298.15–348.15 K.

In the case of $SrCl_2$, no literature ${}^{\phi}C_p(T,m)$ data at higher temperatures are available for comparison.

Conclusions

We have obtained the heat capacities (C_p and ${}^{\phi}C_p$), densities (d) and volumes (${}^{\phi}V$) of $MgCl_2$, $CaCl_2$, and $SrCl_2$ in water as a function of temperature and concentration. Our ${}^{\phi}C_p(T,m)$ data for all three electrolytes are in good agreement with 298.15 K data available in the literature (*5–8*). Our ${}^{\phi}C_p(T,m)$ data at 348.15 and 373.15 K differ considerably from the sparse data (*9*, *23*) for $MgCl_2$ at relatively higher concentrations. This large discrepancy in the two sets of data is attributed to the much lower precision (±60 $J{\cdot}K^{-1}{\cdot}mol^{-1}$ in the ${}^{\phi}C_p$ value at 0.22 $mol{\cdot}kg^{-1}$) attainable by bomb calorimetry C_p measurements in the literature (*9*). The present data are used in an accompanying paper (*18*) to determine reliable $\bar{C}^0_{p,2}(T)$ functions, which can then be used to calculate the thermodynamic properties of ions in water over an extended temperature range.

Registry No. $MgCl_2$, 7786-30-3; $CaCl_2$, 10043-52-4; $SrCl_2$, 10476-85-4.

Literature Cited

(1) Saluja, P. P. S. *J. Nucl. Mater.* **1985**, *130*, 329.
(2) Saluja, P. P. S.; LeBlanc, J. C. "Heat Capacity Data for Selected Cesium- and Iodine-Containing Electrolytes in Water at Elevated Temperatures"; Atomic Energy of Canada Limited Report AECL-8370, 1985.
(3) Saluja, P. P. S.; LeBlanc, J. C.; Hume, H. B. *Can. J. Chem.* **1986**, *64*, 926.
(4) Saluja, P. P. S.; Pitzer, K. S.; Phutela, R. C. *Can. J. Chem.* **1986**, *64*, 1328.
(5) Perron, G.; Desnoyers, J. E.; Millero, F. J. *Can. J. Chem.* **1974**, *52*, 3738.
(6) Desnoyers, J. E.; de Visser, C.; Perron, G.; Picker, P. *J. Solution Chem.* **1976**, *5*, 605.
(7) Spitzer, J. J.; Singh, P. P.; McCurdy, K. G.; Helper, L. G. *J. Solution Chem.* **1978**, *7*, 81.
(8) Perron, G.; Roux, A.; Desnoyers, J. E. *Can. J. Chem.* **1981**, *59*, 3049.
(9) Likke, S.; Bromley, L. A. *J. Chem. Eng. Data* **1973**, *18*, 189.
(10) Ellis, A. J. *J. Chem. Soc. A* **1967**, 660.
(11) Ananthaswamy, J.; Atkinson, G. *J. Chem. Eng. Data* **1985**, *30*, 120.
(12) Wood, R. H. University of Delaware, Newark, DE 19711, private communication, 1983.
(13) Rogers, P. S. Z.; Pitzer, K. S. *J. Phys. Chem.* **1981**, *85*, 2886.
(14) Smith-Magowan, D.; Wood, R. H. *J. Chem. Thermodyn.* **1981**, *13*, 1047.
(15) Busey, R. H.; Holmes, H. F.; Mesmer, R. E. *J. Chem. Thermodyn.* **1984**, *16*, 343.
(16) Picker, P.; Tremblay, E.; Jolicoeur, C. *J. Solution Chem.* **1974**, *3*, 377.
(17) Albert, H. J.; Wood, R. H. *Rev. Sci. Instrum.* **1984**, *55*, 589.
(18) Phutela, R. C.; Pitzer, K. S.; Saluja, P. P. S. *J. Chem. Eng. Data*, following paper in this issue.
(19) Kell, G. S. In *Water, A Comprehensive Treatise*; Franks, F., Ed.; Plenum: New York, 1973; Vol. I, Chapter 10.
(20) Haar, L.; Gallagher, J. S.; Kell, G. S. *NBS/NRC Steam Tables*; Hemisphere: Washington, DC, 1985.
(21) Raznjevic, K. *Handbook of Thermodynamic Tables and Charts-English Translation*; Hemisphere: Washington, DC, 1976, p. 68.
(22) Fine, R. A.; Millero, F. J. *J. Chem. Phys.* **1973**, *59*, 5529.
(23) Eigen, M.; Wicke, E. *Z. Elektrochem. Angew. Phys. Chem.* **1951**, *55*, 354.

Received for review March 25, 1986. Accepted July 23, 1986.

Thermodynamics of Aqueous Magnesium Chloride, Calcium Chloride, and Strontium Chloride at Elevated Temperatures†

Ramesh C. Phutela and Kenneth S. Pitzer*

Department of Chemistry and Lawrence Berkeley Laboratory, University of California, Berkeley, California 94720

Preet P. S. Saluja

Research Chemistry Branch, Atomic Energy of Canada Limited, Whiteshell Nuclear Research Establishment, Pinawa, Manitoba, Canada R0E 1L0

Heat capacities and densities of aqueous $MgCl_2$, $CaCl_2$, and $SrCl_2$ from the accompanying paper are combined with literature data up to 473 K to yield temperature-dependent equations by using the ion-interaction model of Pitzer. These heat capacity equations have been integrated to yield the enthalpy and the Gibbs energy. The enthalpy parameters for 298 K are evaluated in separate calculations using published high-temperature osmotic data as well as heats of dilution, while the Gibbs energy parameters for 298 K are taken from the literature. The range of validity of the final equations is described.

