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# Evaluated Activity and Osmotic Coefficients for Aqueous Solutions: The Alkaline Earth Metal Halides

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A critical evaluation of the mean activity and osmotic coefficients in aqueous solutions of the alkaline earth metal halides at 298.15 K is presented. Osmotic coefficients were calculated from direct vapor pressure measurements, from isopiestic measurements, and from freezing point depression measurements. Activity coefficients were calculated from electromotive force measurements on galvanic cells, both with and without transference, and from diffusion data. Given are empirical coefficients for three different correlating equations, obtained by a weighted least squares fit of the experimental data, and tables consisting of the activity coefficients of the halides, the osmotic coefficients and activity of water, and the excess Gibbs energy of the solution as a function of the molality for each electrolyte system. The literature coverage is through September 1976.

**Key words:** Activity coefficient; alkaline earth metal halides; critical evaluation; electrolyte; excess Gibbs energy; osmotic coefficients; solutions; thermodynamic properties.

## 1. Introduction

The purpose of this paper is to present an evaluation of the activity and osmotic coefficients in aqueous solutions of the alkaline earth metal halides at 298.15 K. The evaluation procedures have been described previously [1,2]<sup>1</sup>. These documents, with the few additional matters discussed herein provide a description of the evaluation procedures we have used. We have chosen to present our evaluation in detail so that any potential users of the data, as well as future data evaluators, can have a better view of the status of the measurements on these systems. We also give coefficients, obtained by a weighted least-squares fit of the experimental data, for three different correlating equations and tables consisting of the mean activity coefficients of the electrolyte, the osmotic coefficient and activity of water, and the excess Gibbs energy of the solution as a function of the molality for each electrolyte system. The literature coverage is through September 1976.

The reader is referred to the glossary of symbols at the end of this paper for the definitions of the various symbols used throughout this paper. In general, we have attempted to adhere to the recommendations of the IUPAC [2a] with regard to nomenclature and units.

## 2. Experimental Methods for the Determination of Mean Activity and Osmotic Coefficients

In a previous paper [1], a rather detailed discussion was given of the experimental basis of the various methods by which activity and osmotic coefficients are

measured. The determination of osmotic coefficients from freezing point depression measurements, requires a somewhat more detailed discussion than was given in ref. [1].

### 2.1. Freezing Point Depression Measurements

Our evaluation procedure calculates the osmotic coefficient,  $\phi$ , using the equations given by Lewis and Randall and Pitzer and Brewer [3] (note that there is a sign error in their equation (26-9)):

$$\begin{aligned} -\frac{\nu M_1 R}{1000} m \phi = & - \left( \frac{\Delta H_{\text{fus}}^{\circ} + \bar{L}_1}{T T_{\text{fus}}} \right) \Theta \\ & + (\Delta C_{\text{fus}}^{\circ} + \bar{J}_1) \left[ \frac{\Theta}{T} + \ln \left( 1 - \frac{\Theta}{T_{\text{fus}}} \right) \right] \\ & + \Delta b \left[ \frac{\Theta^2}{2T} - \frac{T_{\text{fus}} \Theta}{T} - T_{\text{fus}} \ln \left( 1 - \frac{\Theta}{T_{\text{fus}}} \right) \right]. \end{aligned}$$

We follow Lewis and Randall and Pitzer and Brewer [3] and use the values  $\Delta H_{\text{fus}}^{\circ} = 1436 \text{ cal} \cdot \text{mol}^{-1} = 6008 \text{ J} \cdot \text{mol}^{-1}$ ,  $\Delta C_{\text{fus}}^{\circ} = 9.1 \text{ cal} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} = 38.1 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$  for water. We are unaware of any experimental data that lead to a value of  $\Delta b$  for any electrolyte solutions and we therefore use Lewis and Randall's and Pitzer and Brewer's [3] estimated  $\Delta b = -0.047 \text{ cal} \cdot \text{K}^{-2} \cdot \text{mol}^{-1} = -0.197 \text{ J} \cdot \text{K}^{-2} \cdot \text{mol}^{-1}$  which is based on the trend of the heat capacities of pure ice and water near 0 °C.

Values of  $\bar{L}_1$  and  $\bar{J}_1$  are obtained for each system of interest by using, respectively, measured values of the relative apparent molal enthalpy ( $\Phi_L$ ) and the apparent molal heat capacity ( $\Phi_C$ ) and the relationships:

$$\bar{L}_1 = - \frac{M_1 m^{3/2}}{2000} \frac{d \Phi_L}{dm^{1/2}}$$

<sup>1</sup> Figures in brackets indicate literature references at the end of this paper.

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and

$$\bar{J}_1 = -\frac{M_1 m^{3/2}}{2000} \frac{d\Phi_C}{dm^{1/2}}.$$

Since  $\Phi_C$  and  $\Phi_L$  are usually obtained at 25 °C,  $\bar{L}_1$  is calculated at the temperature  $T_{fus}$  using  $(\partial\bar{L}_1/\partial T)_p = \bar{J}_1$  and the calculated value of  $\bar{J}_1$  at 25 °C which is assumed to be constant over the temperature range of interest.

The osmotic coefficients, so obtained at 273.15 K, are used to calculate values at 298.15 K, using the integrated form of the Gibbs-Helmholtz equation:

$$\begin{aligned}\phi_{298.15} &= \phi_{273.15} - \frac{1000}{\nu m M_1} \left[ \frac{-25 \bar{L}_1}{R(298.15)(273.15)} \right. \\ &\quad \left. + \frac{\bar{J}_1(25)}{R(273.15)} - \frac{\bar{J}_1}{R} \ln \frac{298.15}{273.15} \right],\end{aligned}$$

which is derived on the assumption, again, that  $\bar{J}_1$  is constant over the temperature range of interest.

While the above is a nearly rigorous treatment of the experimental data, it is worth emphasizing that both accurately measured freezing point depressions and thermal data ( $\Phi_L$  and  $\Phi_C$ ) are required to obtain accurate values of the osmotic coefficient at both 273.15 and 298.15 K. Indeed, the error in the calculated values of the osmotic coefficients due to any error in the thermal data becomes increasingly larger as the concentrations of the solutions increases. It is for this reason that we have tended to terminate our calculations of osmotic coefficients from freezing point data at a molality of 0.2 to 1.0 mol·kg<sup>-1</sup>. Nevertheless, the value of this method of obtaining osmotic coefficients, and hence activity coefficients, in the dilute region is a very powerful and general one and is in some cases the only sound method available.

## 2.2 Some Comments on the Calculation of Activity and Osmotic Coefficients and on the Evaluation Procedure

Osmotic coefficients are directly calculable from measurable quantities (vapor pressures and freezing point depressions of solutions) using the phenomenological laws of thermodynamics and no additional assumptions are required either in the form of a correlating equation or in assumed potential functions. However, activity coefficients are not directly obtainable either by integration of the Gibbs-Duhem equation or from measurements on electrochemical cells (with or without transference) unless one first assumes some theoretical or correlating equation to handle the necessary extrapolation and integration of the data to infinite dilution. One must therefore expect numerical differences between activity coefficients calculated using different correlating equations. The Debye-Hückel limiting law [4] provides a theoretical function for the very dilute region. The self-consistent approach used in a previous paper [1] is one means of obtaining the coefficients for

selected correlating equations. We have adopted this procedure here and present coefficients for three correlating equations which, for activity coefficients, are:

$$\ln \gamma = -\frac{A_1 I^{1/2}}{1 + B I^{1/2}} + C m + D m^2 + E m^3 + \dots, \quad (1a)$$

$$\ln \gamma = -A_1 I^{1/2} - A_2 I \ln I + \sum_{i=1}^N B_i m^{(i+1)/2}, \quad (2a)$$

$$\ln \gamma = -A_1 I^{1/2} + \sum_{i=1}^N B_i m^{(i+1)/2}. \quad (3a)$$

The Debye-Hückel limiting law [4] is incorporated in the first term in each of the above three equations for the activity coefficient.

The first term of eq (1) is of the form which was derived by Debye and Hückel to account for finite ion size and which has been used successfully to fit data to higher concentrations than the limiting law is valid. In our treatment the coefficient,  $B$ , as well as the higher order coefficients are empirically determined.

A higher order limiting law has been derived theoretically [5] and is given in eq (2a) where the coefficients of the first and second terms are functions only of the temperature, the charge type of the salt, and the properties of the solvent. We have examined the magnitude of the second term in this equation and we find no evidence that it contributes significantly to the integrals in the low concentration range; nor do the activity or osmotic coefficient data for the systems considered herein provide evidence for the verification of this term. It is completely swamped by other effects in the experimental range of concentrations for the systems considered in this paper.

In eq (3a) the limiting law is simply followed by an empirical polynomial in the square root of the molality.

The activity coefficient,  $\gamma$ , the osmotic coefficient,  $\phi$ , the water activity,  $a_w$ , and the excess Gibbs energy,  $\Delta G^{\text{ex}}$ , are related by the following expressions:

$$\phi = -\frac{1000}{\nu m M} \ln a_w = 1 + \frac{1}{m} \int_0^m m d \ln \gamma$$

and

$$\Delta G^{\text{ex}} = \nu m RT (1 - \phi + \ln \gamma).$$

Combining these expressions with eq (1a), (1b) or (1c) leads to equations with common coefficients for the other quantities. These corresponding equations for the osmotic coefficient are, respectively:

$$\begin{aligned}\phi &= 1 + \frac{A_1}{B^3 I} \left\{ -(1 + BI^{1/2}) + 2 \ln (1 + BI^{1/2}) \right. \\ &\quad \left. + 1/(1 + BI^{1/2}) \right\} + \frac{1}{2} C m + \frac{2}{3} D m^2 + \frac{3}{4} E m^3 + \dots, \quad (1b)\end{aligned}$$

$$\phi = 1 - \frac{A_1}{3} I^{1/2} - \frac{A_2}{2} I [\ln I + \frac{1}{2}] + \sum_{i=1}^N B_i \frac{(i+1)}{(i+3)} m^{(i+1)/2}, \quad (2b)$$

and

$$\phi = 1 - \frac{A_1}{3} I^{1/2} + \sum_{i=1}^N B_i \frac{(i+1)}{(i+3)} m^{(i+1)/2}. \quad (3b)$$

For 2-1 electrolytes in water at 25 °C,  $A_1 = 2.3525 \text{ mol}^{-1/2} \cdot \text{kg}^{1/2}$  and  $A_2 = \frac{2}{3} A_1^2 = 0.92238 \text{ mol}^{-1} \cdot \text{kg}$ .

Each of the above correlating equations appears to be justifiable at present and, hence, we have included fits to all three of these equations in this paper. Eqs (1) have two advantages: (1) for most of the systems examined in this paper, fewer coefficients are required to obtain a satisfactory fit to the data and (2) fewer digits in the coefficients are required to calculate a value of the activity or osmotic coefficient to a given degree of precision. Eqs (1), however, suffer from two disadvantages: (1) they are non-linear and hence not as useful as eqs (2) and (3) for application to mixed electrolyte systems and (2) they are not of a form suitable for general application to all binary electrolyte systems in that a negative B value of too large a magnitude is mathematically not allowed.

We have also used activity coefficients based on diffusion measurements. In terms of the laws of thermodynamics (reversible and irreversible) this is not possible [6] unless one first assumes a potential function(s) to represent the various molecular interactions. For activity coefficients calculated from diffusion measurements we have relied upon the analysis of Harned [7]. As noted previously [1], this method of obtaining activity coefficients is applicable only to very dilute solutions.

The proper weighting of the various data sets we are evaluating cannot be entirely made objectively. We have tried to form a judgment as to the accuracy of a given data set by reading the various papers and assessing the merits of the experimental methods used; the general quality of the data obtained from a given laboratory is also a factor. A principal difficulty here is that the numerous details that go into an investigation are only rarely fully described in a given paper. The difficulty in assessing possible systematic errors is mitigated somewhat when data from several different types of measurements are available. These data should, if the systematic and random errors are within bounds, fit together to substantiate the accuracy of the entire data network.

### 3. Discussion of Data Sources

In this section we present in detail (tables 1 to 11) the experimental data upon which our evaluation is based, the calculated values of  $\phi$  and  $\gamma/\gamma_{\text{ref}}$ , and our weightings

of the various data sources. Using these weightings, a fitting of the data was performed, the results of which are the coefficients given in tables 13 to 15. The recommended values of the activity and osmotic coefficients are given in tables 17 to 27 which also give values of the activity of water and of the excess Gibbs energy per kilogram of solvent. Also shown are deviation plots in  $\Delta\phi$  and  $\Delta\gamma$  (figures 1 to 16) and the overall standard deviations in the fit for each system (table 16). In the deviation plots, the symbol Δ means observed minus calculated values. In table 12 are given the various auxiliary data that were used in the calculations of the osmotic and activity coefficients.

The values of  $\gamma_{\text{ref}}$  given in tables 1 to 11, the deviation plots, the values of the activity and the osmotic coefficients, the water activity and the excess Gibbs energy given in tables 17 to 27 are all based on eqs (1) with the coefficients given in table 13. The coefficients for eqs (2) and (3) are given in tables 14 and 15, respectively.

#### 3.1. Magnesium Chloride (Table 1)

Isopiestic measurements are reported by Robinson and Stokes [8] for molalities of 0.1 to 2.0  $\text{mol} \cdot \text{kg}^{-1}$ ; by Stokes [9] for molalities of 1.1 to 5.9  $\text{mol} \cdot \text{kg}^{-1}$  (saturation is reported to be at 5.84  $\text{mol} \cdot \text{kg}^{-1}$ ); by Robinson and Bower [9a] at 0.3 to 4.4  $\text{mol} \cdot \text{kg}^{-1}$ ; by Saad, Padova and Marcus [10] at 0.4 to 2  $\text{mol} \cdot \text{kg}^{-1}$ ; and by Platford [10a] at 0.08 to 2.7  $\text{mol} \cdot \text{kg}^{-1}$ . Osmotic coefficients from these sets of data are in good agreement, although the data of Platford are quite widely scattered.

Serowy and Soika [11] report vapor pressure measurements at temperatures of 20, 24, 30, 35, 40, and 45 °C and molalities from 0.5 to 5.2  $\text{mol} \cdot \text{kg}^{-1}$ . They interpolated their data to report values at 25 °C. Osmotic coefficients from these data are not in good agreement with those from the isopiestic data.

Petit [12] reports vapor pressure measurements over the range  $m = 0.7$  to 4.5  $\text{mol} \cdot \text{kg}^{-1}$ . She claims an accuracy of .001 in the activity of water. However, discrepancies and obvious errors in the reported table of results and a wide scatter of reported results decrease our confidence in her work.

Many measurements of the vapor pressure of water over saturated solutions of magnesium chloride have been made. Greenspan [13] has recently made a critical evaluation of these data and we have included his selected value at 25 °C in our data set.

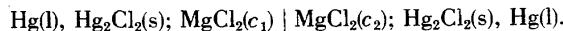
Freezing point depression measurements have been reported by Gibbard and Gossman [14] for solutions from  $m = 0.03$  to 2.0  $\text{mol} \cdot \text{kg}^{-1}$ ; by Menzel [15]<sup>2</sup> from 0.06 to 0.6  $\text{mol} \cdot \text{kg}^{-1}$ ; by Rodebush [16] from 0.9 to 2.5  $\text{mol} \cdot \text{kg}^{-1}$ ; by Loomis [17] from 0.01 to 0.3  $\text{mol} \cdot \text{kg}^{-1}$  and by Rivett [18] from 0.05 to 0.8  $\text{mol} \cdot \text{kg}^{-1}$ . The data of Loomis give osmotic coefficients about 2% higher than corresponding values from the other measurements

<sup>2</sup> Menzel [15] reported his freezing point depression in units of "mole" where 1 mol° = 1.860 °C. These data are given in the Landolt-Bornstein [21] tables, but are erroneously labeled and used as °C.

which agree well with each other. Because of the difficulty of accurate correction to 25°C the data above about 1.0 molal have not been used in this correlation.

Harned and Polestra [19] reported measurements of the diffusion coefficients for MgCl<sub>2</sub> in water. Harned [7] used these data to calculate activity coefficients. These results are the only ones available in the very dilute region.

Geissler [20] measured the emf of the concentration cell with transference:



We have combined his results with available data on transference numbers to calculate activity coefficients. The results are not of sufficient accuracy to be used in this correlation.

### 3.2. Magnesium Bromide (Table 2)

Isopiestic measurements were performed by Robinson and Stokes [22] and by Stokes [23]. Both sets of data were given equal weight, with the exception of one data point at a molality of 1.086 mol·kg<sup>-1</sup> which appears to be an outlier, in arriving at a final set of values.

### 3.3. Magnesium Iodide (Table 3)

Isopiestic measurements were performed by Robinson and Stokes [22] and by Stokes [23]. Both sets of data were weighted equally.

### 3.4. Calcium Bromide (Table 4)

Isopiestic measurements were performed by Robinson [24] and by Robinson and McCoach [25] and freezing point depression measurements by Meyer [26]. The isopiestic measurements were weighted equally, while the less precise freezing point depression measurements were given zero weight in our final fitting. It should be noted, however, that there is a fair amount of scatter in the isopiestic measurements. Also, the isopiestic data [25] extend beyond the solubility at 7.66 mol·kg<sup>-1</sup> [58] and apparently pertain to super-saturated solutions [25a].

### 3.5. Calcium Iodide (Table 5)

Robinson [24] reports a set of isopiestic measurements and Meyer a set of freezing point measurements [26]. The agreement of these two sets of data is probably within their experimental uncertainties.

### 3.6. Strontium Chloride (Table 6)

Isopiestic measurements were performed by Downes [27], Phillips, Watson, and Felsing [28], Robinson [29], and Stokes [23]. Hepburn [30] reports vapor pressure measurements, and Loomis [31] has performed freezing point depression measurements. Emf measurements on

cells without transference are available from Lucasse [33] and from Longhi et al [32]; measurements on cells with transference have been reported by Masaki [34] and Lucasse [33]. These latter measurements cannot be treated in the absence of the prerequisite transference number measurements (note: Masaki's interpretation of his own measurements is incorrect and his measurements appear to yield highly inaccurate activity coefficients using estimated transference numbers). The cell measurements of Hass and Jellinck [35] involve unknown liquid junction potentials and cannot be rigorously treated to yield activity coefficients. Harned [7] reports a set of activity coefficients based on diffusion measurements.

In the dilute region we rely on the analysis of the diffusion data by Harned [7], the results of which merge reasonably well with the freezing point data of Loomis [31]. The most serious problem in evaluating the data for the SrCl<sub>2</sub> system arises in regards to the nonagreement between the various sets of isopiestic data. The four different sets of isopiestic data begin to diverge at  $m = 1.2 \text{ mol}\cdot\text{kg}^{-1}$ , with the data of Robinson [29] showing larger than anticipated deviations from the results of the other three investigations. While the data of Phillips et al. [28] end at  $m = 1.302 \text{ mol}\cdot\text{kg}^{-1}$ , the data of Downes [27] and of Stokes [23] go to higher molalities and are in good agreement with each other but continue to show large systematic differences from the results of Robinson [29]. The data of Hepburn [30] are not precise enough to help resolve this matter. The data of Lucasse [33], with the exception of one measurement at  $m = 2.115 \text{ mol}\cdot\text{kg}^{-1}$ , lie midway between these various data sets. The recent measurements of Longhi et al. [32] on an electrochemical cell without transference show systematic negative differences (from 0.003 to 0.030 in  $\gamma$ ) from the isopiestic data, the freezing point data, and the emf measurements of Lucasse [33]. Our weighting scheme reflects our decision to give the most credence to the two isopiestic data sets that are in good agreement with each other.

