}{2.303K\nu}$$

where K is the dissociation constant for the associated ion pair. It is easily shown that this applies only to concentrations well below 0.01 molal although the correction may be remarkedly large.

At high concentrations two expressions have been found to be useful:

For 1-1 and 2-2 salts

$$\log \gamma_{\pm} = (\text{right side Equation 4}) - E\alpha I^{1/2} [1 - e^{-\alpha I^{1/2}}] \quad (34)$$

For 2-1, 1-2 and other unsymmetrical salts

$$\log \gamma_{\pm} = (\text{right side of Equation 4}) - E \ln(1 + \alpha^2 I) \quad (35)$$

The value of α appears to be near unity for 1-1 salts and about 70 for 2-2 salts. Using 70 for α, the values of B and E computed from Pitzer 1972 data on bivalent sulfates are given in Table 4. It may be noted that even though these data extend to about 4 molal ($I = 16$) the agreement is nearly an order of magnitude better than with the single constant Equation (4) to $I = 6$ as given in Table 2.

Also included in Table 4 are calculated values of the dissociation constant assuming that the equation is also valid at very low concentrations as well as at high. For this to be true

$$K = \frac{2m(\nu - 1)}{2.303\nu E\alpha^2 I} \quad (36)$$

The agreement with Pitzer's K values is not good but is nevertheless remarkable considering the empirical nature and simplicity of the equation. The values for $CaSO_4$ were determined from data between 10^{-4} and 0.02 molal only. For extrapolation to high concentrations, it is estimated that $B_{CaSO_4} = 0.1$ and $E_{CaSO_4} = 0.005$ would do better.

The value of I to be used in all equations is the apparent value, neglecting ion association.

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TABLE 4. BIVALENT METAL SULFATES AT 25°C

Constants in Equation (34) determined from Pitzer's 1972 activity coefficient data. Data to 4m ($I = 16$) were used. α set equal to 70. σ is the standard deviation in $\log \gamma$.

Salt	B	E	σ	K*	K_1 (Pitzer)
$BeSO_4$	0.1385	0.00654	0.045	0.0034	0.0022
$MgSO_4$	0.1042	0.00464	0.009	0.0048	0.0042
$CaSO_4$	0.4463	0.01143	0.002	0.0019	0.0036
$MnSO_4$	0.1226	0.00599	0.027	0.0037	0.0045
$CoSO_4$	0.1244	0.00498	0.006	0.0044	0.0049
$NiSO_4$	0.1056	0.00524	0.008	0.0042	0.0045
$CuSO_4$	0.1285	0.00640	0.008	0.0035	0.0040
$ZnSO_4$	0.1008	0.00483	0.009	0.0046	0.0050
$CdSO_4$	0.0988	0.00526	0.014	0.0042	0.0040

* K values are calculated from equation 36 and are included only for comparison. Do not use for other purposes.

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NOTATION

A_γ = Debye-Hückel constant for activity coefficient = 0.511 kg$^{1/2}$ mol$^{-1/2}$ at 25°C
A_H = Debye-Hückel constant for enthalpy = 688 cal/mole at 25°C
A_j = Debye-Hückel constant for heat capacity = 10.4 cal/deg-mole at 25°C
a = constant in Equation (2); found to be ~ $1.5/|Z_+Z_-|$
a_1 = activity of water in solution
B = a constant per salt; B_+ per cation, B_- per anion
B_0 = the value of $\dot{B}$ at zero ionic strength
$\dot{B}$ = the variable B as defined in Equation (16)
C = arbitrary constant
$\overline{C}_{p1}$ = partial molal heat capacity of water in solution
$\overline{C}_{p_1}^0$ = partial molal heat capacity of water in solution at infinite dilution
= heat capacity of pure water
$\overline{C}_{p2}$ = partial molal heat capacity of salt in solution
$\overline{C}_{p_2}^0$ = partial molal heat capacity of salt in solution at infinite dilution
E = arbitrary constant, see Equations (34) and (35)
F = function defined by Equation (16) and used in Equations (18) to (26)
H = arbitrary constant
I = ionic strength = $\dfrac{\Sigma m_i Z_i^2}{2}$
K = dissociation constant (or may be treated as arbitrary constant). See Equations (34) to (36)
log = logarithm to base 10
ln = logarithm to base e
$\overline{L}_1$ = relative partial molal enthalpy of water in solution
$\overline{L}_2$ = relative partial molal enthalpy of salt in solution
M_1 = molecular weight of solvent (water) = 18.02
m = molality, g-moles/kg of solvent
n = exponent found to be ~ 2 [Equation (2)]
R = universal gas constant = 1.986 cal °K^{-1} mole^{-1}
T = absolute temperature, °K
t = temperature, °C
X defined by Equation (28) and used in Equation (26)
Y defined by Equation (27) and used in Equation (25)
Z = charge number on ion (only absolute values are used)
$|Z_+Z_-|$ = denotes the absolute value of the charge product, for a multi-ion salt = $\dfrac{\Sigma \nu_i Z_i^2}{\Sigma \nu_i}$
$\overline{Z}_{12}$ = arithmetic average charge number of cation 1 and anion 2, see Equation (19)
α = arbitrary constant, see Equations (34) and (35)
β = constant in Equation (1)
Γ = $\gamma^{\frac{1}{Z_+Z_-}}$, see Equations (29) to (31); used by Meissner (1972)
γ = activity coefficient
γ_{12}^0 = activity coefficient of 12 salt if only pure 12 present at the ionic strength of the solution
δ = parameter (per ion) used in Equation (14)
ν = $\Sigma\nu_i$ = sum of stoichiometric number of ions in molecule
ρ = constant in Debye-Hückel equation; related to distance of closest approach of ions in solution. Numerically found to be ~ 1.0 kg$^{1/2}$ mole$^{-1/2}$
$\sigma(\rho I^{1/2})$ = function of $\rho I^{1/2}$, see Equation (6)
ϕ = osmotic coefficient = $\dfrac{-1000}{M_1 \Sigma m_i} \ln a_1$
ϕC_P = apparent molal heat capacity of salt in solution
ϕL = apparent relative molal enthalpy of salt in solution, see Pitzer and Brewer (1961)
$\psi(aI)$ = function of aI, see Equation (7)

Subscripts

+, − refer to cation and anion respectively
± denotes usual mean value for a salt
i denotes individual ion
1, 3, 5 - - - denotes cations (1, 2, 3 - - denotes simply 1st, 2nd, 3rd etc.)
2, 4, 6 - - - denotes anions
M denotes cation
X denotes anion

Superscript

tr denotes trace

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