Introduction

We (*1*) have recently completed a study where thermodynamic data on a number of 1:1 aqueous electrolytes have been analyzed using the ion-interaction model. Apparent molar heat capacities and volumes up to 373 K were fitted to the Pitzer equations and the resulting heat capacity equations were integrated to obtain the enthalpy and Gibbs energy functions. In the present paper, we extend the study to the 2:1 electrolytes $MgCl_2$, $CaCl_2$, and $SrCl_2$. In each case the heat capacity and density have been measured to 373 K by Saluja and LeBlanc (*2*), and are reported in the accompanying paper. We have fitted these data, together with some values from literature, to the appropriate equations.

There is special interest in these results for $MgCl_2$ because they can be combined with similar values for Na_2SO_4 (*3*, *4*) and NaCl (*5*, *6*) to yield indirectly the properties of infinitely dilute $MgSO_4$. Phutela and Pitzer (*4*, *7*) have completed measurements of the heat capacity and density of aqueous $MgSO_4$ to 473 K and used these indirect results for the infinitely dilute standard state of $MgSO_4$ in their general treatment of the thermodynamic properties of aqueous $MgSO_4$. In the case of $MgCl_2$, we have heat capacity data to 453 K from Likke and Bromley (*8*); thus, our treatment for $MgCl_2$ is valid over this extended temperature range.

Our data bases for the apparent molar volumes of all three salts include the measurements of Ellis (*9*) which extend to 473 K and 1.0 $mol{\cdot}kg^{-1}$; thus, our volumetric equations are valid over that range.

---

† Issued as LBL-21304 and as AECL-9042.

We did not undertake comprehensive treatments simultaneously fitting all of the types of data interrelated by thermodynamics. When our heat capacity equations are integrated twice to yield the Gibbs energy, there are two sets of integration constants. The second set, for the Gibbs energy, is accurately known from osmotic measurements at 298 K for all three salts and can be taken from the literature. We had hoped also to take the enthalpy constants from the literature but found it worthwhile, instead, to make new evaluations based primarily on the high-temperature osmotic data but considering also selected heat-of-dilution data.

After this research was in progress, a more extensive treatment for $CaCl_2$ which extends to very high molality and to 373 K was published by Ananthaswamy and Atkinson (*10*). Since their equation is more complex, with 33 parameters, it seems worthwhile to report our simpler equation which represents the heat capacity (with seven parameters) to 0.9 mol·kg^{-1}. With the six integration constants, the integrated equation will be adequate for many applications to mixtures containing $CaCl_2$, as well as to pure $CaCl_2$ at dilute and moderate molality.

Review of Available Data

Heat Capacity Data. There are heat capacity measurements for aqueous $MgCl_2$ at saturation pressure by Likke and Bromley (*8*) to 453 K and at 0.6 MPa in the accompanying paper by Saluja and LeBlanc (*2*) to 373 K in addition to those at atmospheric pressure (0.1 MPa) and 298 K by Perron, Desnoyers, and Millero (*11*) and Perron, Roux, and Desnoyers (*12*). After this research neared completion, we received unpublished data from Wood (*13*) for 10 MPa to 573 K and for 17.5 MPa to 598 K. We decided not to use these additional data in the present fit because the pressure dependence varies dramatically with temperature. Professor Wood will undoubtedly present a comprehensive treatment based on his and other data.

In the case of $CaCl_2$, data to 298 K and 0.1 MPa of Perron et al. (*11*, *12*) and Spitzer et al. (*14*) in addition to those of Saluja et al. (*2*) to 373 K and 0.6 MPa were used. For $SrCl_2$, 298 K data of Perron et al. (*11*) and those of Saluja and LeBlanc (*2*) were used. The data of Perron, Desnoyers, and Millero (*11*) in all the three cases were corrected as suggested by Desnoyers et al. (*15*).

Volumetric Data. In comparison with the heat capacity, there are extensive investigations of the volumetric properties of the systems under present study. For $MgCl_2$, the data used are from ref *2*, *9*, *11*, *12*, *16–25*. There are only two studies at high temperatures. One is by Saluja and LeBlanc (*2*) at 0.6 MPa which extends to 373 K and 0.53 mol·kg^{-1} and the other is by Ellis (*9*) at 2 MPa which extends to 473 K and 1 mol·kg^{-1}. The other studies are in the range 273–323 K with the bulk at 298 K. In the low-temperature range, we had high-concentration and high-pressure data available from various references. But we have data only to 1 mol·kg^{-1} and only at low pressure for high temperatures; consequently, we decided to limit ourselves to the range 273–473 K, to 1 mol·kg^{-1}, and to 2 MPa. All the available data in these limits from the above references were used in the present study.

For $CaCl_2$ and $SrCl_2$, the Saluja and LeBlanc (*2*) data extend to 373 K and Ellis (*9*) data to 473 K. In addition, we have used $CaCl_2$ data at 298 K and 0.1 MPa to 1 mol·kg^{-1} from the ref *11*, *12*, *16*, *25*, *26* and from 278 to 308 K and 0.1 MPa to 1 mol·kg^{-1} from Kumar and Atkinson (*27*). For $SrCl_2$, 298 K and 0.1 MPa data of Perron et al. (*11*) were included in the final fit.