### 3.7. Strontium Bromide (Table 7)

Isopiestic measurements were performed by Robinson [24] and freezing point depression measurements by Meyer [26]. The osmotic coefficients calculated from the freezing point data are not in good agreement with those obtained from the isopiestic measurements. The latter are judged to be much more accurate than the former.

### 3.8. Strontium Iodide (Table 8)

Isopiestic measurements were performed by Robinson [24] and freezing point depression measurements by Meyer [26]. The osmotic coefficients calculated from the freezing point data are not in good agreement with those obtained from the isopiestic measurements. The

latter are judged to be much more accurate than the former.

### 3.9. Barium Chloride (Table 9)

Isopiestic measurements have been performed by Robinson et al., in four separate investigations [29, 36-38]; there are several sets of freezing point measurements [17, 39-43], and four reports of vapor pressure measurements [30, 44-46]. There are also emf measurements on cells with [33, 47-49], and without transference [33, 48, 50, 51], the latter being made useful for our purposes due to the presence of a reasonably precise set of transference number measurements [49]. Finally, there is one set of activity coefficients based on diffusion measurements [7] and another based on ultracentrifuge measurements [52].

The isopiestic data of Phillips, Watson and Felsing [28] relative to  $\text{SrCl}_2$  were not used to obtain osmotic coefficients for  $\text{BaCl}_2$ ; but rather for  $\text{SrCl}_2$  using our final set of calculated osmotic coefficients for  $\text{BaCl}_2$  as the "standard." Moore, Humphries, and Patterson [53] have performed isopiestic measurements on  $\text{BaCl}_2$  relative to  $\text{NaCl}$  at  $80^\circ\text{C}$ . We choose not to treat this data because of the large uncertainties involved in the various temperature corrections. Christenson [54] reports emf measurements on mixed electrolyte solutions which are not useful for our purposes. The emf data of Berestnewa and Kargin [55] and of Hass and Jellinek [35] involve unknown liquid junction potentials and cannot rigorously be used to obtain activity coefficients.

In the most dilute region ( $m \leq 0.007 \text{ mol} \cdot \text{kg}^{-1}$ ), the diffusion data [7] are in good agreement with the freezing point data of Hall and Harkins [41] and, with the exception of two points, of Jones [39]. The data of Bedford [40] show systematic differences from these three data sets. Unfortunately, the emf data of Drucker [47] yield totally unreasonable results and were given zero weight in the fitting. However, in this dilute region, the emf data of Jones and Dole [49] are also in reasonable agreement with the bulk of the freezing point data and the diffusion data, as is one point from the data of Pearce and Gelbach [48] at  $m = 0.005 \text{ mol} \cdot \text{kg}^{-1}$ . In the region  $0.007 \text{ mol} \cdot \text{kg}^{-1} < m < 0.20 \text{ mol} \cdot \text{kg}^{-1}$ , our fit relies heavily on the freezing point data of Gibbard and Fong [43], Hall and Harkins [41], Loomis [17], and Jones [39]—these four data sets being in good agreement.

For the higher molalities, the isopiestic data [29, 36-38] are judged to be the most reliable. The vapor pressure data of Bechtold and Newton [46] and of Newton and Tippets [45] are, with the exception of

data of  $m \leq 0.7 \text{ mol} \cdot \text{kg}^{-1}$ , in good agreement with the overall fit, while the data of Perreau [44] and of Hepburn [30] do not appear to be very reliable. The emf measurements of Jones and Dole [49] and of Tippets and Newton [50], with the exception of two points given zero weight, fit the curve very well over the range  $m = 0.001$  to  $1.03 \text{ mol} \cdot \text{kg}^{-1}$ . The results of Pearce and Gelbach, [48] who measured two different kinds of concentration cells with transference, show an unusual systematic deviation from our final evaluation; i.e., the deviation is positive for the cell using the silver-silver chloride electrodes and negative for the cell using the barium amalgam electrodes. However, their [48] measurements on the cell without transference do not appear to be very reliable. Lacasse's measurements [33] on cells with and without transference scatter randomly about our final fit and provide additional support to the overall accuracy of the correlations. The recent measurements of Ardizzone et al. [51] on cells without transference cover the range  $m = 0.04$  to  $0.30 \text{ mol} \cdot \text{kg}^{-1}$  and are in excellent agreement with the overall fit of the data. The activity coefficients reported by Rush and Johnson [52], based on ultracentrifuge measurements, are in agreement with our correlation within a reasonable estimate of the uncertainties to be attached to their data.

### 3.10. Barium Bromide (Table 10).

Meyer [26] and Rivett [18] report freezing point depression measurements, a set of isopiestic data is available from Robinson [56], and there is also a set of electromotive force measurements on cells with and without transference from Gelbach and Huppke [57]. In the absence of transference number measurements, we are unable to treat the data from concentration cells with transference. The emf measurements on cells without transference do not appear to be very precise, but do provide additional confirmation of the overall accuracy of the isopiestic measurements. The freezing point data of Rivett are, within a reasonable estimate of the accuracy of that data, in agreement with isopiestic measurements.

### 3.11. Barium Iodide (Table 11)

Isopiestic measurements from Robinson [24] and the freezing point depression data of Meyer [26] provide the data for this system. The less precise freezing point data are in fair accord with the more reliable isopiestic data.

Table 1. Osmotic and Activity Coefficient Data for  $MgCl_2$

Robinson and Stokes [8]. Isopiestic measurements, reference salt is KCl. Assigned weight is 1.0. Saad, Padoya and Marcus [10]. Isopiestic measurements, reference salt is NaCl. Assigned weight is 1.0.

$\frac{m_{ref}}{mol \cdot kg^{-1}}$	$m$ $mol \cdot kg^{-1}$	$\phi$	$\frac{m_{ref}}{mol \cdot kg^{-1}}$	$m$ $mol \cdot kg^{-1}$	$\phi$
.1579	.1120	.8625	.5840	.3927	.9149
.2271	.1587	.8691	.9067	.5817	.9687
.2782	.1917	.8781	1.6109	.9510	1.0874
.2808	.1944	.8739	1.6908	.9833	1.1085
.3936	.2656	.8918	2.1587	1.2003	1.1902
.4156	.2795	.8942	2.8543	1.5083	1.3065
.4379	.2933	.8972	3.0070	1.5710	1.3344
.5299	.3492	.9100	3.1222	1.6180	1.3552
.5548	.3644	.9127	3.5077	1.7773	1.4211
.6035	.3924	.9213	4.3027	2.0853	1.5655
.6242	.4040	.9254			
.6818	.4387	.9304			
.7559	.4815	.9395			
.7617	.4840	.9418			
.8516	.5293	.9628			
.9033	.5600	.9654			
1.0750	.6503	.9903			
1.2170	.7212	1.0123			
1.7980	.9856	1.1047			
1.8060	.9906	1.1041			
1.9700	1.0590	1.1305			
2.4870	1.2660	1.2086			
2.7650	1.3670	1.2536			
2.8050	1.3810	1.2603			
3.7320	1.7130	1.3896			
3.9620	1.7840	1.4268			
4.7120	2.0160	1.5386			
Serowy and Soika [11]. Vapor pressure measurements. Assigned weight is 0.2.					
$\frac{m_{ref}}{mol \cdot kg^{-1}}$			$\frac{P/P^\circ}{mol \cdot kg^{-1}}$		$\phi$
			.5000	.9740	.9734
			1.0000	.9410	1.1236
			1.5000	.8990	1.3115
			2.0000	.8440	1.5669
			2.5000	.7850	1.7892
			3.0000	.7180	2.0406
			3.5000	.6440	2.3236
			4.0000	.5680	2.6135
			4.5000	.4970	2.8717
			5.0000	.4290	3.1286
			5.5000	.3660	3.3782

Stokes [9]. Isopiestic measurements, reference salt is KCl. Assigned weight is 1.0.

<u><math>m_{ref}</math></u> $\text{mol} \cdot \text{kg}^{-1}$	<u><math>m</math></u> $\text{mol} \cdot \text{kg}^{-1}$	<u><math>\phi</math></u>	Petit [12]. Vapor pressure measurements. Assigned weight is zero.		
2.1750	1.1430	1.1617	<u><math>m_{ref}</math></u> $\text{mol} \cdot \text{kg}^{-1}$	<u><math>P/P^\circ</math></u>	<u><math>\phi</math></u>
3.5410	1.6450	1.3648	.7000	.9651	.9364*
3.5910	1.6610	1.3729	1.0000	.9420	1.1049*
3.8330	1.7430	1.4071	1.3000	.9254	1.1018*
4.8100	2.0500	1.5495	2.0000	.8450	1.5554*
kes [9]. Isopiestic measurements, reference is 0. Assigned weight is 1.0.			2.1000	.8367	1.5680*
			2.8000	.7523	1.8786*
			3.0000	.7203	2.0207*
			3.4000	.6599	2.2591*
			3.7000	.6078	2.4866*
			4.0000	.5777	2.5355*
			4.5000	.5248	2.6498*
<u><math>m_{ref}</math></u> $\text{mol} \cdot \text{kg}^{-1}$	<u><math>m</math></u> $\text{mol} \cdot \text{kg}^{-1}$	<u><math>\phi</math></u>	* In these tables, an (*) next to a number is used indicate that it is given zero weight in the fitti		
3.3270	2.1680	1.6014			
3.8600	2.4800	1.7534			
4.3790	2.7820	1.8998			
4.4630	2.8290	1.9245			
4.9590	3.1110	2.0644			
5.0040	3.1360	2.0773			
5.2770	3.2870	2.1549			
5.4260	3.3710	2.1956			
6.2450	3.8090	2.4251			
6.2620	3.8190	2.4291			
6.3070	3.8430	2.4412			
6.6580	4.0260	2.5368			
7.3450	4.3730	2.7209			
7.6080	4.5020	2.7902			
8.4270	4.8930	2.9997			
8.6150	4.9820	3.0455			
9.7400	5.4760	3.3213			
0.6100	5.8400	3.5210			
0.8400	5.9250	3.5771			

\* In these tables, an (\*) next to a number is used to indicate that it is given zero weight in the fitting.

Table 1. Continued

Greenspan [13]. Evaluated vapor pressure of saturated solution. Assigned weight is 1.0.

<u>m</u> <u>mol·kg<sup>-1</sup></u>	<u>P/P°</u>	<u>Φ</u>
5.840	0.3278	3.5306

Gibbard and Gosman [14]. Freezing point depression measurements. Assigned weight is 0.5 or 0.0

<u>m</u> <u>mol·kg<sup>-1</sup></u>	<u>F.P. Depression/K</u>	<u>Φ<sub>273.15</sub></u>	<u>Φ<sub>298.15</sub></u>
2.02725	18.3940	1.604	1.549*
2.00220	17.9730	1.587	1.534*
1.95925	17.3890	1.571	1.519*
1.85505	15.8650	1.517	1.470*
1.70825	13.9060	1.448	1.405*
1.23940	8.5640	1.235	1.205*
1.20390	8.2320	1.223	1.194*
1.05860	6.8711	1.162	1.136*
1.01610	6.4892	1.143	1.118
.90805	5.5870	1.102	1.079
.90415	5.5624	1.102	1.079
.72550	4.1959	1.036	1.018
.61180	3.4005	.996	.980
.53480	2.9000	.972	.957
.53415	2.8851	.968	.954
.47585	2.5275	.952	.939
.40445	2.1018	.932	.920
.33250	1.6879	.910	.900
.25645	1.2733	.890	.882
.25000	1.2445	.892	.884
.17460	.8510	.874	.867
.16710	.8144	.874	.867
.14920	.7240	.870	.863
.12180	.5901	.868	.862
.11835	.5732	.868	.862
.07865	.3813	.869	.863
.05675	.2754	.870	.864
.05458	.2653	.870	.866
.03196	.1579	.885	.881
.02805	.1387	.886	.881

See table 12 for the  $\Phi_L$  and  $\Phi_C$  data used in treating all of the freezing point data for  $MgCl_2$ .

Menzel [15]. Freezing point depression measurements. Assigned weight is 0.5.

<u>m</u> <u>mol·kg<sup>-1</sup></u>	<u>F.P. Depression/K</u>	<u>Φ<sub>273.15</sub></u>	<u>Φ<sub>298.15</sub></u>
.06400	.3097	.867	.862
.07970	.3841	.864	.858
.13300	.6482	.874	.867
.27590	1.3838	.899	.890
.39560	2.0646	.936	.924
.53880	2.9165	.970	.955
.67240	3.8130	1.016	.999

Rodebush [16]. Freezing point depression measurements. Assigned weight is 0.5 or 0.0.

<u>m</u> <u>mol·kg<sup>-1</sup></u>	<u>F.P. Depression/K</u>	<u>Φ<sub>273.15</sub></u>	<u>Φ<sub>298.15</sub></u>
.92321	5.7100	1.107	1.085
1.23305	8.4600	1.227	1.197
1.71304	13.7900	1.432	1.389*
2.13841	19.5700	1.612	1.553*
2.54277	25.8600	1.763	1.684*

Loomis [17]. Freezing point depression measurements. Assigned weight is 0.1.

<u>m</u> <u>mol·kg<sup>-1</sup></u>	<u>F.P. Depression/K</u>	<u>Φ<sub>273.15</sub></u>	<u>Φ<sub>298.15</sub></u>
.00996	.0514	.925	.921
.01987	.1014	.915	.910
.04950	.2489	.901	.896
.09878	.4948	.898	.892
.14808	.7444	.901	.895
.19749	1.0039	.911	.904
.24708	1.2699	.921	.913
.29686	1.5557	.939	.930

Rivett [18]. Freezing point depression measurements. Assigned weight is 0.3.

<u>m</u> <u>mol·kg<sup>-1</sup></u>	<u>F.P. Depression/K</u>	<u>Φ<sub>273.15</sub></u>	<u>Φ<sub>298.15</sub></u>
.05620	.2820	.899	.894
.11800	.5800	.881	.875
.16650	.8220	.885	.878
.22550	1.1270	.896	.888
.33910	1.7360	.918	.908
.44390	2.3440	.946	.934
.56660	3.1300	.990	.974
.67370	3.8630	1.027	1.010
.79070	4.7210	1.070	1.050

Harned [7]. Activity coefficients from diffusion measurements. Assigned weight is 1.0.

<u>c/mol·L<sup>-1</sup></u>	<u>y<sub>±</sub></u>
0.0001	0.961
0.0004	0.926
0.001	0.890
0.002	0.854
0.005	0.792
0.007	0.765

No correction was made to convert molarity to molality, nor  $y_{\pm}$  to  $\gamma_{\pm}$ , as the differences are negligible at these concentrations.

Geissler [20]. Activity coefficients from emf measurements. Assigned weight is zero.

<u>c/mol·L<sup>-1</sup></u>	<u>Emf/V</u>	<u><math>\gamma/\gamma_{ref}</math></u>
0.001	- 0.0358	0.9830 * $m_{ref} = 0.0001 \text{ mol} \cdot \text{kg}^{-1}$
0.010	- 0.0704	0.9335 *
0.100	- 0.0994	0.6911 * $\gamma_{ref} = 0.961$
0.500	- 0.1193	0.6519 *
1.000	- 0.1297	0.8164 *
1.500	- 0.1354	0.9394 *
1.750	- 0.1379	1.0355 *
2.000	- 0.1398	1.1011 *

Table 1. Continued

Robinson and Bower [9a]. Isopiestic measurements, reference salt is  $\text{CaCl}_2$ . Assigned weight is 1.0.

$m_{ref}$ $\text{mol} \cdot \text{kg}^{-1}$	$m$ $\text{mol} \cdot \text{kg}^{-1}$	$\phi$
.31211	.30609	.891456
.31662	.31029	.89294
.56061	.54462	.954727
.56109	.54509	.954838
.5625	.54632	.9555429
1.0135	.97	1.09535
1.0198	.9767	1.09652
1.5003	1.4191	1.26917
1.5109	1.4291	1.27293
1.8445	1.7347	1.40265
1.8588	1.7475	1.4086
2.1878	2.05	1.54251
2.2088	2.0686	1.5518
2.4524	2.2908	1.65645
2.4732	2.3101	1.66529
2.6919	2.5076	1.76329
2.6952	2.5091	1.76583
3.204	2.9707	1.99906
3.2061	2.9736	1.99936
3.2213	2.9878	2.00616
3.5689	3.3044	2.16784
3.5888	3.3214	2.17785
3.8882	3.5925	2.31802
3.8898	3.5924	2.31977
4.1086	3.786	2.42395
4.122	3.7967	2.43102

Platford [10a]. Isopiestic measurements, reference salt is  $\text{NaCl}$ . Assigned weight is 0.5.

$m_{ref}$ $\text{mol} \cdot \text{kg}^{-1}$	$m$ $\text{mol} \cdot \text{kg}^{-1}$	$\phi$
.11146	.0801	.863811
.17771	.1248	.878101
.29572	.2088	.869393
.54678	.3779	.889348
.57978	.3819	.933802
.70647	.4724	.922963
1.04964	.6599	.994124
1.14171	.7083	1.01145
1.69143	.9852	1.10687
1.96702	1.1149	1.15484
2.54597	1.3719	1.25697
3.26385	1.6739	1.38189
3.619	1.8139	1.44708
4.24885	2.0596	1.55968
4.51412	2.1624	1.60617
4.93676	2.3174	1.68519
6.14442	2.7551	1.90509

Table 2. Osmotic Coefficient Data for  $MgBr_2$ 

Robinson and Stokes [22]. Isopiestic measurements, reference salt is KCl. Assigned weight is 1.0.

$m_{ref}$ $\text{mol}\cdot\text{kg}^{-1}$	$m$ $\text{mol}\cdot\text{kg}^{-1}$	$\phi$
.1557	.1086	.8773
.1614	.1127	.8757
.1939	.1341	.8809
.2600	.1770	.8899
.5101	.3250	.9416
.5668	.3575	.9502
.6988	.4284	.9764
.7607	.4592	.9913
.8734	.5171	1.0108
1.0600	.6057	1.0483
1.2400	.6845	1.0871
1.3030	.7192	1.0880
1.6590	.8688	1.1532
2.3070	1.0860	1.3010 *
2.8520	1.3040	1.3589
3.6270	1.5560	1.4820
3.6970	1.5760	1.4947
4.0090	1.6670	1.5476
4.0920	1.6970	1.5558
4.3010	1.7610	1.5865
4.4620	1.8020	1.6169
4.7820	1.8940	1.6661

Stokes [23]. Isopiestic measurements, reference salt is  $CaCl_2$ . Assigned weight is 1.0.

$m_{ref}$ $\text{mol}\cdot\text{kg}^{-1}$	$m$ $\text{mol}\cdot\text{kg}^{-1}$	$\phi$
2.6500	2.2980	1.8780
3.4000	2.9330	2.2499
5.1370	4.3450	3.1063
6.5080	5.3140	3.6778
7.0230	5.6100	3.8656

Table 3. Osmotic Coefficient Data for  $MgI_2$ 

Robinson and Stokes [22]. Isopiestic measurements, reference salt is KCl. Assigned weight is 1.0.

$m_{ref}$ $\text{mol}\cdot\text{kg}^{-1}$	$m$ $\text{mol}\cdot\text{kg}^{-1}$	$\phi$
.1518	.1049	.8860
.1789	.1217	.8970
.1867	.1266	.8991
.2982	.1958	.9204
.4233	.2696	.9440
.5934	.3595	0.9889
.8626	.4989	1.0347
1.1520	.6225	1.1094
1.1530	.6263	1.1037
1.1780	.6363	1.1102
1.4490	.7496	1.1631
1.4840	.7598	1.1760
1.7760	.8704	1.2350
1.9330	.9268	1.2665
2.0580	.9707	1.2909
2.6210	1.1620	1.3926
2.8030	1.2180	1.4279
2.8210	1.2190	1.4366
3.5430	1.4400	1.5602
3.8060	1.5150	1.6062
4.1880	1.6210	1.6721
4.4230	1.6880	1.7089
4.6470	1.7430	1.7516
4.8100	1.7870	1.7778

Stokes [23]. Isopiestic measurements, reference salt is  $CaCl_2$ . Assigned weight is 1.0.