Review of Equations. High-temperature activity properties can be calculated by integrating twice the temperature-dependent equation for the heat capacity and by using enthalpy and activity data at 298 K to evaluate integration constants. The basic equations for the osmotic and activity coefficients (ϕ and $\gamma_\pm$), the apparent molar enthalpy ($^\phi L$), the apparent molar heat capacity ($^\phi C_p$), and the apparent molar volume ($^\phi V$) have been derived by Pitzer (*28*) and are summarized in Table I. Here $\beta^{(0)}_{MX}$, $\beta^{(1)}_{MX}$, and C_{MX} are the virial coefficients related to short-range interionic forces. The subscript MX is omitted hereafter. The temperature dependence of these coefficients is determined from the heat capacity data.

The temperature-dependent equation for the apparent molar heat capacity can be integrated to yield the apparent molar enthalpy

$$^\phi L(T,m) = \int_{298}^{T} [^\phi C_p(T',m) - {}^\phi C_p(T',0)]\, dT' + {}^\phi L(298,m) \tag{18}$$

Here and elsewhere 298 is an abbreviation of 298.15 K. The total excess enthalpy $H^{EX} = L = n_2{}^\phi L$, and L is given by

$$L = H - n_1 H^\circ{}_1 - n_2 \bar{H}^\circ{}_2 \tag{19}$$

where n_1 and n_2 are numbers of moles of components 1 and 2 (H_2O and salt, respectively) with standard molar enthalpies $H^\circ{}_1$ for pure water and $\bar{H}^\circ{}_2$ for the salt at infinite dilution.

A second integration of eq 18 gives the excess Gibbs energy

$$G^{EX}(T,m)/n_2 T = - \int_{298}^{T} [^\phi L(T',m)/(T')^2]\, dT' + G^{EX}(298,m)/298 n_2 \tag{20}$$

Appropriate derivatives of G with respect to m yield the activity and osmotic coefficients.

The temperature-dependent equation for the apparent molar volume can be integrated to give the pressure dependence of the Gibbs energy

$$G^{EX}(T,P,m)/n_2 = \int_{P_0}^{P} {}^\phi V(T,P',m)\, dP' + G^{EX}(T,P_0,m)/n_2 \tag{21}$$

Calculations and Results

Heat Capacity. Equation 8 (see Table I) was fitted to the experimental values of the apparent molar heat capacity. The Debye–Hückel parameters for various functions were taken from the equations of Bradley and Pitzer (*29*) for the dielectric constant of water and from equations of Table I. The other properties of water were taken from the equations of Haar, Gallagher, and Kell (*30*).

Since the data for all the solutions extend only to about 1 mol·kg^{-1}, the parameter C^J was not needed. Thus the eq 8 was reduced in practice to

$$^\phi C_p = \bar{C}^\circ{}_{p,2} + (3A_J/b) \ln (1 + bI^{1/2}) - 4RT^2 m \beta^{(0)J} - 8RT^2 m \beta^{(1)J} [1 - (1 + \alpha I^{1/2}) \exp(-\alpha I^{1/2})]/\alpha^2 I \tag{22}$$

where

$$\beta^{(0)J} = (\partial \beta^{(0)L}/\partial T)_p + (2/T)\beta^{(0)L} \tag{23}$$

$$\beta^{(0)L} = (\partial \beta^{(0)}/\partial T)p \tag{24}$$

with similar definitions for $\beta^{(1)L}$ and $\beta^{(1)J}$. Different forms of temperature-dependent equations for $\bar{C}^\circ{}_{p,2}$, $\beta^{(0)J}$, and $\beta^{(1)J}$ were considered, but each of these coefficients could be expressed in terms of the following equations

$$\bar{C}^\circ{}_{p,2} = p_1/T + p_2 + p_3 T + p_4 T^2 + p_5 T^3 \tag{25a}$$

$$\beta^{(0)J} = p_6/T + p_7 + p_8 T \tag{25b}$$

$$\beta^{(1)J} = p_9/T + p_{10} + p_{11} T \tag{25c}$$

where p's are fitting parameters and T is the absolute temperature.

The entire array of data at all temperatures was then fitted in a least-squares calculation adjusting the 11 parameters in eq

Table I. Pitzer Equations for the Thermodynamic Properties of an Aqueous Electrolyte Solution[a]

Osmotic Coefficient

$$\phi - 1 = -|Z_M Z_X| A_\phi I^{1/2}/(1 + bI^{1/2}) + 2(\nu_M \nu_X/\nu) m B^\phi_{MX} + 4((\nu_M \nu_X)^{3/2}/\nu)|Z_M Z_X|^{1/2} m^2 C_{MX} \tag{1}$$

$$B^\phi_{MX} = \beta^{(0)}_{MX} + \beta^{(1)}_{MX} \exp(-\alpha I^{1/2}) \tag{2}$$

Activity Coefficient

$$\ln \gamma_\pm = -|Z_M Z_X| A_\phi [I^{1/2}/(1 + bI^{1/2}) + (2/b) \ln (1 + bI^{1/2})] + 2(\nu_M \nu_X/\nu) m B_{MX} + 6((\nu_M \nu_X)^{3/2}/\nu)|Z_M Z_X|^{1/2} m^2 C_{MX} \tag{3}$$

$$B_{MX} = 2\beta^{(0)}_{MX} + (2\beta^{(1)}_{MX}/\alpha^2 I)\,[1 - (1 + \alpha I^{1/2} - \alpha^2 I/2) \exp(-\alpha I^{1/2})] \tag{4}$$

Apparent Molar Enthalpy

$${}^\phi L = \nu |Z_M Z_X| A_H \ln (1 + bI^{1/2})/2b - 2\nu_M \nu_X R T^2 [m B^L_{MX} + m^2(\nu_M Z_M) C^L_{MX}] \tag{5}$$

$$B^L_{MX} = (\partial \beta^{(0)}_{MX}/\partial T)_p + (\partial \beta^{(1)}_{MX}/\partial T)_p\,(2/\alpha^2 I)[1 - (1 + \alpha I^{1/2}) \exp(-\alpha I^{1/2})] \tag{6}$$

$$C^L_{MX} = (\partial C_{MX}/\partial T)_p \tag{7}$$

Apparent Molar Heat Capacity

$${}^\phi C_p = \bar{C}^\circ{}_{p,2} + \nu |Z_M Z_X| A_J \ln (1 + bI^{1/2})/2b - 2\nu_M \nu_X R T^2 [m B^J_{MX} + m^2(\nu_M Z_M) C^J_{MX}] \tag{8}$$

$$B^J_{MX} = (\partial \beta^L_{MX}/\partial T)_{p,I} + (2/T) B^L_{MX} \tag{9}$$

$$C^J_{MX} = (\partial C^L_{MX}/\partial T)_p + (2/T) C^L_{MX} \tag{10}$$

Apparent Molar Volume

$${}^\phi V = \bar{V}^\circ{}_2 + \nu |Z_M Z_X| A_V \ln (1 + bI^{1/2})/2b + 2\nu_M \nu_X R T [m B^V_{MX} + m^2(\nu_M Z_M) C^V_{MX}] \tag{11}$$

$$B^V_{MX} = (\partial \beta^{(0)}_{MX}/\partial P)_T + 2(\partial \beta^{(1)}_{MX}/\partial P)_T [1 - (1 + \alpha I^{1/2}) \exp(-\alpha I^{1/2})]/\alpha^2 I \tag{12}$$

$$C^V_{MX} = (\partial C_{MX}/\partial P)_T \tag{13}$$

Debye–Hückel Slopes

$$A_\phi = {}^1/_3(2\pi N_o d_w/1000)^{1/2}[e^2(DkT)]^{3/2} \tag{14}$$

$$A_H = 4RT^2(\partial A_\phi/\partial T)_p \tag{15}$$

$$A_J = (\partial A_H/\partial T)_p \tag{16}$$

$$A_V = -4RT(\partial A_\phi/\partial P)_T \tag{17}$$

[a] Definition of symbols: b = a general constant with value 1.2 $\mathrm{kg}^{1/2}\cdot\mathrm{mol}^{-1/2}$; α = 2.0 $\mathrm{kg}^{1/2}\cdot\mathrm{mol}^{-1/2}$; β's and C are ion-interaction parameters specific to each solute MX; m = molality of the solute; I = ionic strength $(1/2\sum m_i Z_i^2)$; ν = total number of ions formed from dissociation of salt MX ($\nu = \nu_M + \nu_X$); Z_M and Z_X are the charges on ions M and X. $\bar{C}^\circ{}_{p,2}$ = apparent molar heat capacity of the solute at infinite dilution; $\bar{V}^\circ{}_2$ = apparent molar volume of the solute at infinite dilution; D = dielectric constant of water.

Table II. Parameters for Eq 25 for the Apparent Molar Heat Capacity

parameter	$MgCl_2$	$CaCl_2$	$SrCl_2$
$p_1/(\mathrm{J\cdot mol^{-1}})$	-7.39872×10^6	-1.26721×10^6	-8.26696×10^5
$p_2/(\mathrm{J\cdot mol^{-1}\cdot K^{-1}})$	7.96487×10^4	7.41013×10^3	4.58928×10^3
$p_3/(\mathrm{J\cdot mol^{-1}\cdot K^{-2}})$	-3.25868×10^2	-1.15222×10^1	-7.05950
$p_4/(\mathrm{J\cdot mol^{-1}\cdot K^{-3}})$	5.98722×10^{-1}		
$p_5/(\mathrm{J\cdot mol^{-1}\cdot K^{-4}})$	-4.21187×10^{-4}		
$p_6/(\mathrm{kg\cdot mol^{-1}\cdot K^{-1}})$	3.10184×10^{-2}	-1.31585×10^{-1}	-2.19115×10^{-2}
$p_7/(\mathrm{kg\cdot mol^{-1}\cdot K^{-2}})$	-2.26558×10^{-4}	7.37742×10^{-4}	5.66565×10^{-5}
$p_8/(\mathrm{kg\cdot mol^{-1}\cdot K^{-3}})$	3.83769×10^{-7}	-1.03737×10^{-6}	
$p_9/(\mathrm{kg\cdot mol^{-1}\cdot K^{-1}})$	-4.68652×10^{-1}		-6.72129×10^{-2}
$p_{10}/(\mathrm{kg\cdot mol^{-1}\cdot K^{-2}})$	2.90617×10^{-3}	5.24873×10^{-5}	2.54614×10^{-4}
$p_{11}/(\mathrm{kg\cdot mol^{-1}\cdot K^{-3}})$	-4.27438×10^{-6}		
range	0–0.9 *m* 298–453 K	0–1 *m* 298–373 K	0–1 *m* 298–373 K