$m_{ref}$ $\text{mol}\cdot\text{kg}^{-1}$	$m$ $\text{mol}\cdot\text{kg}^{-1}$	$\phi$
2.5690	2.0810	1.9700
2.7470	2.2330	2.0522
3.0990	2.5010	2.2480
4.1600	3.3140	2.8336
4.2930	3.4020	2.9163
5.0750	3.9700	3.3313
6.0320	4.6160	3.7845
6.7700	5.0090	4.1226

Table 4. Osmotic Coefficient Data for  $\text{CaBr}_2$ 

Robinson [24]. Isopiestic measurements, reference salt is  $\text{KCl}$ . Assigned weight is 1.0.

Meyer [26]. Freezing point depression measurements. Assigned weight is zero.

$m_{ref}$ $\text{mol}\cdot\text{kg}^{-1}$	$m$ $\text{mol}\cdot\text{kg}^{-1}$	$\varnothing$	$m$ $\text{mol}\cdot\text{kg}^{-1}$	F.P. Depression/K	$\varnothing_{273.15}$	$\varnothing_{298.15}$
.1507	.1058	.8722	0.05203	0.264	0.909	0.906 *
.1986	.1386	.8725	0.08635	0.441	0.915	0.912 *
.2650	.1818	.8828	0.13605	0.703	0.926	0.921 *
.3730	.2531	.8875				- Values for higher molalities were not considered -
.3916	.2642	.8920				
.6420	.4135	.9297				
.9382	.5711	.9833				
1.1940	.6995	1.0238				
1.2470	.7250	1.0322				
1.6150	.8932	1.0911				
1.8540	.9972	1.1271				
1.9170	1.0230	1.1375				
2.1060	1.0980	1.1691				
2.4500	1.2410	1.2135				
2.8410	1.3820	1.2768				
3.5610	1.6430	1.3751				
3.8740	1.7480	1.4200				
4.2200	1.8670	1.4644				
4.8230	2.0560	1.5501				

Robinson and McCoach [25]. Isopiestic measurements, reference salt is  $\text{CaCl}_2$ . Assigned weight is 1.0.

$m_{ref}$ $\text{mol}\cdot\text{kg}^{-1}$	$m$ $\text{mol}\cdot\text{kg}^{-1}$	$\varnothing$
1.5240	1.4230	1.2928
1.8970	1.7660	1.4364
2.3090	2.1400	1.6105
2.3210	2.1520	1.6149
2.7640	2.5540	1.8129
2.8010	2.5840	1.8323
3.0260	2.7910	1.9339
3.3870	3.1160	2.1037
3.8880	3.5650	2.3399
4.1580	3.7850	2.4789
4.3120	3.9220	2.5492
4.9650	4.4350	2.8738
5.9520	5.1440	3.3272
6.6550	5.5950	3.6047
6.8930	5.7260	3.6951
7.4700	5.9840	3.9141
7.8310	6.1700	4.0074
8.0670	6.2860	4.0610
8.3750	6.4060	4.1395
8.7300	6.5830	4.1908
8.8380	6.6300	4.2084
9.4980	6.8630	4.3369
9.8150	6.9650	4.4057
10.4100	7.2160	4.5287

Robinson and McCoach [25]. Isopiestic measurements, reference salt is  $\text{H}_2\text{SO}_4$ . Assigned weight is 1.0.

$m_{ref}$ $\text{mol}\cdot\text{kg}^{-1}$	$m$ $\text{mol}\cdot\text{kg}^{-1}$	$\varnothing$
16.10	7.636	4.689
16.81	7.922	4.771
17.97	8.406	4.887
19.61	9.210	4.971

Table 5. Osmotic Coefficient Data for  $\text{CaI}_2$ 

Robinson [24]. Isopiestic measurements, reference is KCl. Assigned weight is 1.0.

$m_{ref}$ $\text{mol}\cdot\text{kg}^{-1}$	$m$ $\text{mol}\cdot\text{kg}^{-1}$	$\phi$
.1160	.0815	.8764
.2074	.1408	.8962
.3559	.2350	.9127
.4366	.2814	.9324
.6107	.3791	.9650
.7692	.4610	.9985
.7832	.4715	.9940
1.0310	.5943	1.0389
1.2760	.7022	1.0909
1.4080	.7628	1.1101
1.6750	.8728	1.1594
1.7820	.9122	1.1826
2.2170	1.0880	1.2453
2.3660	1.1340	1.2797
2.9510	1.3430	1.3690
3.3230	1.4510	1.4425
3.6550	1.5680	1.4833
4.0580	1.6880	1.5494
4.1820	1.7280	1.5660
4.3970	1.7930	1.5980
4.6120	1.8550	1.6315
4.6450	1.8640	1.6370
4.8400	1.9150	1.6710

Meyer [26]. Freezing point depression measurements. Assigned weight is 0.10.

$m$ $\text{mol}\cdot\text{kg}^{-1}$	F.P. Depression/K	$\phi_{273.15}$	$\phi_{298.15}$
0.03992	0.197	0.884	0.881
0.08799	0.430	0.876	0.873
0.12172	0.594	0.875	0.870

- Values for higher molalities were not considered -

In the absence of any measurements,  $\phi_L$  data for  $\text{CaBr}_2$  and  $\phi_C$  data for  $\text{CaCl}_2$  was used (see table 12).

Table 6. Osmotic and Activity Coefficient Data for  $\text{SrCl}_2$ 

Downes [27]. Isopiestic measurements, reference salt is KCl. Assigned weight is 1.0.

Robinson [29]. Isopiestic measurements, reference salt is KCl. Assigned weight is 0.50.

$m_{ref}$ $\text{mol}\cdot\text{kg}^{-1}$	$m$ $\text{mol}\cdot\text{kg}^{-1}$	$\phi$	$m_{ref}$ $\text{mol}\cdot\text{kg}^{-1}$	$m$ $\text{mol}\cdot\text{kg}^{-1}$	$\phi$
.1503	.1083	.8499	.1627	.1195	.8324
.1741	.1254	.8476	.2194	.1574	.8471
.2179	.1561	.8484	.2749	.1935	.8598
.2759	.1963	.8506	.5757	.3942	.8752
.4996	.3456	.8674	.8290	.5501	.9018
.5418	.3728	.8714	.8434	.5601	.9011
.6043	.4118	.8791	1.1070	.7120	.9317
.6807	.4594	.8870	1.3280	.8320	.9589
.9371	.6113	.9176	1.5460	.9452	.9859
.9696	.6307	.9203	1.7140	1.0280	1.0080
1.1022	.7045	.9375	1.8430	1.0940	1.0210
1.2070	.7416	.9763 *	2.1860	1.2590	1.0603
1.2531	.7877	.9548	2.3080	1.3170	1.0733
1.3659	.8480	.9681	2.6490	1.4720	1.1119
1.5793	.9571	.9951	3.1280	1.6820	1.1646
1.6236	.9800	.9999	3.5010	1.8370	1.2070
1.7770	1.0563	1.0183	4.0210	2.0430	1.2670
1.9495	1.1378	1.0408	4.0830	2.0680	1.2735
2.2309	1.2708	1.0732	4.3140	2.1570	1.2997
2.2506	1.2770	1.0779	4.5830	2.2580	1.3306
2.3184	1.3087	1.0853			
2.4274	1.3578	1.0982			
2.7081	1.4806	1.1319			
2.8800	1.5507	1.1548			
2.9089	1.5668	1.1554			
2.9762	1.5959	1.1628			
3.1115	1.6487	1.1813			
3.3918	1.7626	1.2146			
3.4487	1.7834	1.2227			
3.8305	1.9321	1.2685			
4.1555	2.0541	1.3080			
4.5158	2.1866	1.3510			

Phillips, Watson, and Felsing [28]. Isopiestic measurements, reference salt is  $\text{BaCl}_2$ . Assigned weight is 0.80.

$m_{ref}$ $\text{mol}\cdot\text{kg}^{-1}$	$m$ $\text{mol}\cdot\text{kg}^{-1}$	$\phi$
1.4079	1.3020	1.083
1.4020	1.2964	1.083
1.0040	.9440	.999
.7868	.7490	.951
.7831	.7455	.951
.6929	.6630	.932
.4550	.4380	.891
.3997	.3865	.880
.2374	.2290	.886
.0410	.0396	.886
.0339	.0328	.891

Stokes [23]. Isopiestic measurements, reference salt is  $\text{CaCl}_2$ . Assigned weight is 1.0.

$m_{ref}$ $\text{mol}\cdot\text{kg}^{-1}$	$m$ $\text{mol}\cdot\text{kg}^{-1}$	$\phi$
1.0780	1.0150	1.0112
1.1020	1.1120	1.0348
1.3250	1.1350	1.0432
1.3250	1.3710	1.1042
1.7310	1.8020	1.2276
1.9480	2.0280	1.3023
2.0340	2.1230	1.3295
2.3310	2.4370	1.4359
2.3950	2.5110	1.4559
2.6910	2.8270	1.5661
2.7690	2.9090	1.5965
2.3340	3.5200	1.8120
3.7990	4.0380	1.9837

Hepburn [30]. Vapor pressure measurements. Assigned weight is 0.02.

$m$ $\text{mol}\cdot\text{kg}^{-1}$	$-\log_{10}(P/P^{\circ})$	$\phi$
.40000	0.0075	.7977
.60000	0.0115	.8156
.99500	0.0226	.9665
1.49500	0.0403	1.1470
2.24600	0.0713	1.3509
2.87200	0.1049	1.5544
3.24500	0.1278	1.6761
3.40300	0.1381	1.7321
3.51700	0.1470	1.7897

The evaluated osmotic coefficients calculated for  $\text{BaCl}_2$  in this paper were used to calculate  $\phi_{ref}$  and thence  $\phi$  for  $\text{SrCl}_2$ .

Table 6. Continued

Loomis [31]. Freezing point depression measurements. Longhi, Mussini, and Vaghi [32]. Activity coefficients from emf measurements. Assigned weight is 0.50.

$m$	F.P. $\text{mol}\cdot\text{kg}^{-1}$	$\phi_{273.15}$	$\phi_{298.15}$	$\text{Ag(s), AgCl(s); SrCl}_2(m_{\text{ref}}) \mid \text{Sr}_x\text{Hg(1)} \mid \text{SrCl}_2(m)$
0.010038	0.0508	0.907	0.904	$\text{AgCl(s), Ag(s)}$
0.019994	0.1015	0.910	0.906	
0.050271	0.2445	0.872	0.868	$m_{\text{ref}} = 0.010089$
0.100893	0.4834	0.859	0.855	$\gamma_{\text{ref}} = 0.7250$
0.203631	0.9608	0.846	0.841	$m$

- A value at a higher molality was not considered -

See table 12 for the  $\phi_L$  and  $\phi_C$  data used in these calculations.

Harned [7]. Activity coefficients from diffusion measurements. Assigned weight is 0.70.

$c/\text{mol}\cdot\text{L}^{-1}$	$y_{\pm}$
0.0001	0.961
0.0004	0.926
0.0010	0.889
0.0020	0.853
0.0050	0.790
0.0070	0.762
0.0100	0.732

No correction was made to convert molarity to molality nor  $y_{\pm}$  to  $\gamma_{\pm}$ , as the differences are negligible at these concentrations.

Lucasse [33]. Activity coefficients from emf measurements. Assigned weight is 0.70.

$\text{Ag(s), AgCl(s); SrCl}_2(m_{\text{ref}}) \mid \text{Sr}_x\text{Hg(1)} \mid \text{SrCl}_2(m)$ ;  
 $\text{AgCl(s), Ag(s)}$

$$m_{\text{ref}} = 0.01 \text{ mol}\cdot\text{kg}^{-1} \quad \gamma_{\text{ref}} = 0.7258$$

$m$	Emf/V	$\gamma/\gamma_{\text{ref}}$
.029080	.035242	.85812
.089960	.072224	.72418
.116700	.079787	.67928
.345800	.117060	.60300
1.049000	.161225	.62526
1.403000	.176760	.69959
2.115000	.203119	.91967
3.015000	.235650	1.50053

The above values of  $(\gamma/\gamma_{\text{ref}})$  are averages calculated from the measurements performed at various mole fractions ( $x = .0007544$  to  $0.02136$ ) of strontium in the mercury amalgam.

Table 7. Osmotic Coefficient Data for  $\text{SrBr}_2$ 

Robinson [24]. Isopiestic measurements, reference salt is KCl. Assigned weight is 1.0.

$m_{\text{ref}}$ $\text{mol} \cdot \text{kg}^{-1}$	$m$ $\text{mol} \cdot \text{kg}^{-1}$	$\phi$
.1256	.0896	.8617
.1648	.1166	.8639
.2834	.1933	.8778
.3519	.2413	.8790
.4548	.3056	.8939
.4941	.3323	.8923
.8255	.5257	.9396
.9330	.5829	.9580
1.0550	.6524	.9686
1.2100	.7331	.9901
1.4270	.8362	1.0266
1.6720	.9517	1.0613
1.6680	.9518	1.0585
1.9400	1.0790	1.0919
1.9930	1.0950	1.1066
2.0500	1.1190	1.1153
2.1470	1.1610	1.1283
2.1920	1.1780	1.1365
2.4960	1.3060	1.1761
3.0070	1.5080	1.2444
3.4310	1.6100	1.346 / *
3.4310	1.6590	1.3069
3.6990	1.7580	1.3407
4.2490	1.9420	1.4189
4.7950	2.1230	1.4911

Meyer [26]. Freezing point depression measurements. Assigned weight is zero.

$m$ $\text{mol} \cdot \text{kg}^{-1}$	F.P. Depression/K	$\phi_{273.15}$	$\phi_{298.15}$
0.0583	0.245	0.753	0.751 *
0.1071	0.566	0.947	0.945 *

- Values for higher molalities were not considered -

\*<sub>L</sub> data for  $\text{SrBr}_2$  is from table 12; the \*<sub>C</sub> data for  $\text{SrCl}_2$  was used in the absence of any direct measurements (also see table 12).

Table 8. Osmotic Coefficient Data for  $\text{SrI}_2$ 

Robinson [24]. Isopiestic measurements, reference salt is KCl. Assigned weight is 1.0.

$m_{\text{ref}}$ $\text{mol} \cdot \text{kg}^{-1}$	$m$ $\text{mol} \cdot \text{kg}^{-1}$	$\phi$
.1361	.0952	.8773
.2315	.1572	.8941
.4339	.2827	.9225
.5202	.3322	.9392
.6186	.3883	.9542
.9436	.5605	1.0077
.9654	.5721	1.0102
1.1600	.6645	1.0466
1.3550	.7544	1.0794
1.7040	.9367	1.1530
2.0060	1.0240	1.1914
2.0720	1.0540	1.1973
2.5540	1.2340	1.2756
3.2910	1.4890	1.3908
3.3880	1.5230	1.4040
3.3980	1.5240	1.4076
4.5090	1.8700	1.5770
4.7510	1.9450	1.6103
4.8430	1.9690	1.6263

Meyer [26]. Freezing point depression measurements. Assigned weight is zero.

$m$ $\text{mol} \cdot \text{kg}^{-1}$	F.P. Depression/K	$\phi_{273.15}$	$\phi_{298.15}$
0.0241	0.130	0.963	0.963 *
0.0727	0.385	0.949	0.947 *
0.1106	0.586	0.950	0.948 *

- Values for higher molalities were not considered -

In the absence of any measurements, \*<sub>L</sub> data for  $\text{SrBr}_2$  and \*<sub>C</sub> data for  $\text{SrCl}_2$  was used (see table 12).

Table 9. Osmotic and Activity Coefficient Data for BaCl<sub>2</sub>

Robinson [29]. Isopiestic measurements, reference salt is KCl. Assigned weight is 0.30.

$m \text{ mol} \cdot \text{kg}^{-1}$	$\phi$
0.05	0.861
0.10	0.843
0.20	0.835
0.3	0.836
0.4	0.842
0.5	0.8565
0.6	0.873
0.7	0.888
0.8	0.904
0.9	0.919
1.0	0.9345
1.1	0.950
1.2	0.966
1.3	0.983
1.4	1.000
1.5	1.017
1.6	1.033
1.7	1.049
1.8	1.064

The author did not give the isopiestic molalities and hence the raw data could not be recalculated.

Robinson [36]. Isopiestic measurements, reference salt is KCl. Assigned weight is 1.0.

$m_{\text{ref}} \text{ mol} \cdot \text{kg}^{-1}$	$m \text{ mol} \cdot \text{kg}^{-1}$	$\phi$
.1209	.0881	.8443
.1558	.1134	.8407
.2034	.1475	.8393
.2106	.1529	.8377
.2139	.1553	.8375
.4526	.3213	.8462
.6696	.4649	.8623
.7360	.5088	.8657
.8278	.5660	.8752
1.1750	.7809	.9023
1.4360	.9302	.9288
1.9620	1.2270	.9716
2.1480	1.3220	.9914
2.2940	1.4050	.9997
2.3950	1.4540	1.0110
2.4620	1.4920	1.0146
2.4720	1.4970	1.0155
2.7730	1.6490	1.0425
3.0460	1.7820	1.0679

Robinson [37]. Isopiestic measurements, reference salt is NaCl. Assigned weight is 1.0.

$m_{\text{ref}} \text{ mol} \cdot \text{kg}^{-1}$	$m \text{ mol} \cdot \text{kg}^{-1}$	$\phi$
1.2292	.8497	.9113
1.2866	.8862	.9171
1.3409	.9193	.9237
1.4235	.9726	.9307
1.5278	1.0380	.9408
1.7981	1.2038	.9686
1.8132	1.2133	.9699
1.8871	1.2578	.9777
2.0344	1.3472	.9922
2.0598	1.3614	.9956
2.1186	1.3965	1.0017
2.1240	1.4002	1.0019
2.3449	1.5318	1.0243
2.4820	1.6147	1.0371
2.4824	1.6169	1.0359
2.5225	1.6400	1.0403
2.7599	1.7813	1.0634
2.7677	1.7884	1.0627

Robinson and Bower [38]. Isopiestic measurements, reference salt is NaCl. Assigned weight is 1.0.

$m_{\text{ref}} \text{ mol} \cdot \text{kg}^{-1}$	$m \text{ mol} \cdot \text{kg}^{-1}$	$\phi$
.5044	.3638	.8516
.5063	.3645	.8531
.9728	.6832	.8871
1.2328	.8507	.9131
1.5683	1.0634	.9447
1.6226	1.0983	.9490
1.8749	1.2498	.9769
1.9873	1.3149	.9904
2.0021	1.3245	.9914
2.3615	1.5466	1.0227
2.6185	1.6998	1.0481
2.7147	1.7610	1.0551

Bechtold and Newton [46]. Vapor pressure measurements. Assigned weight is 0.80.

$m \text{ mol} \cdot \text{kg}^{-1}$	$P/P^\circ$	$\phi$
.01017	0.99975	.4512 *
.09505	0.99608	.7632 *
.19087	0.99151	.8253 *
.47231	0.97866	.8440 *
.87460	0.95774	.9123
1.23237	0.93746	.9684
1.60010	0.91483	1.0281

Newton and Tippetts [45]. Vapor pressure measurements. Assigned weight is 0.80.