Table III. Parameters for Eq 27 for the Apparent Molar Volume

parameter	$MgCl_2$	$CaCl_2$	$SrCl_2$
$q_1/(\mathrm{cm^3\cdot K\cdot mol^{-1}})$	-3.85979×10^5	-3.96192×10^5	1.19602×10^5
$q_2/(\mathrm{cm^3\cdot mol^{-1}})$	4.30260×10^3	4.24159×10^3	-1.22812×10^3
$q_3/(\mathrm{cm^3\cdot mol^{-1}\cdot K^{-1}})$	-1.80513×10^1	-1.72824×10^1	4.26680
$q_4/(\mathrm{cm^3\cdot mol^{-1}\cdot K^{-2}})$	3.44723×10^{-2}	3.26408×10^{-2}	-4.80302×10^{-3}
$q_5/(\mathrm{cm^3\cdot mol^{-1}\cdot K^{-3}})$	-2.55222×10^{-5}	-2.42826×10^{-5}	
$q_6/(\mathrm{kg\cdot K\cdot mol^{-1}\cdot MPa^{-1}})$	6.31185	-4.97093	7.65753×10^{-1}
$q_7/(\mathrm{kg\cdot mol^{-1}\cdot MPa^{-1}})$	-5.59578×10^{-2}	4.23731×10^{-2}	-2.14925×10^{-3}
$q_8/(\mathrm{kg\cdot mol^{-1}\cdot K^{-1}\cdot MPa^{-1}})$	1.64166×10^{-4}	-1.17984×10^{-4}	
$q_9/(\mathrm{kg\cdot mol^{-1}\cdot K^{-2}\cdot MPa^{-1}})$	-1.57572×10^{-7}	1.07995×10^{-7}	
$q_{10}/(\mathrm{kg\cdot K\cdot mol^{-1}\cdot MPa^{-1}})$	2.82852	2.55671	
$q_{11}/(\mathrm{kg\cdot mol^{-1}\cdot MPa^{-1}})$	-9.85529×10^{-3}	-8.90863×10^{-3}	-7.54375×10^{-4}
range	0–1 *m* 273–473 K	0–1 *m* 278–473 K	0–1 *m* 298–473 K

25. All 11 parameters were needed in the case of $MgCl_2$ (Table II). For $CaCl_2$ and $SrCl_2$, only the first three parameters were needed for the intercept, $\bar{C}^\circ{}_{p,2}$. For $CaCl_2$, $\beta^{(1)J}$ could be expressed by the constant term P_{10}. For $SrCl_2$, the $\beta^{(0)J}$ and $\beta^{(1)J}$ each required first two terms of eq 25b and 25c.

Initially, all the data points were given equal weights. However, we found that for $MgCl_2$ the values of Saluja and LeBlanc (*2*) and Likke and Bromley (*8*) differed by as much as 15 $\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$ at 373 K. Hence, all the data in the region 353–373 K were given lesser weights. All the data for $CaCl_2$ and $SrCl_2$ were given equal weights. The weighted standard deviation of the fit for $MgCl_2$ was 3.6, for $CaCl_2$ 5.4, and for $SrCl_2$ 4.8 $\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$.

***Volumetric Properties*.** The treatment of the data for the apparent molar volumes was similar in that the parameter $C^V{}_{MX}$ was not required because the data extend only up to 1 $\mathrm{mol\cdot kg^{-1}}$. Hence, eq 11 was reduced to the following

$${}^\phi V = \bar{V}^\circ{}_2 + (3A_V/b) \ln (1 + bI^{1/2}) + 4RTm\beta^{(0)V} + 8RTm\beta^{(1)V}[1 - (1 + \alpha I^{1/2}) \exp(-\alpha I^{1/2})]/\alpha^2 I \tag{26}$$

where $\beta^{(0)V} = (\partial \beta^{(0)}/\partial P)T$, with a similar definition for $\beta^{(1)V}$. Again different parametric forms of the fitting parameters were tried, and the necessary parameters in this case could be defined by the following equations

$$\bar{V}^\circ{}_2 = q_1/T + q_2 + q_3 T + q_4 T^2 + q_5 T^3 \tag{27a}$$

$$\beta^{(0)V} = q_6/T + q_7 + q_8 T + q_9 T^2 \tag{27b}$$

$$\beta^{(1)V} = q_{10}/T + q_{11} \tag{27c}$$

where q's are the fitting parameters. All 11 parameters were required for $MgCl_2$ and $CaCl_2$ (Table III). For $SrCl_2$, only seven parameters were required to fit the whole array of data.

For $MgCl_2$, a bulk of the points up to 323 K were given equal weights except a few points at very low molality, which showed large deviations and were assigned lower weights. The data of Dunn (*16*) and Vasilev et al. (*18*) at 298 K showed larger deviations and were assigned smaller weights. The high-temperature data of Ellis (*9*) were assigned lower weights with decreasing molality and with increasing temperature. For $CaCl_2$ and $SrCl_2$, all the data points were given equal weights except those of Ellis (*9*), which were weighted the same as for $MgCl_2$. The standard deviations of the fit for $MgCl_2$, $CaCl_2$, and $SrCl_2$ were 0.18, 0.62, and 0.71 $cm^3 mol^{-1}$, respectively.

***Pressure Dependence of Thermodynamic Properties*.** One can obtain the pressure dependence of the thermodynamic properties from the volumetric results using the following relationships:

$$(\partial G/\partial P)_T = V \tag{28}$$

$$(\partial H/\partial P)_T = V - T(\partial V/\partial T)_p \tag{29}$$

$$(\partial C_p/\partial P)_T = -T(\partial^2 V/\partial T^2)_p \tag{30}$$

$$(\partial \beta^{(0)J}/\partial P)_T = (\partial^2 \beta^{(0)V}/\partial T^2)_p + (2/T)(\partial \beta^{(0)V}/\partial T)_p \tag{31}$$

A relation similar to eq 31 follows for the pressure dependence of $\beta^{(1)J}$. Equation 30 gives the pressure effects on the heat capacities described in this paper.

***Enthalpy and Gibbs Energy*.** The enthalpy parameter, $\beta^{(0)L}$, is given by

$$T^2\beta^{(0)L} = \int_{298}^{T} (T')^2\beta^{(0)J}\,dT' + 298^2\beta^{(0)L}(298) \tag{32}$$

where $\beta^{(0)L}(298)$ is the value of enthalpy parameter at 298.15 K. Substitution of eq 25b into the above equation yields

$$\beta^{(0)L} = [(T^2 - 298^2)p_6/2 + (T^3 - 298^3)p_7/3 + (T^4 - 298^4)p_8/4 + 298^2\beta^{(0)L}(298)]/T^2 \tag{33}$$

The pressure dependence may also be introduced by the relationship

$$\beta^{(0)L}(P) = \int_{P_0}^{P} (\partial \beta^{(0)V}/\partial T)_p\,dP' + \beta^{(0)L}(P_0) \tag{34}$$

where P_0 is the pressure at which $\beta^{(0)L}$ is known. By adding this pressure dependence, eq 33 becomes

$$\beta^{(0)L} = [(T^2 - 298^2)p_8/2 + (T^3 - 298^3)p_7/3 + (T^4 - 298^4)p_8/4 + 298^2\beta^{(0)L}(298,P_0)]/T^2 + [-q_6/T^2 + q_8 + 2q_9T](P - P_0) \tag{35}$$

Similar equations apply for $\beta^{(1)L}$ and C^L. C^J and C^V were found to be unnecessary; thus, only the term $298^2C^L(298,P_0)/T^2$ remains.

A second integration yields the excess Gibbs energy. Again, for the ion-interaction parameter, we get

$$\beta^{(0)} = \int_{298}^{T} \beta^{(0)L}\,dT' + \beta^{(0)}(298) \tag{36}$$

The pressure dependence of $\beta^{(0)}$ is given by

$$\partial\beta^{(0)}/\partial P = \beta^{(0)V} \tag{37}$$

Combining equations 36 and 37, we get

$$\beta^{(0)} = (T/2 + 298^2/2T - 298)p_6 + (T^2/6 + 298^3/3T - 298^2/2)p_7 + (T^3/12 + 298^4/4T - 298^3/3)p_8 + (298 - 298^2/T)\beta^{(0)L}(298,P_0) + [q_6/T + q_7 + q_8T + q_9T^2](P - P_0) + \beta^{(0)}(298,P_0) \tag{38}$$

Again similar relations apply for $\beta^{(1)}$ and C although in our case the equation for C is simplified to the two terms in $C^L(298,P_0)$ and $C(298,P_0)$.

Table IV. Values for the Ion-Interaction Parameters and Their Derivatives at 298.15 K

parameter	$MgCl_2$	$CaCl_2$	$SrCl_2$
$\beta^{(0)}/(kg \cdot mol^{-1})$	3.5093×10^{-1} [a]	3.0534×10^{-1} [b]	2.8344×10^{-1} [c]
$\beta^{(1)}/(kg \cdot mol^{-1})$	1.6508[a]	1.7083[b]	1.6256[c]
$C/(kg^2 \cdot mol^{-2})$	2.301×10^{-3} [a]	7.612×10^{-4} [b]	-3.150×10^{-4} [c]
$\beta^{(0)L}/(kg \cdot mol^{-1} \cdot K^{-1})$	-9.8786×10^{-5}	1.8215×10^{-4}	4.3709×10^{-4}
$\beta^{(1)L}/(kg \cdot mol^{-1} \cdot K^{-1})$	2.666×10^{-3}	3.554×10^{-3}	3.674×10^{-3}
$C^L/(kg^2 \cdot mol^{-2} \cdot K^{-1})$	-7.624×10^{-5}	-4.754×10^{-5}	-5.076×10^{-5}
$\beta^{(0)J}/(kg \cdot mol^{-1} \cdot K^{-2})$	-8.101×10^{-6}	-1.289×10^{-5}	-1.684×10^{-5}
$\beta^{(1)J}/(kg \cdot mol^{-1} \cdot K^{-2})$	5.990×10^{-5}	5.249×10^{-5}	2.918×10^{-5}
$\beta^{(0)V}/(kg \cdot mol^{-1} \cdot MPa^{-1})$	1.512×10^{-4}	1.236×10^{-4}	4.191×10^{-4}
$\beta^{(1)V}/(kg \cdot mol^{-1} \cdot MPa^{-1})$	-3.684×10^{-4}	-3.334×10^{-4}	-7.544×10^{-4}

[a] From ref *31*. [b] From ref *33*. [c] From ref *32*.

The integrations of $\bar{C}^\circ_{p,2}$ to yield the enthalpy and Gibbs energy as a function of temperature for the salt in its standard state are similar and yield

$$\bar{H}^\circ_2 = \ln(T/298)p_1 + (T - 298)p_2 + (T^2 - 298^2)p_3/2 + (T^3 - 298^3)p_4/3 + (T^4 - 298^4)p_5/4 + [-q_1/T^2 + q_3 + 2q_4T + 3q_5T^2](P - P_0) + \bar{H}^\circ_2(298,P_0) \tag{39}$$

$$\bar{G}^\circ_2/T = [(\ln T)/T + 1/T - 1/298 - (\ln 298)/T]p_1 + (1 - 298/T - \ln(T/298))p_2 + (2(298) - T - 298^2/T)p_3/2 + ((3/2)298^2 - T^2/2 - 298^3/T)p_4/^3 + ((4/3)298^3 - T^3/3 - 298^4/T)p_5/^4 + \bar{H}^\circ_2(298,P_0)[1/T - 1/298] + [q_1/T^2 + q_2/T + q_3 + q_4T + q_5T^2](P - P_0) + \bar{G}^\circ_2(298,P_0)/298 \tag{40}$$

Table IV gives the ion-interaction parameters and their derivatives at 298.15 K. The Gibbs energy parameters for these systems are known accurately and were used as such. The parameters for $MgCl_2$ and $SrCl_2$ were taken from the work of Rard and Miller (*31*, *32*), whereas for $CaCl_2$ the parameters were taken from the previous work of Phutela and Pitzer (*33*). All of the remaining parameters were obtained in this study as described above or in the following section.