$m \text{ mol} \cdot \text{kg}^{-1}$	$P/P^\circ$	$\phi$
.30600	0.9868	.8025 *
.68480	0.9681	.8748 *
.91430	0.9555	.9200
1.17680	0.9408	.9583
1.58900	0.9158	1.0229
1.78800	0.9021	1.0649

Hepburn [30]. Vapor pressure measurements. Assigned weight is 0.05.

$m \text{ mol} \cdot \text{kg}^{-1}$	$-\log_{10}(P/P^\circ)$	$\phi$
.50800	0.0088	.7372 *
.60600	0.0105	.7372 *
1.00700	0.0184	.7775 *
1.28500	0.0254	.8411 *
1.56800	0.0371	1.0068
1.65500	0.0397	1.0208
1.78800	0.0430	1.0233

Table 9. Continued

Perreau [44]. Vapor pressure measurements. Assigned weight is 0.02.

$m$ $\text{mol} \cdot \text{kg}^{-1}$	P torr*	$\phi$
.41960	17.20	.8498
.87200	16.79	.9204
1.01750	16.69	.8973
1.20450	16.53	.9058
1.31280	16.38	.9595
1.44320	16.17	1.0381
1.57640	15.96	1.1036

\* 1 torr = 101325/760 Pa

Bedford [40]. Freezing point depression measurements. Assigned weight is 0.20.

$m$ $\text{mol} \cdot \text{kg}^{-1}$	F.P. Depression/K	$\phi_{273.15}$	$\phi_{298.15}$
0.0010	0.00531	0.952	0.950
0.0020	0.01042	0.934	0.932
0.0040	0.02048	0.918	0.915
0.0060	0.03042	0.909	0.906
0.0080	0.04024	0.901	0.899
0.0100	0.05000	0.896	0.893

$\psi_L$  and  $\psi_C$  data from table 12 was used in treating all of the freezing point data for  $\text{BaCl}_2$ .

Gibbard and Fong [43]. Freezing point depression measurements. Assigned weight is 0.80.

$m$ $\text{mol} \cdot \text{kg}^{-1}$	F.P. Depression/K	$\phi_{273.15}$	$\phi_{298.15}$
0.03305	0.1614	0.875	0.872
0.06830	0.3242	0.851	0.848
0.1080	0.5090	0.845	0.842
0.1201	0.5642	0.842	0.840
0.1814	0.8466	0.837	0.836
0.2443	1.1431	0.839	0.838
0.2651	1.2406	0.839	0.839
0.3143	1.4794	0.844	0.844
0.3855	1.8196	0.847	0.848

- Values for higher molalities was not considered -

Hall and Harkins [41]. Freezing point depression measurements. Assigned weight is 0.60.

$m$ $\text{mol} \cdot \text{kg}^{-1}$	F.P. Depression/K	$\phi_{273.15}$	$\phi_{298.15}$
0.00273	0.0144	0.945	0.943
0.00534	0.02765	0.928	0.925
0.01142	0.0577	0.906	0.902
0.02092	0.1458	0.876	0.873
0.05611	0.2682	0.857	0.854
0.11358	0.5319	0.840	0.837

Jablczynski and Legat [42]. Freezing point depression measurements. Assigned weight is 0.02.

- Values for higher molalities were not considered -

Jones [39]. Freezing point depression measurements. Assigned weight is 0.50.

$m$ $\text{mol} \cdot \text{kg}^{-1}$	F.P. Depression/K	$\phi_{273.15}$	$\phi_{298.15}$
0.001001	0.0054	0.967	0.965
0.002001	0.0109	0.976	0.974 *
0.002999	0.0161	0.962	0.960 *
0.003994	0.0209	0.938	0.936
0.004988	0.0261	0.938	0.935
0.005979	0.0309	0.926	0.924
0.006970	0.0360	0.926	0.923
0.008013	0.0412	0.921	0.919
0.008999	0.0458	0.912	0.909
0.009983	0.0507	0.910	0.907
0.02004	0.1002	0.896	0.893
0.02966	0.1465	0.885	0.882
0.03910	0.1899	0.870	0.867
0.04836	0.2310	0.856	0.853
0.05743	0.2742	0.856	0.853
0.07023	0.3333	0.851	0.848
0.07887	0.3716	0.844	0.842
0.08735	0.4108	0.843	0.840
0.09566	0.4478	0.839	0.836
0.10381	0.4814	0.831	0.829

Loomis [17]. Freezing point depression measurements. Assigned weight is 0.50.

$m$ $\text{mol} \cdot \text{kg}^{-1}$	F.P. Depression/K	$\phi_{273.15}$	$\phi_{298.15}$
0.010032	0.04990	0.891	0.889
0.020069	0.09900	0.884	0.881
0.050210	0.23850	0.851	0.848
0.10055	0.46900	0.836	0.834
0.20166	0.93100	0.828	0.827

Lucasse [33]. Emf measurements. Assigned weight is 0.90.

$m$ $\text{mol} \cdot \text{kg}^{-1}$	Emf/V	$\gamma/\gamma_{\text{ref}}$
.030160	.035492	.83277
.100400	.074225	.68345
.297800	.109247	.57171 $m_{\text{ref}}=0.0100$
.971000	.153272	.54954
1.521000	.171888	.56869 $\gamma_{\text{ref}}=0.7211$
1.650000	.177190	.60154

Table 9. Continued

Lucasse [33]. Emf measurements. Assigned weight is 0.60.

Ag(s), AgCl(s); BaCl<sub>2</sub>(m<sub>ref</sub>)|BaCl<sub>2</sub>(m); AgCl(s), Ag(s)

m mol·kg <sup>-1</sup>	Emf/V	$\gamma/\gamma_{ref}$	m mol·kg <sup>-1</sup>	Emf/V	$\gamma/\gamma_{ref}$
.019230	-.009273	.902610	.001001	.071624	1.224789 *
.038150	-.018526	.794453	.002002	.061321	1.136839 * m <sub>ref</sub> =0.100378
.079770	-.028049	.681221	.005007	.043615	1.326083 * mol·kg <sup>-1</sup>
.179100	-.039423	.620394	.010014	.032411	1.313104 * mol·kg <sup>-1</sup>
.242600	-.042784	.568588	.020034	.020907	1.334101 * $\gamma_{ref}$ =0.4925
.392700	-.049087	.532111	.050123	.009503	1.089868 *
.597100	-.054769	.515788	.001001	.057820	1.455951 *
.812200	-.059970	.547819	.002002	.047516	1.351402 * m <sub>ref</sub> =0.050123
			.005007	.035512	1.116763 * mol·kg <sup>-1</sup>
			.010014	.022908	1.204456 * mol·kg <sup>-1</sup>
			.020034	.011704	1.201281 * $\gamma_{ref}$ =0.5590

- Values for higher molalities were not considered -

Pearce and Gelbach [48]. Emf measurements. Assigned weight is 0.10.

Ag(s), AgCl(s); BaCl<sub>2</sub>(m<sub>ref</sub>)|Ba<sub>x</sub>Hg(1)|BaCl<sub>2</sub>(m); AgCl(s), Ag(s)

m mol·kg <sup>-1</sup>	Emf/V	$\gamma/\gamma_{ref}$	m mol·kg <sup>-1</sup>	Emf/V	$\gamma/\gamma_{ref}$
.005000	.017746	.95089	.001001	.035612	1.160860 * m <sub>ref</sub> =0.010014
.010000	.039793	.84247	.002002	.023308	1.215034 * mol·kg <sup>-1</sup>
.030000	.075666	.71232	.005007	.010704	1.041171 * $\gamma_{ref}$ =0.7210
.050000	.093071	.67139	.001001	.024808	1.120576 * m <sub>ref</sub> =0.005007
.100000	.114239	.58140	.002002	.015005	1.009338 * mol·kg <sup>-1</sup>
.300000	.149591	.48499	$\gamma_{ref}$ =0.8213		$\gamma_{ref}$ =0.7823
1.000000	.190865	.42459 *			
1.256000	.218254	.68807 *			

Pearce and Gelbach [48]. Emf measurements. Assigned weight is 0.10.

Ag(s), AgCl(s); BaCl<sub>2</sub>(m<sub>ref</sub>)|BaCl<sub>2</sub>(m); AgCl(s), Ag(s)

m mol·kg <sup>-1</sup>	Emf/V	$\gamma/\gamma_{ref}$	m mol·kg <sup>-1</sup>	Emf/V	$\gamma/\gamma_{ref}$
.030000	-.034452	.771784	.001001	.035612	1.160860 * m <sub>ref</sub> =0.010014
.300000	-.065432	.543661	.002002	.023308	1.215034 * mol·kg <sup>-1</sup>
		$\gamma_{ref}$ =0.8213	.005007	.010704	1.041171 * $\gamma_{ref}$ =0.7210
.100000	-.032131	.704484	.001001	.024808	1.120576 * m <sub>ref</sub> =0.005007
1.000000	-.063331	.585933	.002002	.015005	1.009338 * mol·kg <sup>-1</sup>
.050000	-.033741	.753330	$\gamma_{ref}$ =0.7211		$\gamma_{ref}$ =0.7823
		$\gamma_{ref}$ =-0.005			
		$\gamma_{ref}$ =0.7824			

Pearce and Gelbach [48]. Emf measurements. Assigned weight is 0.10.

Ba<sub>x</sub>Hg(1)|BaCl(m<sub>ref</sub>)|BaCl<sub>2</sub>(m)|Ba<sub>x</sub>Hg(1)

m mol·kg <sup>-1</sup>	Emf/V	$\gamma/\gamma_{ref}$	m mol·kg <sup>-1</sup>	Emf/V	$\gamma/\gamma_{ref}$
.030000	-.042054	.696277	.001001	.035612	1.160860 * m <sub>ref</sub> =0.010014
.300000	-.085069	.466236	.002002	.023308	1.215034 * mol·kg <sup>-1</sup>
		$\gamma_{ref}$ =0.8213	.005007	.010704	1.041171 * $\gamma_{ref}$ =0.7210
.100000	-.041034	.642425	.001001	.024808	1.120576 * m <sub>ref</sub> =0.005007
1.000000	-.090010	.509491	$\gamma_{ref}$ =0.7211		$\gamma_{ref}$ =0.7823
.050000	-.042054	.687306	$\gamma_{ref}$ =-0.005		$\gamma_{ref}$ =0.7824

Drucker [47]. Emf measurements. Assigned weight is zero.

Hg(s), HgCl(s); BaCl<sub>2</sub>(m<sub>ref</sub>)|BaCl<sub>2</sub>(m); HgCl(s), Hg(s)

Drucker's measurements were performed at a temperature of ~ 17 °C. The transference numbers at this temperature were estimated from the data at 25 °C (see table 12) and the ( $\partial t_+^0 / \partial T$ ) data of Keenan et al. [59] on CaCl<sub>2</sub>. The concentration dependence of  $t_+$  at 17 °C was assumed to be the same as at 25 °C since this was the case observed for CaCl<sub>2</sub>[59]. The densities of the solutions were calculated by letting  $\phi^0 = 0.99880 \text{ g} \cdot \text{cm}^{-3}$  and assuming the concentration dependence to be the same as at 25 °C. The rigorous adjustment of  $\gamma/\gamma_{ref}$  at 17 °C to be 25 °C was judged to be a negligible correction and was not performed.

Ardizzone, Longhi, Mussini, and Rondinini [51]. Emf measurements. Assigned weight is 0.80.

Ag(s), AgCl(s); BaCl<sub>2</sub>(m<sub>ref</sub>)|Ba<sub>x</sub>Hg(1)|BaCl<sub>2</sub>(m); AgCl(s), Ag(s)

m mol·kg <sup>-1</sup>	Emf/V	$\gamma/\gamma_{ref}$	m mol·kg <sup>-1</sup>	Emf/V	$\gamma/\gamma_{ref}$
0.040		1.08662	0.100	0.91464	m <sub>ref</sub> =0.0630
0.130		0.85423	0.160	0.84132	mol·kg <sup>-1</sup>
0.210		0.80121	0.250	0.76833	$\gamma_{ref}$ =0.5362

The above values of ( $\gamma/\gamma_{ref}$ ) are averages calculated from the measurements performed at various mole fractions ( $x = 0.001186$  to  $0.004350$ ) of barium in the mercury amalgam.

Table 9. Continued

Rush and Johnson [52]. Ultracentrifuge measurements.  
Assigned weight is 0.40.

Jones and Dole [49]. Emf measurements. Assigned weight is 0.70.

<u>m</u> <u>mol·kg<sup>-1</sup></u>	<u>Emf/V</u>	<u>γ/γ<sub>ref</sub></u>	<u>m</u> <u>mol·kg<sup>-1</sup></u>	<u>Y</u>
.001003	.058420	1.591015	0.6114	0.399
.005015	.033271	1.375199	0.9266	0.400
.010032	.022758	1.276613 <sup>m</sup> <sub>ref</sub> =0.050210 The authors did not give adequate raw data to permit	1.2500	0.412
.025089	.009423	1.130461 <sup>m</sup> <sub>ref</sub> <sup>-1</sup> mol·kg <sup>-1</sup> recalculation of their results.	1.5856	0.434
.100552	-.009223	.882589		
.252434	-.021337	.760506 <sup>γ</sup> <sub>ref</sub> =0.5589		
.508677	-.030820	.710648		
1.034306	-.041034	.722072		

Tippette and Newton [50]. Emf measurements. Assigned weight is 0.90.

Hg(1), Hg<sub>2</sub>Cl<sub>2</sub>(s); BaCl<sub>2</sub>(<sup>m</sup><sub>ref</sub>) | Ba(2 phase amalgam) | BaCl<sub>2</sub>(m); Hg<sub>2</sub>Cl<sub>2</sub>(s), Hg(1)

<u>m</u> <u>mol·kg<sup>-1</sup></u>	<u>Emf/V</u>	<u>γ/γ<sub>ref</sub></u>
.056290	.003501	.97273
.068970	.010504	.95208
.115900	.027009	.86946
.119400	.027809	.86169
.130300	.030610	.84913
.153900	.035912	.82494 <sup>m</sup> <sub>ref</sub> =0.0500
.237300	.050017	.77146
.454600	.071524	.70363 mol·kg <sup>-1</sup>
.485600	.073525	.69381 <sup>γ</sup> <sub>ref</sub> =0.5593
.702100	.087530	.69015
.880700	.087630	.55162 *
.997500	.096433	.61200 *
1.527100	.121041	.75703
1.778300	.128744	.79391

Harned [7]. Diffusion measurements. Assigned weight is 1.0.

<u>c/mol·L<sup>-1</sup></u>	<u>y<sub>±</sub></u>
0.0001	0.961
0.0004	0.926
0.0010	0.888
0.0020	0.850
0.0050	0.783
0.0070	0.754

No correction was made to convert molarity to molality nor  $y_{\pm}$  to  $\gamma_{\pm}$ , as the differences are negligible at these concentrations.

Table 10. Osmotic and Activity Coefficient Data for  $\text{BaBr}_2$ 

Rivett [18]. Freezing point depression measurements.  
Assigned weight is 0.10.

$\frac{m}{\text{mol}\cdot\text{kg}^{-1}}$	F.P. Depression/K	$\phi_{273.15}$	$\phi_{298.15}$
0.0865	0.420	0.870	0.869
0.1873	0.909	0.870	0.868

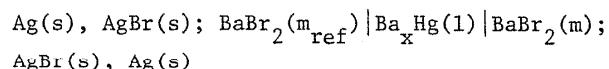
- Values for higher molalities were not considered -

$\phi_L$  data for  $\text{BaBr}_2$  is from table 12; the  $\phi_C$  data for  $\text{BaCl}_2$  was used in the absence of any direct measurements (also see table 12).

Robinson [56]. Isopiestic measurements, reference salt is KCl. Assigned weight is 1.0.

$\frac{m_{\text{ref}}}{\text{mol}\cdot\text{kg}^{-1}}$	$\frac{m}{\text{mol}\cdot\text{kg}^{-1}}$	$\phi$
.1253	.09092	.8472
.2178	.1557	.8502
.4035	.2800	.8669
.4355	.3012	.8690
.5932	.4008	.8867
.7140	.4900	.8721 *
.8110	.5303	.9151
.9640	.6212	.9290
1.1200	.7098	.9508
1.4470	.8847	.9843
1.5530	.9342	1.0021
1.7720	1.0470	1.0243
2.4290	1.3560	1.1004
2.5520	1.4140	1.1123
2.5860	1.4300	1.1155
2.7720	1.5070	1.1403
3.1170	1.6600	1.1755
3.3750	1.7690	1.2036
4.1650	2.0930	1.2870
4.7360	2.3210	1.3445

Gelbach and Huppke [57]. Emf measurements. Assigned weight is 0.40.



$\frac{m}{\text{mol}\cdot\text{kg}^{-1}}$	Emf/V	$\gamma/\gamma_{\text{ref}}$
0.005	0.018306	0.96481
0.010	0.042024	0.89267
0.030	0.077436	0.74581
0.050	0.094742	0.70113 $m_{\text{ref}} = 0.003$
0.100	0.116489	0.61637 $\text{mol}\cdot\text{kg}^{-1}$
0.300	0.153342	0.53457 $\gamma_{\text{ref}} = 0.8239$
0.500	0.172989	0.53402
1.000	0.198747	0.52095 *

Table 11. Osmotic Coefficient Data for BaI<sub>2</sub>

Robinson [24]. Isopiestic measurements, reference salt is KCl.  
Assigned weight is 1.0.

$m_{ref}$	$m$	$\phi$
$\text{mol}\cdot\text{kg}^{-1}$	$\text{mol}\cdot\text{kg}^{-1}$	
.1329	.0940	.8681
.2186	.1484	.8953
.4372	.2865	.9171
.7784	.4755	.9796
1.0380	.6083	1.0220
1.3540	.7565	1.0756
1.5250	.8337	1.1021
1.6960	.9038	1.1341
1.8460	.9686	1.1552
2.3130	1.1630	1.2182
2.5540	1.2550	1.2542
2.6470	1.3000	1.2580
3.1360	1.4740	1.3327
3.4120	1.5660	1.3761
3.9400	1.7480	1.4472
4.4120	1.9010	1.5131
4.7440	1.9980	1.5649

Meyer [26]. Freezing point depression measurements. Assigned weight is zero.

$m$	F.P.	$\phi_{273.15}$	$\phi_{298.15}$
$\text{mol}\cdot\text{kg}^{-1}$	Depression/K		
0.0279	0.143	0.919	0.917 *
0.0593	0.300	0.907	0.905 *
0.1022	0.511	0.896	0.895 *

- Values for higher molalities were not considered -

$\phi_L$  data for BaBr<sub>2</sub> and  $\phi_C$  data for BaCl<sub>2</sub> was used in the absence of any direct measurements (see table 12).

Table 12. Auxiliary Data Used in Calculations of Osmotic and Activity Coefficients

Relative Apparent Molal Enthalpy Data

$$\phi_L^{\circ}/J \cdot mol^{-1} = \sum_{i=1}^n \alpha_i m_i^{1/2}$$

<u>System</u>	<u><math>\alpha_1</math></u>	<u><math>\alpha_2</math></u>	<u><math>\alpha_3</math></u>	<u><math>\alpha_4</math></u>	<u><math>\alpha_5</math></u>	<u><math>\alpha_6</math></u>
MgCl <sub>2</sub>	10479.7	-20703.7	31055.9	-23606.1	9041.39	-1317.91
CaCl <sub>2</sub>	9703.6	-16833.1	21521.9	-15011.1	5463.78	-763.778
CaBr <sub>2</sub>	10291.7	-35241.8	138565.0	-358111.0	372514.0	-
SrCl <sub>2</sub>	10423.0	-31744.7	146405.0	-545729.0	$1.03420 \times 10^6$	-731278.0
SrBr <sub>2</sub>	9911.78	-26154.2	42397.1	-27852.2	-	-
BaCl <sub>2</sub>	9946.6	-20223.5	27330.0	-22874.1	10439.6	-1968.45
BaBr <sub>2</sub>	10303.9	33103.0	84282.3	-139133.0	104683.0	-

The above coefficients were obtained by a least squares fit to the evaluated  $\phi_L^{\circ}$  data given in ref. [60], and which, in the low concentration region, appear to be largely based on the results of Lange and Streeck [61]. It should be noted that in our least squares fit that we have not fixed the value of  $\alpha_1$  to a theoretical value.

Apparent Molal Heat Capacity Data

$$\phi_c^{\circ}/J \cdot mol^{-1} \cdot K^{-1} = \phi_c^{\circ} + \sum_{i=1}^n \beta_i m_i^{1/2}$$

<u>System</u>	<u><math>\phi_c^{\circ}</math></u>	<u><math>\beta_1</math></u>	<u><math>\beta_2</math></u>
MgCl <sub>2</sub>	-257.7	88.75	-
CaCl <sub>2</sub>	-276.3	102.2	3.28
SrCl <sub>2</sub>	-282.0	150.38	-62.6
BaCl <sub>2</sub>	-292.0	150.38	-38.3

The data for MgCl<sub>2</sub> is based on an empirical fit to the calorimetric data of Rutskov [62], Vasileev et al. [63], and Perron et al. [64]. For CaCl<sub>2</sub> data from Perron et al. [64] were combined with data given by Lewis and Randall and Pitzer and Brewer [3]. The other coefficients are based entirely on the calorimetric measurements of Perron et al. [64]. As in the case of the fit of the  $\phi_L^{\circ}$  data, we have not fixed the value of  $\beta_1$  to a theoretical value for either MgCl<sub>2</sub> or CaCl<sub>2</sub>.

Table 12. Continued

System	$t_+^{\circ}$	<u>Transference Number Data</u>			
		<u>A<sub>1</sub></u>	<u>A<sub>2</sub></u>	<u>A<sub>3</sub></u>	<u>A<sub>4</sub></u>
MgCl <sub>2</sub>	0.4100	-0.1672	0.0034	-	-
BaCl <sub>2</sub>	0.4542	-0.1791	0.2859	0.3812	0.1727

The coefficients of the transference number equation for BaCl<sub>2</sub> are based on a least squares fit to the transference numbers reported by Jones and Dole [49] and a value of  $t_+^{\circ} = 0.4547$ . This latter value was calculated using the  $\Lambda^{\circ}$  values for BaCl<sub>2</sub> and CaCl<sub>2</sub> given by Harned and Owen [65] together with a  $t_+^{\circ} = 0.4381$  for CaCl<sub>2</sub>, which is an average of the data of Keenan et al. [59] and of Longsworth [66]. Earlier, and less precise, transference number were reported by several different workers [67-70]; see figure 16 for a summary of the available data from the literature.

For MgCl<sub>2</sub>,  $t_+^{\circ}$  was calculated via a scheme similar to that used in obtaining  $t_+^{\circ}$  for Ba<sup>2+</sup> in aqueous BaCl<sub>2</sub>. The coefficients given above are based on a fit to this  $t_+^{\circ}$  value and data from three other sources [71-73]. We note that the experimental values of the transference numbers for this system are not very precise.

Density Data

$$\rho/g \cdot ml^{-1} = \rho^{\circ} + B_1 c + B_2 c^{3/2} + B_3 c^2 \text{ where } c \text{ is the concentration in units of moles per cubic decimeter.}$$

System	$\rho^{\circ}$	<u>B<sub>1</sub></u>	<u>B<sub>2</sub></u>	<u>B<sub>3</sub></u>	<u>References</u>
MgCl <sub>2</sub>	0.99707	0.0808	-0.0077	0.0005	[63, 64, 74, 75]
SrCl <sub>2</sub>	0.99707	0.0700	-0.0022	-	[74]
BaCl <sub>2</sub>	0.997074	0.184762	-0.006758	-	[76]

Osmotic Coefficient Data

The evaluated osmotic coefficients given by Hamer and Wu [77] were used for NaCl and KCl. We use the evaluation of Staples and Nuttall for both CaCl<sub>2</sub> (note here that we have used the coefficients appropriate to their eq. 40) and H<sub>2</sub>SO<sub>4</sub>. Although the evaluation on sulfuric acid is still tentative, the calculated osmotic coefficients are in good agreement with a recent evaluation [78] of that data.

Additional auxiliary data follow:

$$\Delta H_{fus}^{\circ} = 6008 \text{ J} \cdot \text{mol}^{-1} \quad [3]$$

$$\Delta C_{fus}^{\circ} = 38.1 \text{ J} \cdot \text{mol}^{-1} \text{ K}^{-1} \quad [3]$$

$$\Delta b = -0.197 \text{ J} \cdot \text{K}^{-2} \cdot \text{mol}^{-1} \quad [3]$$

$$T_{fus} = 273.15 \text{ K for water} \quad [2a]$$

$$R = 8.31441 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \quad [79]$$

$$F = 96484.56 \text{ C} \cdot \text{mol}^{-1} \quad [79]$$

$$A = 1.17625 \text{ kg}^{1/2} \cdot \text{mol}^{-1/2} \quad [1]$$

$$P^{\circ} = 3168.6 \text{ Pa (23.7627 torr)} \\ \text{for water at } 25 \text{ }^{\circ}\text{C} \quad [80]$$

$$B_T = -992 \text{ cm}^3 \cdot \text{mol}^{-1} \text{ at } 25 \text{ }^{\circ}\text{C} \quad [81]$$

Table 13a. Coefficients of Equations (1a) and (1b)

System	B	C	D	E	F	G	H	I
MgCl <sub>2</sub>	1.745234565	0.3091590213	0.1755567018	-2.315139694x10 <sup>-2</sup>	1.280641813x10 <sup>-3</sup>	-	-	-
MgBr <sub>2</sub>	1.664936670	0.6114054954	0.1095425731	-7.901867257x10 <sup>-3</sup>	-	-	-	-
MgI <sub>2</sub>	1.730883515	0.740885433	0.134564402	-9.496760588x10 <sup>-3</sup>	-	-	-	-
CaCl <sub>2</sub> [1]	1.600017243	0.2566899947	0.1510517824	-3.770550309x10 <sup>-2</sup>	9.905782658x10 <sup>-3</sup>	-1.6948798336x10 <sup>-3</sup>	1.349599530x10 <sup>-4</sup>	-3.942075413x10 <sup>-6</sup>
CaBr <sub>2</sub>	1.793589168	0.3244255774	0.2086318113	-5.661908925x10 <sup>-2</sup>	1.215649977x10 <sup>-2</sup>	-1.293030637x10 <sup>-3</sup>	4.849426545x10 <sup>-5</sup>	-
CaI <sub>2</sub>	1.766008019	0.5946380078	9.289406005x10 <sup>-2</sup>	-	-	-	-	-
SrCl <sub>2</sub>	1.498397739	0.2633867503	7.973317963x10 <sup>-2</sup>	-5.398408661x10 <sup>-3</sup>	-	-	-	-
SrBr <sub>2</sub>	1.779766562	0.2554248269	0.1496435300	-1.462397669x10 <sup>-2</sup>	-	-	-	-
SrI <sub>2</sub>	1.916437263	0.4205813750	0.1615996077	-1.623333549x10 <sup>-2</sup>	-	-	-	-
BaCl <sub>2</sub>	1.371515905	0.2729656762	-	-	-	-	-	-
BaBr <sub>2</sub>	1.513071093	0.3427681720	2.869661079x10 <sup>-2</sup>	-	-	-	-	-
BaI <sub>2</sub>	1.807342728	0.5135200156	6.295856273x10 <sup>-2</sup>	-	-	-	-	-

$$\ln \gamma = - \frac{A_1 I^{1/2}}{1 + B I^{1/2}} + Cm + Dm^2 + Em^3 + \dots \quad (1a)$$

$$\phi = 1 + \frac{A_1}{B^3 I} \left\{ - (1 + B I^{1/2}) + 2 \ln (1 + B I^{1/2}) \right. \\ \left. + 1/(1 + B I^{1/2}) \left\{ + \frac{1}{2} Cm + \frac{2}{3} Dm^2 + \frac{3}{4} Em^3 + \dots \right. \right\} \right\} \quad (1b)$$

$A_1 = 2.3525 \text{ mol}^{-1/2} \cdot \text{kg}^{1/2}$  for the above systems.

Table 13b. Standard Deviations of the Coefficients of Equations (1a) and (1b)

System	Bx10 <sup>3</sup>	Cx10 <sup>3</sup>	Dx10 <sup>3</sup>	Ex10 <sup>3</sup>	Fx10 <sup>3</sup>	Gx10 <sup>3</sup>	Hx10 <sup>3</sup>	Ix10 <sup>3</sup>
MgCl <sub>2</sub>	31.2	17.4	9.6	2.26	0.182	-	-	-
MgBr <sub>2</sub>	25.7	11.3	4.1	0.45	-	-	-	-
MgI <sub>2</sub>	57.8	23.1	8.53	1.02	-	-	-	-
CaCl <sub>2</sub> [1]	8.7	10.8	10.7	5.3	1.4	0.2	0.01	0.0003
CaBr <sub>2</sub>	151	92.3	66.3	24.3	4.5	0.41	0.014	-
CaI <sub>2</sub>	47.9	21.8	7.32	-	-	-	-	-
SrCl <sub>2</sub>	20.0	16.3	8.16	1.30	-	-	-	-
SrBr <sub>2</sub>	47.0	34.4	26.0	6.72	-	-	-	-
SrI <sub>2</sub>	47.8	30.9	23.8	6.36	-	-	-	-
BaCl <sub>2</sub>	6.4	2.9	-	-	-	-	-	-
BaBr <sub>2</sub>	15.5	10.4	3.47	-	-	-	-	-
BaI <sub>2</sub>	70.9	27.9	9.15	-	-	-	-	-

Table 14a. Coefficients of Equations (2a) and (2b)

System	B <sub>1</sub>	B <sub>2</sub>	B <sub>3</sub>	B <sub>4</sub>	B <sub>5</sub>	B <sub>6</sub>	B <sub>7</sub>	B <sub>8</sub>	B <sub>9</sub>
MgCl <sub>2</sub>	1.5177 <sub>37348</sub>	7.75759 <sub>3094</sub>	-4.13444 <sub>1316</sub>	1.92098 <sub>2603</sub>	-0.526958 <sub>7461</sub>	6.00945 <sub>1209</sub>	x10 <sup>-2</sup>	-	-
MgBr <sub>2</sub>	1.5112 <sub>42175</sub>	8.6219 <sub>3341</sub>	-5.33850 <sub>0811</sub>	2.68864 <sub>6717</sub>	-0.759490 <sub>6226</sub>	0.087067 <sub>58632</sub>	-	-	-
MgI <sub>2</sub>	2.7657 <sub>20791</sub>	5.22965 <sub>9380</sub>	-1.10040 <sub>2869</sub>	0.11722 <sub>60761</sub>	-	-	-	-	-
CaCl <sub>2</sub> [1]	-1.3981 <sub>92476</sub>	21.29097 <sub>223</sub>	-33.10951 <sub>856</sub>	36.599960 <sub>12</sub>	-25.677586 <sub>01</sub>	11.3349977 <sub>4</sub>	-3.0486152 <sub>00</sub>	0.45508931 <sub>92</sub>	-2.883352 <sub>369</sub>
CaBr <sub>2</sub>	2.4377 <sub>53200</sub>	4.39757 <sub>8906</sub>	1.19781 <sub>3134</sub>	-2.397370 <sub>473</sub>	1.301745 <sub>559</sub>	-0.3162767 <sub>000</sub>	2.87269 <sub>7395</sub>	x10 <sup>-2</sup>	-
CaI <sub>2</sub>	2.2573 <sub>19730</sub>	6.1783 <sub>40798</sub>	-1.9632 <sub>95105</sub>	0.3636 <sub>840859</sub>	-	-	-	-	-
SrCl <sub>2</sub>	-1.2913 <sub>62164</sub>	19.0984 <sub>8118</sub>	-25.61053 <sub>236</sub>	23.82305 <sub>618</sub>	-13.07326 <sub>267</sub>	3.858152 <sub>527</sub>	-0.472723 <sub>0522</sub>	-	-
SrBr <sub>2</sub>	1.8804 <sub>90724</sub>	6.2994 <sub>07207</sub>	-2.0020 <sub>57845</sub>	0.3639 <sub>314011</sub>	-	-	-	-	-
SrI <sub>2</sub>	2.3308 <sub>63656</sub>	5.8371 <sub>65577</sub>	-1.6955 <sub>74538</sub>	0.2942 <sub>121323</sub>	-	-	-	-	-
BaCl <sub>2</sub>	-3.6840 <sub>28391</sub>	31.8290 <sub>4197</sub>	-54.2629 <sub>1911</sub>	54.7580 <sub>6114</sub>	-28.2778 <sub>4025</sub>	5.81846 <sub>7173</sub>	-	-	-
BaBr <sub>2</sub>	-1.1134 <sub>81407</sub>	18.3148 <sub>5172</sub>	-22.7551 <sub>2079</sub>	18.3570 <sub>1684</sub>	-7.75533 <sub>5889</sub>	1.31769 <sub>8451</sub>	-	-	-
BaI <sub>2</sub>	1.8249 <sub>22230</sub>	7.2509 <sub>23378</sub>	-3.0420 <sub>81158</sub>	0.6952 <sub>546547</sub>	-	-	-	-	-

$$\ln \gamma = - A_1 I^{1/2} - A_2 I \ln I + \sum_{i=1}^N B_i m^{(i+1)/2}$$

$$\phi = 1 - \frac{A_1}{3} I^{1/2} - \frac{A_2}{2} I \left[ \ln I + \frac{1}{2} \right] + \sum_{i=1}^N B_i \frac{(i+1)}{(i+3)} m^{(i+1)/2}$$

A<sub>1</sub> = 2.3525 mol<sup>-1/2</sup>·kg<sup>1/2</sup> and A<sub>2</sub> = 0.92238 mol<sup>-1</sup>·kg for the above systems

Table 14b. Standard Deviations of Coefficients of Equations (2a) and (2b)

System	B <sub>1</sub>	B <sub>2</sub>	B <sub>3</sub>	B <sub>4</sub>	B <sub>5</sub>	B <sub>6</sub>	B <sub>7</sub>	B <sub>8</sub>	B <sub>9</sub>
MgCl <sub>2</sub>	0.733	0.424	0.555	0.358	0.113	0.014	-	-	-
MgBr <sub>2</sub>	0.163	0.539	0.73	0.49	0.161	0.0206	-	-	-
MgI <sub>2</sub>	0.077	0.131	0.0774	0.0153	-	-	-	-	-
CaCl <sub>2</sub> [1]	0.08	0.50	1.2	1.6	1.3	0.58	0.16	0.025	0.002
CaBr <sub>2</sub>	0.492	1.61	2.25	1.65	0.661	0.137	0.0116	-	-
CaI <sub>2</sub>	0.169	0.442	0.404	0.124	-	-	-	-	-
SrCl <sub>2</sub>	0.314	1.86	4.38	5.25	3.4	1.13	0.15	-	-
SrBr <sub>2</sub>	0.0981	0.249	0.221	0.0657	-	-	-	-	-
SrI <sub>2</sub>	0.0927	0.238	0.213	0.064	-	-	-	-	-
BaCl <sub>2</sub>	0.309	2.09	5.36	6.54	3.83	0.866	-	-	-
BaBr <sub>2</sub>	0.257	1.45	3.20	3.43	1.78	0.356	-	-	-
BaI <sub>2</sub>	0.193	0.484	0.429	0.128	-	-	-	-	-

Table 15a. Coefficients of Equations (3a) and (3b)

System	B <sub>1</sub>	B <sub>2</sub>	B <sub>3</sub>	B <sub>4</sub>	B <sub>5</sub>	B <sub>6</sub>	B <sub>7</sub>	B <sub>8</sub>
MgCl <sub>2</sub>	11.4515 <sub>534</sub>	-23.24459 <sub>218</sub>	33.30581 <sub>304</sub>	-30.88833 <sub>451</sub>	18.348782 <sub>21</sub>	-6.688545 <sub>031</sub>	1.3561596 <sub>77</sub>	-0.1167946 <sub>304</sub>
MgBr <sub>2</sub>	10.5731 <sub>6706</sub>	-17.47516 <sub>454</sub>	20.24871 <sub>172</sub>	-14.64636 <sub>159</sub>	6.419302 <sub>25</sub>	-1.546677 <sub>652</sub>	0.156203 <sub>0230</sub>	-
MgI <sub>2</sub>	9.1516 <sub>22470</sub>	-10.28923 <sub>092</sub>	7.09203 <sub>7004</sub>	-2.38881 <sub>0288</sub>	0.314394 <sub>92420</sub>	-	-	-
CaCl <sub>2</sub> [1]	10.2643 <sub>0765</sub>	-18.05044 <sub>031</sub>	21.84262 <sub>561</sub>	-16.799684 <sub>41</sub>	8.139673 <sub>440</sub>	-2.3771904 <sub>79</sub>	0.3783336 <sub>173</sub>	-2.506441 <sub>862</sub> × 10 <sup>-2</sup>
CaBr <sub>2</sub>	10.1937 <sub>7186</sub>	-16.09445 <sub>200</sub>	16.84968 <sub>738</sub>	-10.619650 <sub>62</sub>	3.934862 <sub>324</sub>	-0.7790418 <sub>832</sub>	6.2879429 <sub>73</sub> × 10 <sup>-2</sup>	-
CaI <sub>2</sub>	10.5289 <sub>9170</sub>	-15.81674 <sub>254</sub>	14.7218 <sub>6083</sub>	-7.0563 <sub>21298</sub>	1.3669 <sub>63987</sub>	-	-	-
SrCl <sub>2</sub>	9.0670 <sub>99395</sub>	-13.3670 <sub>9115</sub>	13.10785 <sub>523</sub>	-7.66019 <sub>5471</sub>	2.44950 <sub>1826</sub>	-0.327326 <sub>3337</sub>	-	-
SrBr <sub>2</sub>	9.9636 <sub>96833</sub>	-14.9731 <sub>5500</sub>	13.6228 <sub>0283</sub>	-6.3684 <sub>65403</sub>	1.2020 <sub>05524</sub>	-	-	-
SrI <sub>2</sub>	10.7612 <sub>6121</sub>	-16.8462 <sub>4517</sub>	16.0971 <sub>3447</sub>	-7.8952 <sub>52388</sub>	1.56130 <sub>2140</sub>	-	-	-
BaCl <sub>2</sub>	8.5893 <sub>36778</sub>	-11.9769 <sub>0210</sub>	10.5978 <sub>3433</sub>	-5.0867 <sub>62800</sub>	1.0094 <sub>47230</sub>	-	-	-
BaBr <sub>2</sub>	10.0269 <sub>6445</sub>	-17.4760 <sub>3685</sub>	21.0183 <sub>7443</sub>	-15.4066 <sub>5243</sub>	6.19774 <sub>7886</sub>	-1.04170 <sub>9254</sub>	-	-
BaI <sub>2</sub>	10.4141 <sub>4787</sub>	-15.9681 <sub>8515</sub>	15.4677 <sub>4299</sub>	-7.9275 <sub>71436</sub>	1.6594 <sub>92515</sub>	-	-	-

$$\ln \gamma = -A_1 T^{1/2} + \sum_{i=1}^N B_i m^{(i+1)/2}$$

$$\phi = 1 - \frac{A_1}{3} T^{1/2} + \sum_{i=1}^N \frac{B_i}{(i+3)} m^{(i+1)/2}$$

A<sub>1</sub> = 2.3525 mol<sup>-1/2</sup> · kg<sup>1/2</sup> for the above systems.