***Determination of Enthalpy Parameters*.** We initially expected to take values of the enthalpy parameters for 298 K from the literature (*34*) but found that considerable improvement was now possible in view of recent measurements. Although a simultaneous fit of all parameters (including $p_1 - p_{11}$) could be made, this is complex and we expect that publication of new measurements would render such a treatment obsolete before many years. Consequently, we took an intermediate course and determined new enthalpy parameters for 298 K which yield (in the integrated equations with $p_1 - p_{11}$ already determined) quite good agreement with the high-temperature osmotic data of Holmes and Mesmer (*35*, *36*) and various measurements of the heat of dilution (*37*–*41*).

In this relatively simple least-squares regression, the parameter $\beta^{(1)L}(298)$ is sensitive to data at low molality and is determined primarily by the heat-of-dilution data below 0.1 mol·kg^{-1} from Lange and Streeck (*37*). The $\beta^{(0)L}(298)$ parameter is determined primarily by data at intermediate molality (0.1 to 1.0 mol·kg^{-1}). Both enthalpies and osmotic coefficients are fitted quite well in this range of composition to 473 K for $MgCl_2$ and $SrCl_2$ or to 445 K for $CaCl_2$.

At molality above 1 mol·kg^{-1} the triple interaction parameter, C, becomes important, but there is no guidance from the present heat capacity data which do not extend into this range. Nevertheless, for $MgCl_2$ there is good agreement to 2 mol·kg^{-1}

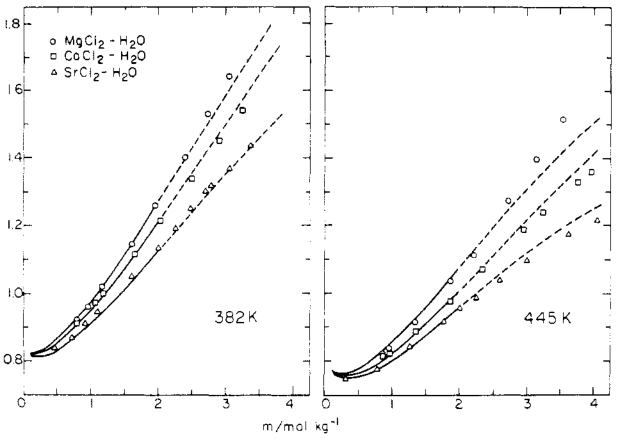

Figure 1. Osmotic coefficients for $MgCl_2$ and $CaCl_2$ at 382.0 K and 445.4 K, and $SrCl_2$ at 382.96 K and 443.92 K. The points are experimental data from Holmes et al. (*35*, *36*). The curves are calculated from the equations and parameters of this paper.

Table V. Standard-State Heat Capacities and Volumes at 298.15 K

	$-\bar{C}^\circ_{p,2}/(J\cdot mol^{-1}\cdot K^{-1})$		$\bar{V}^\circ_2/(cm^3\cdot mol^{-1})$	
	this research (0.6 MPa)	lit. (0.1 MPa)	this research (0.6 MPa)	lit. (0.1 MPa)
$MgCl_2$	264.8	269,^{a} 252.5^b	13.96	14.49,^{e} 14.02,^{f} 15.00^b
$CaCl_2$	275.5	282,^{a} 278.3^b 275.7,^{c} 282.0^d	17.98	17.81,^{e} 17.65,^{f} 18.35,^{b} 18.86,^{g} 16.1^d
$SrCl_2$	288.3	289^a	18.22	17.50,^{e} 18.26^f

^{a} From the single ion values from ref *16*. ^{b} From ref *12*. ^{c} From ref *10*. ^{d} From ref *14*. ^{e} From the single ion values from ref *42*. ^{f} From ref *11*. ^{g} From ref *26*.

for the osmotic coefficient (±0.010) to 473 K and for enthalpies (±0.05 kJ·mol^{-1}) near 300 K. For $CaCl_2$ the good agreement for the osmotic coefficient extends to 2 mol·kg^{-1} and 445 K. For $SrCl_2$ the agreement is not as good (±0.02 for ϕ), but it extends in composition to 3.7 mol·kg^{-1} below 420 K, to 2.5 mol·kg^{-1} at 444 K, and to 1.3 mol·kg^{-1} at 474 K. The only heat-of-dilution data above 1 mol·kg^{-1} for $CaCl_2$ or $SrCl_2$ are of limited accuracy and were not used.

Figure 1 shows the osmotic coefficient for the three electrolyte solutions at 382 K and 445 K. Even though our heat capacity equations are valid only to 1 mol·kg^{-1}, the calculated and experimental values of the osmotic coefficient are in good agreement to 2 mol·kg^{-1}.

Standard-State Properties. Table V compares our results for the standard-state heat capacity and volume with values reported in the literature for 298.15 K. In some cases single-ion values are reported (*15*, *42*) and these are summed as appropriate. Strictly, our values are for 0.6 MPa while the literature values are for 0.1 MPa, but the effect of this pressure difference is small in comparison to the difference between values in Table V where the agreement is quite good.

Registry No. $MgCl_2$, 7786-30-3; $CaCl_2$, 10043-52-4; $SrCl_2$, 10476-85-4.