Table 15b. Standard Deviations of the Coefficients of Equations (3a) and (3b)

System	B <sub>1</sub>	B <sub>2</sub>	B <sub>3</sub>	B <sub>4</sub>	B <sub>5</sub>	B <sub>6</sub>	B <sub>7</sub>	B <sub>8</sub>
MgCl <sub>2</sub>	0.439	2.28	5.18	6.42	4.64	1.95	0.442	0.042
MgBr <sub>2</sub>	0.285	1.26	2.36	2.31	1.23	0.338	0.0375	-
MgI <sub>2</sub>	0.216	0.54	0.525	0.225	0.0356	-	-	-
CaCl <sub>2</sub> [1]	0.047	0.23	0.45	0.46	0.27	0.09	0.02	0.001
CaBr <sub>2</sub>	0.48	1.58	2.2	1.61	0.645	0.134	0.0113	-
CaI <sub>2</sub>	0.401	1.54	2.30	1.53	0.377	-	-	-
SrCl <sub>2</sub>	0.172	0.764	1.33	1.11	0.448	0.0697	-	-
SrBr <sub>2</sub>	0.222	0.82	1.18	0.748	0.176	-	-	-
SrI <sub>2</sub>	0.190	0.718	1.06	0.696	0.169	-	-	-
BaCl <sub>2</sub>	0.146	0.716	1.26	0.944	0.256	-	-	-
BaBr <sub>2</sub>	0.269	1.51	3.36	3.6	1.86	0.373	-	-
BaI <sub>2</sub>	0.489	1.87	2.77	1.82	0.441	-	-	-

Table 16. Standard Deviations for Observations of Unit Weight for  $\phi$  or  $\ln \gamma$ 

## Equation

System	equations (1)	equations (2)	equations (3)
MgCl <sub>2</sub>	0.00724	0.00749	0.00734
MgBr <sub>2</sub>	0.00441	0.00431	0.00526
MgI <sub>2</sub>	0.00889	0.00928	0.0108
CaCl <sub>2</sub> [1]	0.0045	0.0054	0.0048
CaBr <sub>2</sub>	0.0140	0.0144	0.0141
CaI <sub>2</sub>	0.00545	0.00578	0.00549
SrCl <sub>2</sub>	0.00937	0.00922	0.00949
SrI <sub>2</sub>	0.00267	0.00300	0.00232
BaCl <sub>2</sub>	0.00923	0.00960	0.00933
BaBr <sub>2</sub>	0.00426	0.00442	0.00463
BaI <sub>2</sub>	0.00668	0.00597	0.00607

Table 17. Recommended Values for the Mean Activity Coefficient and Osmotic Coefficient of  
 $\text{MgCl}_2$  in  $\text{H}_2\text{O}$  at 298.15 K

$m/\text{mol}\cdot\text{kg}^{-1}$	$\gamma$	$\phi$	$a_w$	$\Delta G^{\text{ex}}/\text{J}\cdot\text{kg}^{-1}$
.001	.8893	.9627	.999948	-1.
.002	.8522	.9501	.999897	-2.
.003	.8265	.9415	.999847	-3.
.004	.8065	.9347	.999798	-4.
.005	.7899	.9292	.999749	-6.
.006	.7758	.9245	.999700	-8.
.007	.7634	.9224	.999652	-10.
.008	.7525	.9168	.999604	-12.
.009	.7426	.9135	.999556	-14.
.010	.7336	.9106	.999508	-16.
.020	.6721	.8916	.999037	-43.
.030	.6352	.8813	.998572	-75.
.040	.6094	.8749	.998110	-110.
.050	.5899	.8708	.997650	-148.
.060	.5745	.8681	.997189	-188.
.070	.5619	.8663	.996728	-231.
.080	.5513	.8653	.996266	-274.
.090	.5424	.8648	.995802	-319.
.100	.5347	.8648	.995337	-365.
.200	.4935	.8760	.990576	-866.
.300	.4827	.8963	.985573	-1403.
.400	.4796	.9206	.980295	-1949.
.500	.4855	.9475	.974721	-2492.
.600	.4962	.9765	.968330	-3022.
.700	.5111	1.0073	.962608	-3532.
.800	.5296	1.0398	.956038	-4019.
.900	.5515	1.0738	.949111	-4477.
1.00	.5769	1.1292	.941815	-4923.
1.250	.6561	1.2034	.921921	-5829.
1.500	.7622	1.3047	.899629	-6458.
1.750	.8943	1.4123	.874965	-6819.
2.000	1.0655	1.5250	.848029	-6866.
2.250	1.2328	1.6421	.818987	-6577.
2.500	1.5584	1.7629	.788056	-5934.
2.750	1.9076	1.8865	.755495	-4922.
3.000	2.3498	2.0125	.721589	-3529.
3.250	2.9103	2.1403	.686640	-1742.
3.500	3.6211	2.2696	.650952	446.
3.750	4.5231	2.4000	.614828	3845.
4.000	5.6692	2.5313	.578552	6060.
4.250	7.1273	2.6634	.542392	9498.
4.500	8.9854	2.7962	.506587	13365.
4.750	11.3582	2.9299	.471354	17664.
5.000	14.3960	3.0645	.436875	22402.
5.250	18.2979	3.2003	.403329	27583.
5.500	23.3290	3.3377	.370786	33212.
5.750	29.8468	3.4771	.339410	39297.
5.840	32.6458	3.5279	.328412	41602.
5.925	35.5476	3.5762	.318175	43832.

$\frac{m}{\text{mol}\cdot\text{kg}^{-1}}$	$\sigma(\phi)$	$\sigma(\ln\gamma)$	$\sigma(\gamma)$
6.00	.0049	.0076	.2921
3.00	.0015	.0055	.0130
1.00	.0012	.0050	.0029
.10	.0014	.0043	.0023
.01	.0005	.0011	.0008

Table 18. Recommended Values for the Mean Activity Coefficient and Osmotic Coefficient of  $\text{MgBr}_2$  in  $\text{H}_2\text{O}$  at 298.15 K

$m/\text{mol}\cdot\text{kg}^{-1}$	$\gamma$	$\phi$	$a_w$	$\Delta G^{\text{ex}}/\text{J}\cdot\text{kg}^{-1}$
.001	.8892	.9627	.999948	-1.
.002	.8520	.9500	.999897	-2.
.003	.8262	.9413	.999847	-3.
.004	.8062	.9346	.999798	-4.
.005	.7896	.9290	.999749	-6.
.006	.7755	.9243	.999700	-8.
.007	.7631	.9203	.999652	-10.
.008	.7522	.9167	.999604	-12.
.009	.7423	.9135	.999556	-14.
.010	.7334	.9107	.999508	-16.
.020	.6724	.8922	.999036	-43.
.030	.6363	.8827	.998570	-75.
.040	.6114	.8773	.998105	-110.
.050	.5928	.8742	.997640	-148.
.060	.5783	.8726	.997174	-187.
.070	.5667	.8720	.996707	-229.
.080	.5572	.8721	.996236	-272.
.090	.5492	.8728	.995764	-316.
.100	.5426	.8740	.995288	-361.
.200	.5123	.8976	.990345	-842.
.300	.5109	.9303	.985030	-1343.
.400	.5218	.9666	.979320	-1836.
.500	.5405	1.00051	.973205	-2307.
.600	.5651	1.0451	.966676	-2749.
.700	.5949	1.0866	.959725	-3154.
.800	.6298	1.1292	.952348	-3520.
.900	.6698	1.1730	.944539	-3841.
1.000	.7151	1.2179	.936296	-4115.
1.250	.8541	1.3345	.913786	-4576.
1.500	1.0372	1.4570	.888588	-4691.
1.750	1.2769	1.5849	.860790	-4432.
2.000	1.5902	1.7177	.830548	-3775.
2.250	2.0006	1.8548	.798074	-2701.
2.500	2.5390	1.9958	.763634	-1191.
2.750	3.2471	2.1402	.727541	769.
3.000	4.1804	2.2873	.690140	3192.
3.250	5.413	2.4367	.6518	6091.
3.500	7.042	2.5879	.6129	9475.
3.750	9.199	2.7403	.5738	13352.
4.000	12.054	2.8934	.5350	17728.
4.250	15.831	3.0466	.4967	22610.
4.500	20.823	3.1994	.4593	27999.
4.750	27.408	3.3512	.4230	33899.
5.000	36.074	3.5015	.3882	40310.
5.250	47.441	3.6498	.3550	47232.
5.500	62.288	3.7954	.3236	54661.
5.610 (sat)	70.166	3.8585	.3104	58089.

$\frac{m}{\text{mol}\cdot\text{kg}}^{-1}$	$\sigma(\phi)$	$\sigma(\ln y)$	$\sigma(\gamma)$
5.6	0.0036	0.0067	0.4651
3.0	0.0025	0.0063	0.0264
1.0	0.0012	0.0057	0.0041
0.10	0.0014	0.0040	0.0022
0.01	0.0004	0.0010	0.0007

Table 19. Recommended Values for the Mean Activity Coefficient and Osmotic Coefficient of  $MgI_2$  in  $H_2O$  at 298.15 K

$m/mol \cdot kg^{-1}$	$\gamma$	$\phi$	$a_w$	$\Delta G^{ex}/J \cdot kg^{-1}$
.001	.8896	.9629	.999948	-1.
.002	.8528	.9505	.999897	-2.
.003	.8274	.9420	.999847	-3.
.004	.8076	.9354	.999798	-4.
.005	.7913	.9301	.999749	-6.
.006	.7775	.9256	.999700	-8.
.007	.7654	.9217	.999651	-10.
.008	.7547	.9183	.999603	-12.
.009	.7451	.9152	.999555	-14.
.010	.7363	.9125	.999507	-16.
.020	.6772	.8955	.999033	-42.
.030	.6426	.8872	.998563	-73.
.040	.6190	.8829	.998093	-108.
.050	.6016	.8808	.997623	-145.
.060	.5883	.8802	.997150	-183.
.070	.5777	.8805	.996674	-223.
.080	.5692	.8815	.996196	-265.
.090	.5623	.8831	.995714	-307.
.100	.5565	.8851	.995228	-350.
.200	.5353	.9169	.990138	-806.
.300	.5430	.9575	.984595	-1267.
.400	.5641	1.0018	.978576	-1708.
.500	.5942	1.0484	.972068	-2116.
.600	.6318	1.0968	.965059	-2480.
.700	.6768	1.1468	.957542	-2797.
.800	.7291	1.1983	.949509	-3060.
.900	.7892	1.2512	.940956	-3265.
1.000	.8579	1.3054	.931879	-3411.
1.250	1.0736	1.4465	.906903	-3490.
1.500	1.3687	1.5949	.878713	-3135.
1.750	1.7724	1.7501	.847449	-2314.
2.000	2.3264	1.9115	.813334	-999.
2.250	3.0900	2.0784	.776671	833.
2.500	4.1475	2.2502	.737831	3203.
2.750	5.6184	2.4264	.697239	6128.
3.000	7.6727	2.6062	.655362	9626.
3.250	10.552	2.7891	.6127	13710.
3.500	14.598	2.9743	.5697	18391.
3.750	20.296	3.1613	.5269	23681.
4.000	28.330	3.3493	.4848	29588.
4.250	39.665	3.5377	.4437	36117.
4.500	55.649	3.7260	.4041	43274.
4.750	78.163	3.9133	.3662	51062.
5.000	109.808	4.0991	.3303	59482.
5.010	111.311	4.1065	.3289	59832.

$m/mol \cdot kg^{-1}$	$\sigma(\phi)$	$\sigma(\ln\gamma)$	$\sigma(\gamma)$
5.0	0.0074	0.0135	1.4814
3.0	0.0039	0.0126	0.0967
1.0	0.0022	0.0119	0.0102
0.1	0.0030	0.0088	0.0049
0.01	0.0010	0.0022	0.0016

Table 20. Recommended Values for the Mean Activity of Coefficient and Osmotic Coefficient of  $\text{CaCl}_2$  in  $\text{H}_2\text{O}$  at 298.15 K [1]

$m/\text{mol}\cdot\text{kg}^{-1}$	$\gamma$	$\phi$	$a_w$	$\Delta G^{\text{ex}}/\text{J}\cdot\text{kg}^{-1}$
.001	.8885	.9623	.999948	-1.
.002	.8508	.9493	.999897	-2.
.003	.8245	.9403	.999848	-3.
.004	.8039	.9332	.999798	-5.
.005	.7869	.9274	.999749	-6.
.006	.7724	.9224	.999701	-8.
.007	.7596	.9181	.999653	-10.
.008	.7483	.9142	.999605	-12.
.009	.7380	.9107	.999557	-14.
.010	.7287	.9076	.999510	-17.
.020	.6644	.8866	.999042	-44.
.030	.6256	.8748	.998583	-77.
.040	.5982	.8671	.998127	-113.
.050	.5773	.8619	.997674	-153.
.060	.5607	.8582	.997221	-195.
.070	.5470	.8555	.996769	-239.
.080	.5355	.8536	.996316	-285.
.090	.5256	.8524	.995863	-332.
.100	.5171	.8516	.995408	-380.
.200	.4692	.8568	.990782	-912.
.300	.4508	.8721	.985960	-1492.
.400	.4442	.8915	.980912	-2091.
.500	.4442	.9134	.975621	-2695.
.600	.4486	.9370	.970072	-3296.
.700	.4564	.9621	.964256	-3886.
.800	.4670	.9884	.958163	-4461.
.900	.4801	1.0159	.951785	-5017.
1.000	.4956	1.0444	.945117	-5551.
1.250	.5440	1.1198	.927142	-6773.
1.500	.6070	1.2004	.907271	-7805.
1.750	.6861	1.2857	.885497	-8621.
2.000	.7842	1.3754	.861853	-9199.
2.250	.9049	1.4690	.836413	-9519.
2.500	1.0529	1.5660	.809293	-9565.
2.750	1.2339	1.6661	.780655	-9323.
3.000	1.4550	1.7685	.750702	-8780.
3.250	1.724	1.8728	.7197	-7926.
3.500	2.052	1.9781	.6879	-6752.
3.750	2.448	2.0836	.6555	-5252.
4.000	2.926	2.1885	.6231	-3421.
4.250	3.497	2.2918	.5907	-1260.
4.500	4.176	2.3926	.5588	1233.
4.750	4.976	2.4898	.5277	4054.
5.000	5.907	2.5826	.4976	7198.
5.250	6.980	2.6701	.4688	10656.
5.500	8.199	2.7515	.4414	14419.
5.750	9.565	2.8260	.4155	18475.
6.000	11.072	2.8932	.3913	22811.
6.250	12.709	2.9526	.3689	27410.
6.500	14.461	3.0041	.3481	32258.
6.750	16.304	3.0476	.3290	37338.
7.000	18.215	3.0833	.3115	42632.
7.250	20.171	3.1117	.2954	48124.
7.462(sat)	21.847	3.1304	.2830	52925.
7.500	22.148	3.1332	.2808	53798.
7.750	24.132	3.1488	.2674	59638.
8.000	26.111	3.1592	.2551	65632.
8.250	28.09	3.166	.2438	71766.
8.500	30.07	3.169	.2332	78031.
8.750	32.07	3.171	.2233	84419.
9.000	34.11	3.171	.2138	90924.
9.250	36.23	3.172	.2048	97542.
9.500	38.43	3.173	.1961	104272.
9.750	40.73	3.175	.1877	111110.
10.000	43.12	3.176	.1796	118055.

For standard deviations of calculated values, see ref. [1].

Table 21. Recommended Values for the Mean Activity Coefficient and Osmotic Coefficient of  $\text{CaBr}_2$  in  $\text{H}_2\text{O}$  at 298.15 K

$m/\text{mol}\cdot\text{kg}^{-1}$	$\gamma$	$\phi$	$a_w$	$\Delta G^{\text{ex}}/\text{J}\cdot\text{kg}^{-1}$
.001	.8896	.9629	.999948	-1.
.002	.8527	.9504	.999897	-2.
.003	.8272	.9418	.999847	-3.
.004	.8073	.9352	.999798	-4.
.005	.7909	.9297	.999749	-6.
.006	.7769	.9251	.999700	-8.
.007	.7647	.9211	.999652	-10.
.008	.7538	.9176	.999603	-12.
.009	.7441	.9144	.999555	-14.
.010	.7352	.9116	.999507	-16.
.020	.6745	.8932	.999035	-43.
.030	.6383	.8834	.998569	-74.
.040	.6130	.8774	.998105	-109.
.050	.5940	.8736	.997642	-147.
.060	.5789	.8712	.997179	-186.
.070	.5667	.8698	.996715	-228.
.080	.5564	.8690	.996250	-271.
.090	.5478	.8688	.995783	-315.
.100	.5404	.8690	.995315	-360.
.200	.5016	.8822	.990509	-851.
.300	.4909	.9044	.985443	-1374.
.400	.4919	.9304	.980086	-1903.
.500	.4999	.9590	.974417	-2426.
.600	.5130	.9896	.968420	-2932.
.700	.5302	1.0218	.962082	-3417.
.800	.5511	1.0554	.955394	-3875.
.900	.5756	1.0903	.948346	-4302.
1.000	.6036	1.1265	.940935	-4695.
1.250	.6897	1.2215	.920793	-5513.
1.500	.8014	1.3224	.898339	-6066.
1.750	.9441	1.4287	.873605	-6328.
2.000	1.1255	1.5400	.846657	-6273.
2.250	1.3561	1.6561	.817593	-5881.
2.500	1.6504	1.7771	.786534	-5134.
2.750	2.0277	1.9031	.753631	-4012.
3.000	2.5143	2.0341	.719069	-2500.
3.250	3.146	2.1700	.6831	-578.
3.500	3.970	2.3110	.6459	1767.
3.750	5.053	2.4567	.6078	4554.
4.000	6.482	2.6070	.5692	7796.
4.250	8.376	2.7612	.5303	11508.
4.500	10.893	2.9189	.4917	15703.
4.750	14.244	3.0790	.4536	20392.
5.000	18.705	3.2408	.4165	25583.
5.250	24.635	3.4029	.3808	31284.
5.500	32.487	3.5641	.3467	37498.
5.750	42.823	3.7228	.3145	44227.
6.000	56.321	3.8776	.2844	51467.
6.250	73.763	4.0269	.2566	59213.
6.500	96.009	4.1690	.2312	67456.
6.750	123.953	4.3023	.2081	76181.
7.000	158.434	4.4254	.1875	85379.
7.250	200.144	4.5369	.1690	95008.
7.500	249.517	4.6358	.1527	105068.
7.660 (sat)	285.193	4.6921	.1433	111715.
7.750	306.638	4.7213	.1384	115523.
8.000	371.202	4.7930	.1259	126349.
8.250	442.57	4.851	.1150	137515.
8.500	519.93	4.897	.1055	148994.
8.750	602.63	4.931	.0971	160760.
9.000	694.66	4.956	.0898	172790.
9.210	769.53	4.973	.0841	183085.
$\frac{m}{\text{mol}\cdot\text{kg}^{-1}}$		$\sigma(\phi)$	$\sigma(\ln\gamma)$	$\sigma(\gamma)$
9.2	0.0135	0.0264	20.222	
7.0	0.0049	0.0231	3.665	
5.0	0.0060	0.0224	0.420	
3.0	0.0048	0.0235	0.0590	
1.0	0.0044	0.0219	0.0132	
0.1	0.0062	0.0193	0.0104	
0.01	0.0023	0.0054	0.0039	

Table 22. Recommended Values for the Mean Activity Coefficient and Osmotic Coefficient of  
CaI<sub>2</sub> in H<sub>2</sub>O at 298.15 K

$m/mol \cdot kg^{-1}$	$\gamma$	$\phi$	$a_w$	$\Delta G^{ex}/J \cdot kg^{-1}$
.001	.8897	.9629	.999948	-1.
.002	.8529	.9505	.999897	-2.
.003	.8275	.9420	.999847	-3.
.004	.8077	.9355	.999798	-4.
.005	.7914	.9301	.999749	-6.
.006	.7776	.9256	.999700	-8.
.007	.7655	.9217	.999651	-10.
.008	.7547	.9182	.999603	-12.
.009	.7451	.9152	.999555	-14.
.010	.7363	.9124	.999507	-16.
.020	.6768	.8950	.999033	-42.
.030	.6418	.8863	.998564	-74.
.040	.6177	.8815	.998096	-108.
.050	.5998	.8788	.997628	-145.
.060	.5859	.8776	.997158	-184.
.070	.5748	.8773	.996687	-224.
.080	.5657	.8777	.996212	-266.
.090	.5581	.8786	.995735	-309.
.100	.5518	.8799	.995256	-353.
.200	.5237	.9042	.990274	-820.
.300	.5234	.9365	.984930	-1303.
.400	.5350	.9720	.979206	-1777.
.500	.5541	1.0093	.973094	-2230.
.600	.5790	1.0481	.966584	-2653.
.700	.6089	1.0881	.959669	-3041.
.800	.6438	1.1294	.952342	-3390.
.900	.6837	1.1718	.944596	-3695.
1.000	.7288	1.2154	.936425	-3954.
1.100	.7795	1.2601	.927825	-4165.
1.200	.8364	1.3059	.918791	-4324.
1.300	.9001	1.3530	.909320	-4430.
1.400	.9713	1.4011	.899411	-4480.
1.500	1.0508	1.4505	.889063	-4472.
1.600	1.1396	1.5010	.878277	-4406.
1.700	1.2390	1.5526	.867054	-4277.
1.800	1.3502	1.6055	.855400	-4086.
1.900	1.4747	1.6595	.843318	-3830.
1.915	1.4946	1.6677	.841469	-3786.

$\frac{m}{mol \cdot kg}^{-1}$	$\sigma(\phi)$	$\sigma(\ln \gamma)$	$\sigma(\gamma)$
2.0	0.0032	0.0094	0.0152
1.0	0.0019	0.0080	0.0058
0.1	0.0023	0.0068	0.0038
0.01	0.0008	0.0018	0.0013

Table 23. Recommended Values for the Mean Activity Coefficient and Osmotic Coefficient of  $\text{SrCl}_2$  in  $\text{H}_2\text{O}$  at 298.15 K

$m/\text{mol}\cdot\text{kg}^{-1}$	$\gamma$	$\phi$	$a_w$	$\Delta G^{\text{ex}}/\text{J}\cdot\text{kg}^{-1}$
.001	.8880	.9620	.999948	-1.
.002	.8498	.9488	.999897	-2.
.003	.8232	.9395	.999848	-3.
.004	.8023	.9323	.999798	-5.
.005	.7850	.9262	.999750	-6.
.006	.7701	.9211	.999701	-8.
.007	.7571	.9165	.999653	-10.
.008	.7455	.9125	.999606	-12.
.009	.7351	.9089	.999558	-15.
.010	.7255	.9056	.999511	-17.
.020	.6595	.8834	.999046	-45.
.030	.6195	.8706	.998589	-78.
.040	.5911	.8621	.998138	-115.
.050	.5694	.8562	.997689	-156.
.060	.5521	.8519	.997241	-199.
.070	.5378	.8487	.996794	-244.
.080	.5257	.8464	.996347	-291.
.090	.5153	.8447	.995900	-340.
.100	.5063	.8435	.995452	-390.
.200	.4550	.8454	.990903	-941.
.300	.4336	.8579	.986187	-1547.
.400	.4241	.8743	.981276	-2178.
.500	.4209	.8930	.976158	-2820.
.600	.4219	.9131	.970824	-3463.
.700	.4260	.9345	.965265	-4101.
.800	.4324	.9568	.959475	-4731.
.900	.4409	.9800	.953447	-5347.
1.000	.4513	1.0041	.947176	-5948.
1.250	.4846	1.0677	.930406	-7363.
1.500	.5283	1.1358	.912037	-8632.
1.750	.5829	1.2078	.892049	-9728.
2.000	.6496	1.2835	.870456	-10632.
2.250	.7303	1.3626	.847308	-11327.
2.500	.8270	1.4446	.822684	-11797.
2.750	.9427	1.5292	.796697	-12029.
3.000	1.0808	1.6161	.769485	-12012.
3.250	1.245	1.7049	.7412	-11737.
3.500	1.441	1.7953	.7121	-11194.
3.518 (sat)	1.456	1.8019	.7099	-11144.
3.750	1.673	1.8869	.6822	-10376.
4.000	1.949	1.9793	.6519	-9278.
4.038	1.995	1.9934	.6472	-9086.

$\frac{m}{\text{mol}\cdot\text{kg}^{-1}}$	$\sigma(\phi)$	$\sigma(\ln\gamma)$	$\sigma(\gamma)$
4.0	0.0078	0.0095	0.0185
3.0	0.0032	0.0052	0.0056
1.0	0.0015	0.0039	0.0018
0.1	0.0010	0.0030	0.0015
0.01	0.0003	0.0007	0.0005

Table 24. Recommended Values for the Mean Activity Coefficient and Osmotic Coefficient of  $\text{SrBr}_2$  in  $\text{H}_2\text{O}$  at 298.15 K

$m/\text{mol}\cdot\text{kg}^{-1}$	$\gamma$	$\phi$	$a_w$	$\Delta G^{\text{ex}}/\text{J}\cdot\text{kg}^{-1}$
.001	.8895	.9628	.999948	-1.
.002	.8525	.9503	.999897	-2.
.003	.8268	.9416	.999847	-3.
.004	.8068	.9349	.999798	-4.
.005	.7904	.9294	.999749	-6.
.006	.7763	.9247	.999700	-8.
.007	.7640	.9207	.999652	-10.
.008	.7530	.9171	.999604	-12.
.009	.7432	.9139	.999556	-14.
.010	.7343	.9110	.999508	-16.
.020	.6729	.8921	.999036	-43.
.030	.6362	.8818	.998571	-75.
.040	.6104	.8754	.998109	-110.
.050	.5908	.8711	.997649	-148.
.060	.5753	.8683	.997188	-188.
.070	.5626	.8664	.996728	-230.
.080	.5520	.8652	.996266	-273.
.090	.5429	.8645	.995804	-318.
.100	.5350	.8642	.995340	-364.
.200	.4921	.8728	.990610	-866.
.300	.4769	.8900	.985673	-1407.
.400	.4731	.9108	.980502	-1961.
.500	.4758	.9340	.975077	-2517.
.600	.4830	.9590	.969382	-3064.
.700	.4939	.9856	.963400	-3597.
.800	.5079	1.0137	.957117	-4112.
.900	.5249	1.0432	.950522	-4603.
1.000	.5447	1.0740	.943605	-5069.
1.100	.5672	1.1061	.936356	-5506.
1.200	.5927	1.1394	.928771	-5912.
1.300	.6211	1.1737	.920843	-6283.
1.400	.6527	1.2091	.912571	-6619.
1.500	.6876	1.2456	.903953	-6917.
1.600	.7260	1.2829	.894993	-7176.
1.700	.7683	1.3212	.885692	-7393.
1.800	.8146	1.3602	.876057	-7567.
1.900	.8652	1.4000	.866093	-7698.
2.000	.9206	1.4405	.855811	-7782.
2.100	.9810	1.4816	.845221	-7820.
2.123	.9957	1.4911	.842743	-7822.

$\frac{m}{\text{mol}\cdot\text{kg}^{-1}}$	$\sigma(\phi)$	$\sigma(\ln\gamma)$	$\sigma(\gamma)$
2.0	0.0021	0.0063	0.0056
1.0	0.0010	0.0057	0.0031
0.1	0.0017	0.0056	0.0030
0.01	0.0007	0.0016	0.0012

Table 25. Recommended Values for the Mean Activity Coefficient and Osmotic Coefficient of SrI<sub>2</sub> in H<sub>2</sub>O at 298.15 K

$m/mol \cdot kg^{-1}$	$\gamma$	$\phi$	$a_w$	$\Delta G^{ex}/J \cdot kg^{-1}$
.001	.8903	.9633	.999948	-1.
.002	.8540	.9511	.999897	-2.
.003	.8290	.9428	.999847	-3.
.004	.8095	.9365	.999798	-4.
.005	.7935	.9313	.999748	-6.
.006	.7799	.9269	.999699	-8.
.007	.7681	.9232	.999651	-10.
.008	.7576	.9199	.999602	-12.
.009	.7481	.9169	.999554	-14.
.010	.7396	.9143	.999506	-16.
.020	.6814	.8976	.999030	-42.
.030	.6470	.8892	.998559	-72.
.040	.6233	.8844	.998090	-106.
.050	.6056	.8817	.997620	-143.
.060	.5917	.8803	.997150	-181.
.070	.5806	.8797	.996677	-220.
.080	.5714	.8798	.996203	-261.
.090	.5636	.8803	.995727	-304.
.100	.5571	.8812	.995249	-347.
.200	.5257	.9004	.990315	-808.
.300	.5212	.9272	.985079	-1291.
.400	.5281	.9573	.979517	-1772.
.500	.5422	.9897	.973610	-2238.
.600	.5617	1.0239	.967342	-2680.
.700	.5859	1.0598	.960698	-3094.
.800	.6147	1.0973	.953666	-3474.
.900	.6479	1.1362	.946235	-3817.
1.000	.6856	1.1764	.938398	-4119.
1.100	.7283	1.2180	.930147	-4377.
1.200	.7761	1.2609	.921481	-4589.
1.300	.8296	1.3049	.912396	-4753.
1.400	.8892	1.3500	.902896	-4867.
1.500	.9555	1.3962	.892983	-4927.
1.600	1.0291	1.4434	.882662	-4934.
1.700	1.1108	1.4914	.871943	-4884.
1.800	1.2014	1.5404	.860836	-4777.
1.900	1.3018	1.5901	.849353	-4611.
1.970	1.3785	1.6253	.841098	-4459.

$\frac{m}{mol \cdot kg}^{-1}$	<u><math>\sigma(\phi)</math></u>	<u><math>\sigma(\ln\gamma)</math></u>	<u><math>\sigma(\gamma)</math></u>
2.0	0.0020	0.0055	0.0078
1.0	0.0010	0.0052	0.0036
0.1	0.0016	0.0054	0.0030
0.01	0.0007	0.0016	0.0012

Table 26. Recommended Values for the Mean Activity Coefficient and Osmotic Coefficient of BaCl<sub>2</sub> in H<sub>2</sub>O at 298.15 K

$m/mol \cdot kg^{-1}$	$\gamma$	$\phi$	$a_w$	$\Delta G^{ex}/J \cdot kg^{-1}$
.001	.8873	.9616	.999948	-1.
.002	.8486	.9481	.999898	-2.
.003	.8215	.9386	.999848	-3.
.004	.8002	.9310	.999799	-5.
.005	.7825	.9247	.999750	-6.
.006	.7673	.9193	.999702	-8.
.007	.7539	.9146	.999654	-10.
.008	.7420	.9104	.999606	-12.
.009	.7312	.9065	.999559	-15.
.010	.7214	.9030	.999512	-17.
.020	.6532	.8791	.999050	-45.
.030	.6115	.8650	.998598	-80.
.040	.5819	.8555	.998152	-118.
.050	.5591	.8487	.997709	-160.
.060	.5409	.8436	.997268	-204.
.070	.5258	.8397	.996828	-251.
.080	.5130	.8367	.996389	-300.
.090	.5020	.8344	.995950	-350.
.100	.4924	.8326	.995510	-402.
.200	.4365	.8301	.991068	-980.
.300	.4115	.8386	.986496	-1621.
.400	.3983	.8507	.981777	-2295.
.500	.3911	.8645	.976909	-2987.
.600	.3877	.8791	.971895	-3688.
.700	.3867	.8941	.966740	-4394.
.800	.3875	.9093	.961446	-5100.
.900	.3897	.9247	.956019	-5804.
1.000	.3929	.9401	.950462	-6501.
1.100	.3970	.9555	.944779	-7192.
1.200	.4019	.9709	.938974	-7875.
1.300	.4074	.9863	.933052	-8548.
1.400	.4135	1.0016	.927014	-9210.
1.500	.4202	1.0169	.920866	-9861.
1.600	.4273	1.0322	.914611	-10499.
1.700	.4349	1.0474	.908252	-11125.
1.785(sat)	.4417	1.0603	.902768	-11647.

$\frac{m}{mol \cdot kg}^{-1}$	$\sigma(\phi)$	$\sigma(\Delta G^{ex})$	$\sigma(\gamma)$
2.0	0.0020	0.0030	0.0014
1.7	0.0016	0.0026	0.0011
1.0	0.0008	0.0021	0.0008
0.1	0.0005	0.0012	0.0006
0.01	0.0001	0.0003	0.0002

Table 27. Recommended Values for the Mean Activity Coefficient and Osmotic Coefficient of BaBr<sub>2</sub> in H<sub>2</sub>O at 298.15 K

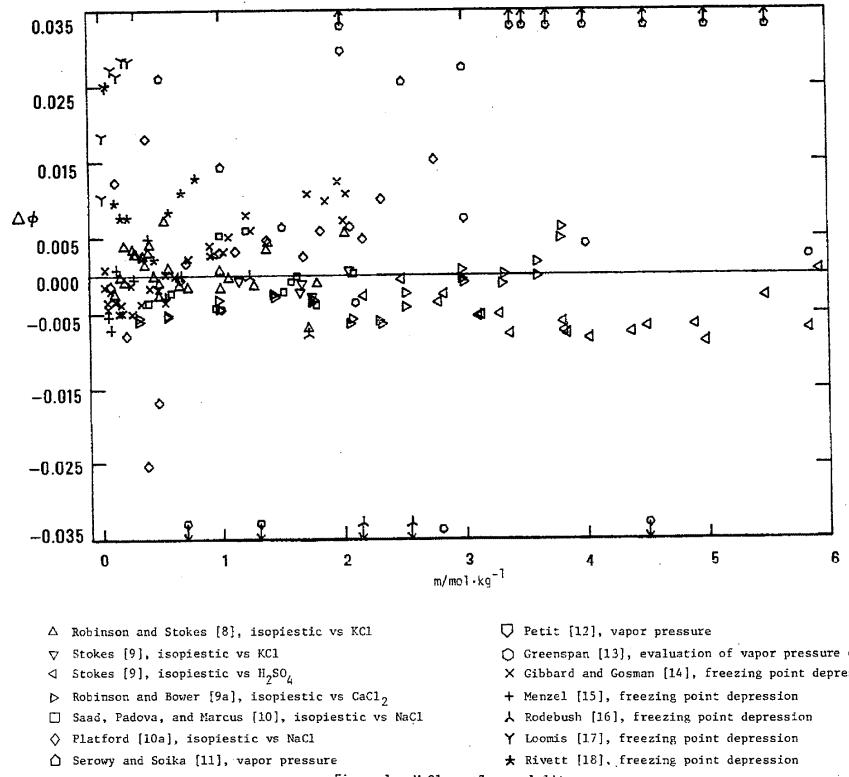
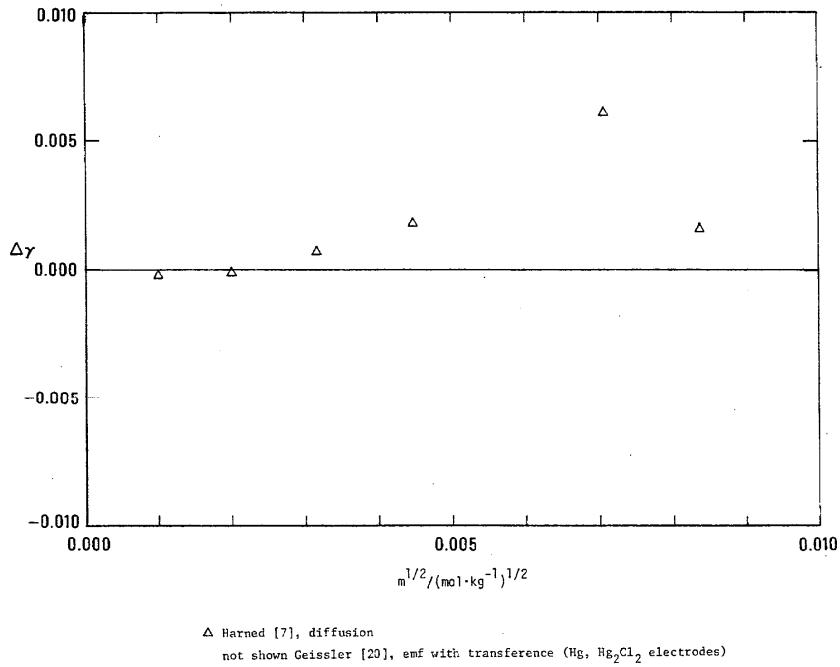
$m/mol \cdot kg^{-1}$	$\gamma$	$\phi$	$a_w$	$\Delta G^{\text{ex}}/J \cdot kg^{-1}$
.001	.8881	.9621	.999948	-1.
.002	.8501	.9490	.999897	-2.
.003	.8235	.9398	.999848	-3.
.004	.8028	.9326	.999798	-5.
.005	.7856	.9266	.999750	-6.
.006	.7708	.9215	.999701	-8.
.007	.7579	.9170	.999653	-10.
.008	.7464	.9131	.999605	-12.
.009	.7360	.9095	.999558	-14.
.010	.7266	.9063	.999510	-17.
.020	.6613	.8846	.999044	-44.
.030	.6218	.8724	.998587	-78.
.040	.5940	.8644	.998133	-115.
.050	.5728	.8590	.997682	-155.
.060	.5559	.8551	.997231	-197.
.070	.5420	.8524	.996781	-242.
.080	.5303	.8504	.996330	-288.
.090	.5203	.8491	.995878	-336.
.100	.5117	.8483	.995426	-385.
.200	.4634	.8536	.990816	-926.
.300	.4444	.8686	.986016	-1516.
.400	.4369	.8869	.981010	-2127.
.500	.4355	.9067	.975795	-2744.
.600	.4379	.9275	.970370	-3361.
.700	.4432	.9490	.964735	-3971.
.800	.4506	.9709	.958890	-4570.
.900	.4598	.9932	.952836	-5156.
1.000	.4705	1.0159	.946573	-5725.
1.100	.4828	1.0390	.940100	-6276.
1.200	.4963	1.0624	.933419	-6808.
1.300	.5113	1.0861	.926530	-7318.
1.400	.5275	1.1101	.919433	-7805.
1.500	.5451	1.1345	.912129	-8269.
1.600	.5641	1.1592	.904620	-8707.
1.700	.5844	1.1842	.896905	-9120.
1.800	.6062	1.2096	.888988	-9506.
1.900	.6295	1.2353	.880869	-9864.
2.000	.6544	1.2613	.872550	-10194.
2.100	.6809	1.2876	.864034	-10495.
2.200	.7092	1.3143	.855323	-10766.
2.300	.7393	1.3414	.846419	-11006.
2.321	.7459	1.3471	.844525	-11052.