Literature Cited

(1) Saluja, P. P. S.; Pitzer, K. S.; Phutela, R. C. *Can. J. Chem.* **1986**, *64*, 1328.
(2) Saluja, P. P. S.; LeBlanc, J. C. *J. Chem. Eng. Data*, preceding article in this issue.
(3) Rogers, P. S. Z.; Pitzer, K. S. *J. Phys. Chem.* **1981**, *85*, 2886; **1982**, *86*, 2110.
(4) Phutela, R. C.; Pitzer, K. S. *J. Chem. Eng. Data* **1986**, *31*, 320.
(5) Rogers, P. S. Z.; Pitzer, K. S. *J. Phys. Chem. Ref. Data* **1982**, *11*, 15.
(6) Pitzer, K. S.; Peiper, J. C.; Busey, R. H. *J. Phys. Chem. Re. Data* **1984**, *13*, 1.
(7) Phutela, R. C.; Pitzer, K. S. *J. Phys. Chem.* **1986**, *90*, 895.
(8) Likke, S.; Bromley, L. R. A. *J. Chem. Eng. Data* **1973**, *18*, 189.
(9) Ellis, A. J. *J. Chem. Soc. A* **1967**, 660.
(10) Ananthaswamy, J.; Atkinson, G. *J. Chem. Eng. Data* **1985**, *30*, 120.
(11) Perron, G.; Desnoyers, J. E.; Millero, F. J. *Can. J. Chem.* **1974**, *52*, 3738.
(12) Perron, G.; Roux, A.; Desnoyers, J. E. *Can. J. Chem.* **1981**, *59*, 3049.
(13) Wood, R. H., University of Delaware, private communication, 1985.
(14) Spitzer, J. J.; Singh, P. P.; McCurdy, K. G.; Hepler, L. G. *J. Solution Chem.* **1978**, *7*, 81.
(15) Desnoyers, J. E.; de Visser, C.; Perron, G.; Picker, P. *J. Solution Chem.* **1976**, *5*, 605.
(16) Dunn, L. A. *Trans. Faraday Soc.* **1966**, *62*, 2348.
(17) Millero, F. J.; Knox, J. H. *J. Chem. Eng. Data* **1973**, *18*, 407.
(18) Vasilev, Y. A.; Fedyainov, N. V.; Kurenkov, V. V. *Russ. J. Phys. Chem.* **1973**, *47*, 1570.
(19) Chen, C. T.; Emmet, R. T.; Millero, F. J. *J. Chem. Eng. Data* **1977**, *22*, 201.
(20) Chen, C. T. A.; Chen, J. H.; Millero, F. J. *J. Chem. Eng. data* **1980**, *25*, 307.
(21) Phang, S.; Stokes, R. H. *J. Solution Chem.* **1980**, *9*, 947.
(22) Surdo, A. L.; Alzola, E. M.; Millero, F. J. *J. Chem. Thermodyn.* **1982**, *14*, 649.
(23) Romankiw, L. A.; Chou, I. M. *J. Chem. Eng. Data* **1983**, *28*, 300.
(24) Miller, D. G.; Rard, J. A.; Eppstein, L. B.; Albright, J. G. *J. Phys. Chem.* **1984**, *88*, 5739.
(25) Gates, J. A.; Wood, R. H. *J. Chem. Eng. Data* **1985**, *30*, 44.
(26) Kumar, A.; Atkinson, G.; Howell, R. D. *J. Solution Chem.* **1982**, *11*, 857.
(27) Kumar, A.; Atkinson, G. *J. Phys. Chem.* **1983**, *87*, 5504.
(28) Pitzer, K. S. *Activiy Coefficients in Electrolyte Solutions*; Pytkowitz, R. M., Ed.; CRC Press: Boca Raton, FL, 1979; Vol. I, Chapter 7.
(29) Bradley, D. J.; Pitzer, K. S. *J. Phys. Chem.* **1979**, *83*, 1599.
(30) Haar, L.; Gallagher, J. S.; Kell, G. S. *NBS/NRC Steam Tables*; Hemisphere: Washington, DC, 1985; *Proceeding of the Eighth Symposium on Thermophysical Properties*; Senger, J. V., Ed.; American Soceity of Mechanical Engineers: New York, 1981; Vol. 2, p 298.
(31) Rard, J. A.; Miller, D. G. *J. Chem. Eng. Data* **1981**, *26*, 38.
(32) Rard, J. A.; Miller, D. G. *J. Chem. Eng. Data* **1982**, *27*, 169.
(33) Phutela, R. C.; Pitzer, K. S. *J. Solution Chem.* **1983**, *3*, 201.
(34) Silvester, L. F.; Pitzer, K. S. *J. Solution Chem.* **1978**, *7*, 327.
(35) Holmes, H. F.; Baes, C. F., Jr.; Mesmer, R. E. *J. Chem. Thermodn.* **1978**, *10*, 983.
(36) Holmes, H. F.; Mesmer, R. E. *J. Chem. Thermodyn.* **1981**, *13*, 1025.
(37) Lange, E.; Streeck, H. *Z. Phys. Chem. (Leipzig)* **1931**, *A152*, 1.
(38) Leung, W. H.; Millero, F. J. *J. Solution Chem.* **1975**, *4*, 145.
(39) Leung, W. H.; Millero, F. J. *J. Chem. Thermodyn.* **1975**, *7*, 1067.
(40) Snipes, H. P.; Charles, M.; Ensor, D. D. *J. Chem. Eng. Data* **1975**, *20*, 287.
(41) Mayrath, J. E.; Wood, R. H. *J. Chem. Eng. Data* **1983**, *28*, 56.
(42) Millero, F. J. *Water and Aqueous Solutions*; Horne, R. A., Ed.; Wiley-Interscience: New York, 1972; Chapter 13.

Received for review March 25, 1986. Accepted July 15, 1986. The work at Berkeley was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Division of Engineering and Geosciences of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.