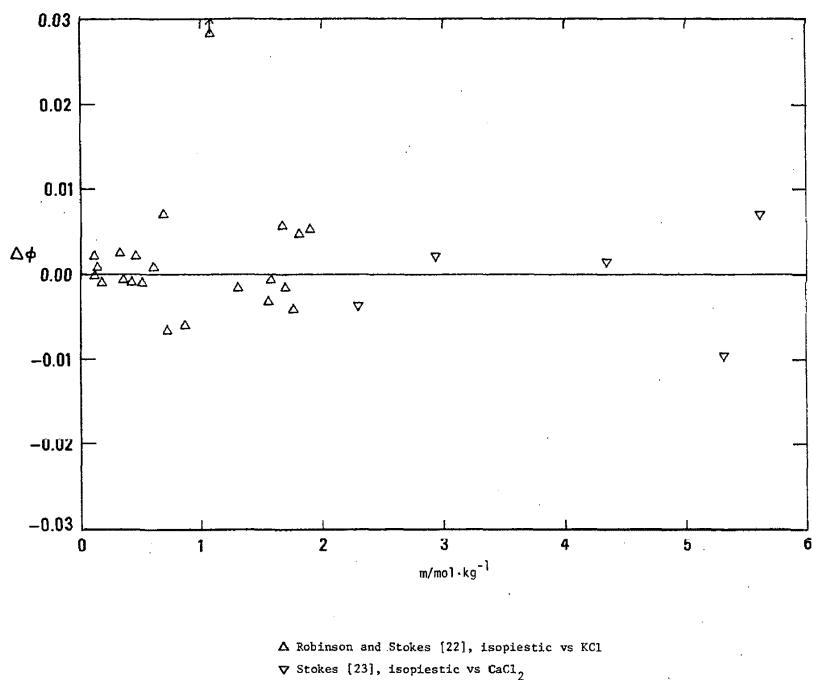
$\frac{m}{mol \cdot kg}^{-1}$	$\sigma(\phi)$	$\sigma(\ln\gamma)$	$\sigma(\gamma)$
2.3	0.0031	0.0050	0.0037
2.0	0.0019	0.0041	0.0027
1.0	0.0014	0.0037	0.0017
0.1	0.0008	0.0024	0.0013
0.01	0.0003	0.0006	0.0004

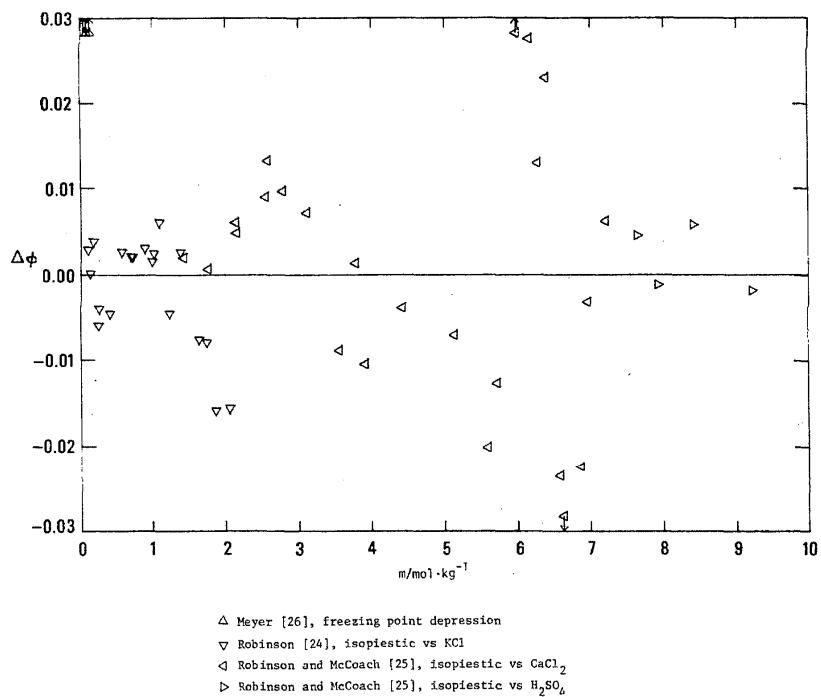
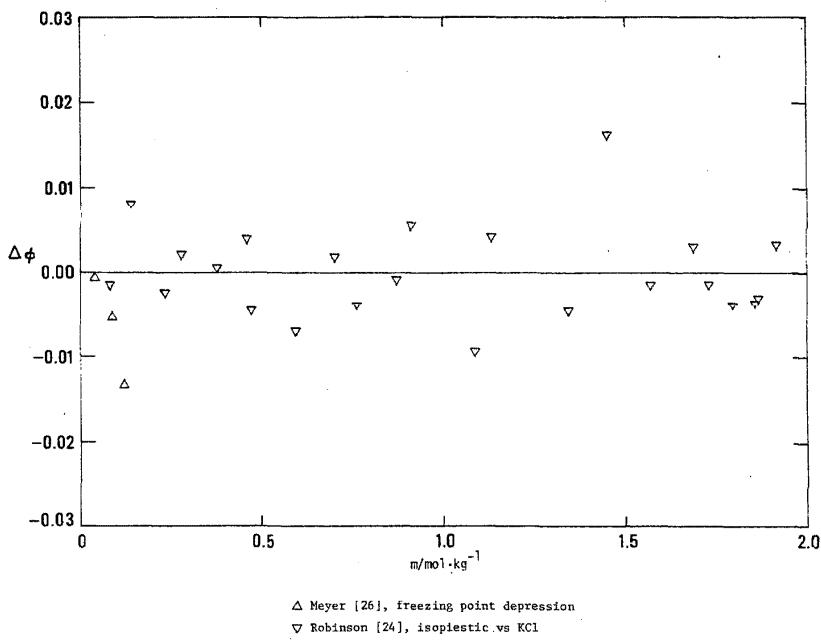
Table 28. Recommended Values for the Mean Activity Coefficient and Osmotic Coefficient of BaI<sub>2</sub> in H<sub>2</sub>O at 298.15 K

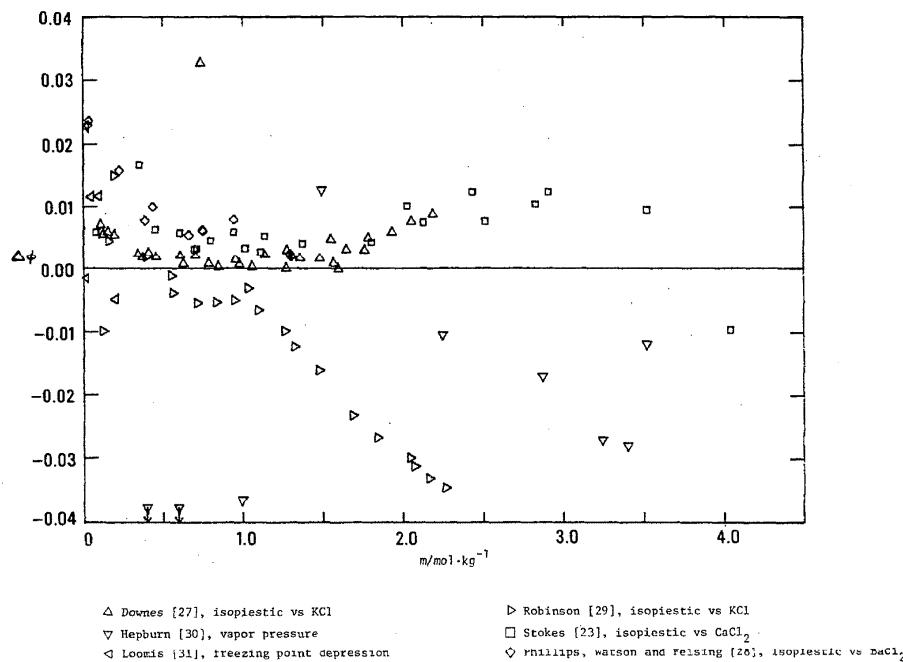
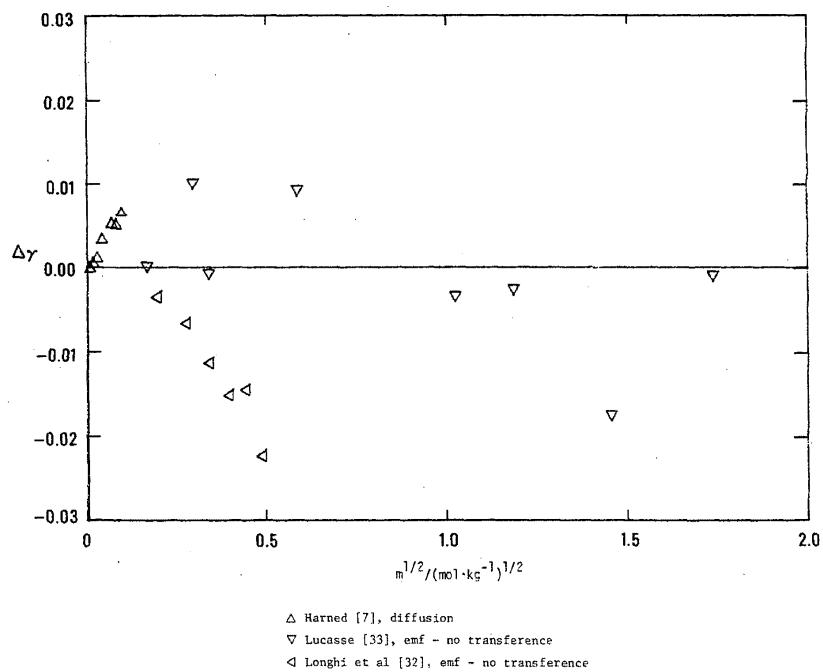
$m/mol \cdot kg^{-1}$	$\gamma$	$\phi$	$a_w$	$\Delta G^{ex}/J \cdot kg^{-1}$
.001	.8898	.9630	.999948	-1.
.002	.8532	.9507	.999897	-2.
.003	.8278	.9422	.999847	-3.
.004	.8081	.9357	.999798	-4.
.005	.7919	.9303	.999749	-6.
.006	.7781	.9258	.999700	-8.
.007	.7660	.9220	.999651	-10.
.008	.7553	.9186	.999603	-12.
.009	.7457	.9155	.999555	-14.
.010	.7370	.9128	.999507	-16.
.020	.6777	.8954	.999033	-42.
.030	.6426	.8866	.998563	-73.
.040	.6185	.8816	.998096	-108.
.050	.6004	.8788	.997628	-145.
.060	.5863	.8773	.997159	-183.
.070	.5750	.8767	.996689	-224.
.080	.5657	.8768	.996216	-266.
.090	.5579	.8774	.995741	-309.
.100	.5513	.8784	.995264	-352.
.200	.5199	.8987	.990333	-822.
.300	.5156	.9263	.985093	-1313.
.400	.5224	.9565	.979534	-1802.
.500	.5358	.9881	.973652	-2276.
.600	.5539	1.0207	.967443	-2728.
.700	.5760	1.0541	.960905	-3154.
.800	.6017	1.0884	.954033	-3548.
.900	.6309	1.1233	.946825	-3908.
1.000	.6636	1.1591	.939279	-4232.
1.100	.7000	1.1955	.931392	-4517.
1.200	.7402	1.2327	.923163	-4762.
1.300	.7844	1.2707	.914590	-4964.
1.400	.8331	1.3094	.905673	-5123.
1.500	.8865	1.3489	.896413	-5235.
1.600	.9452	1.3891	.886810	-5301.
1.700	1.0095	1.4302	.876866	-5319.
1.800	1.0800	1.4720	.866584	-5287.
1.900	1.1575	1.5145	.855967	-5204.
1.998	1.2407	1.5570	.845242	-5072.

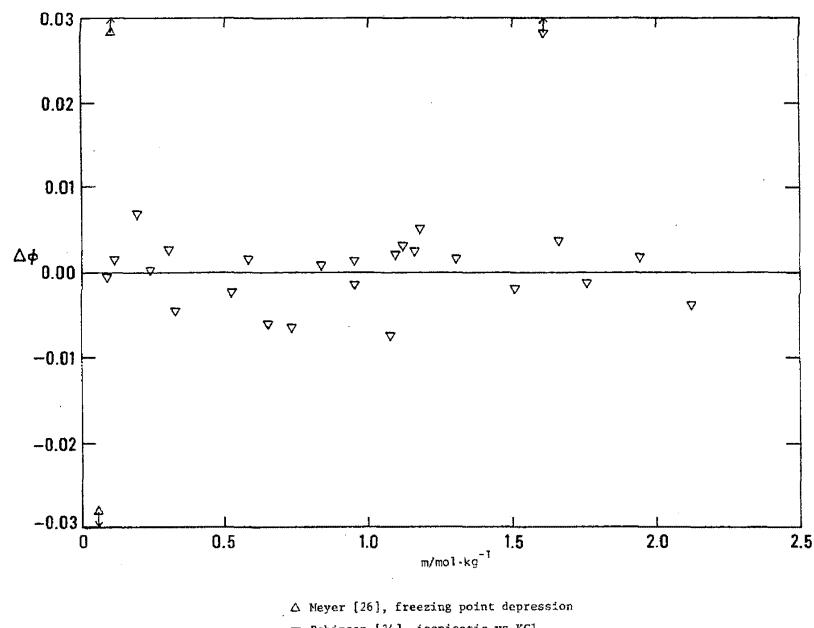
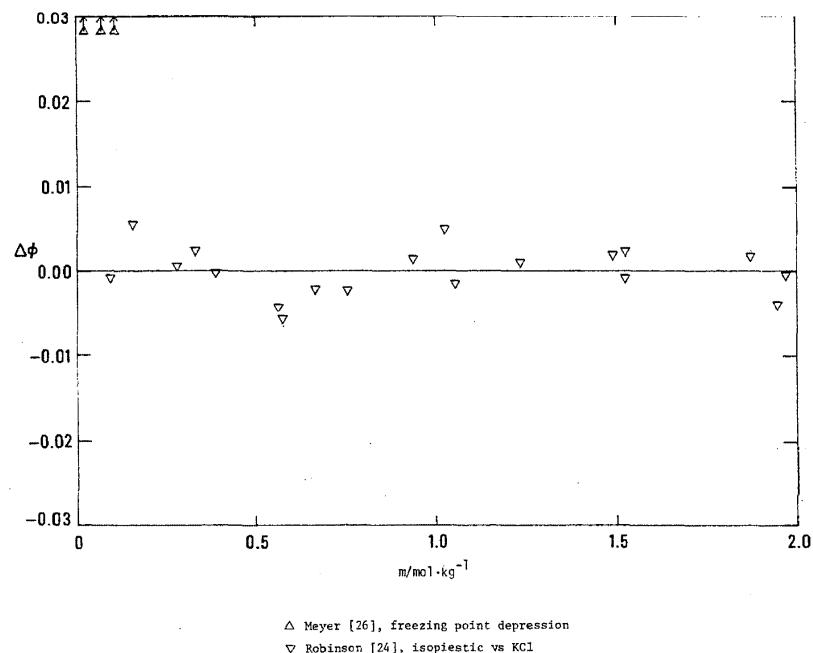
$\frac{m}{mol \cdot kg}^{-1}$	$\sigma(\phi)$	$\sigma(\ln\gamma)$	$\sigma(\gamma)$
2.0	0.0045	0.0141	0.0175
1.0	0.0023	0.0126	0.0084
0.1	0.0034	0.0102	0.0056
0.01	0.0012	0.0026	0.0020

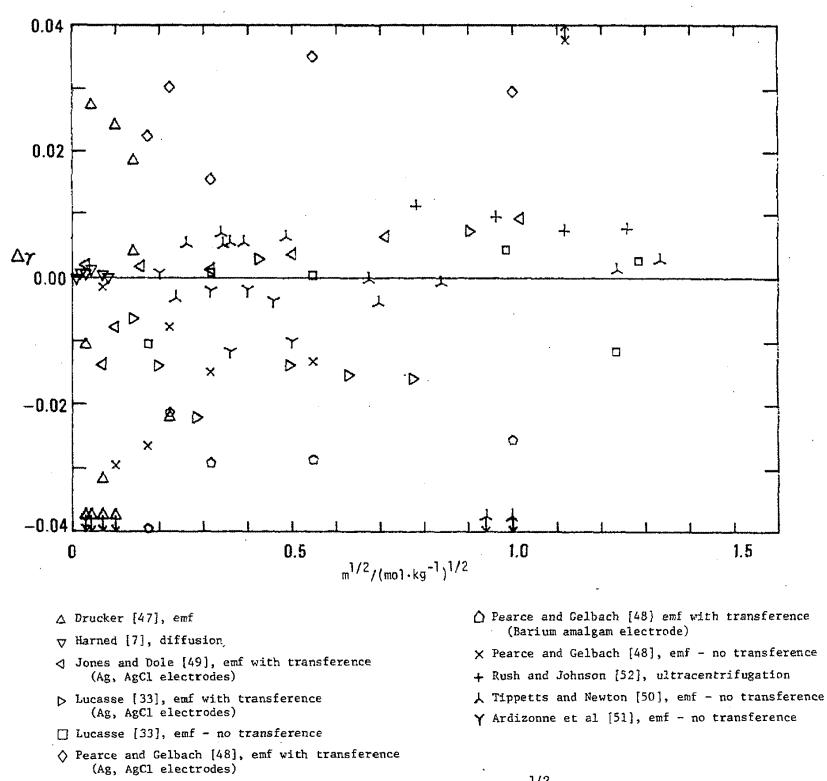
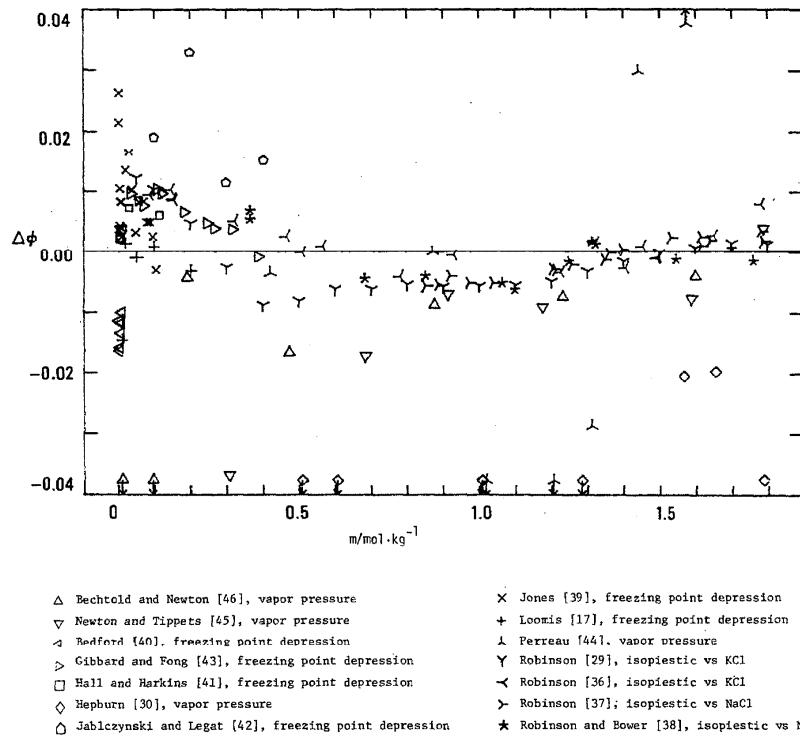
Figure 1.  $MgCl_2$ :  $\Delta\phi$  vs molalityFigure 2.  $MgCl_2$ :  $\Delta\gamma$  vs molality  $^{1/2}$

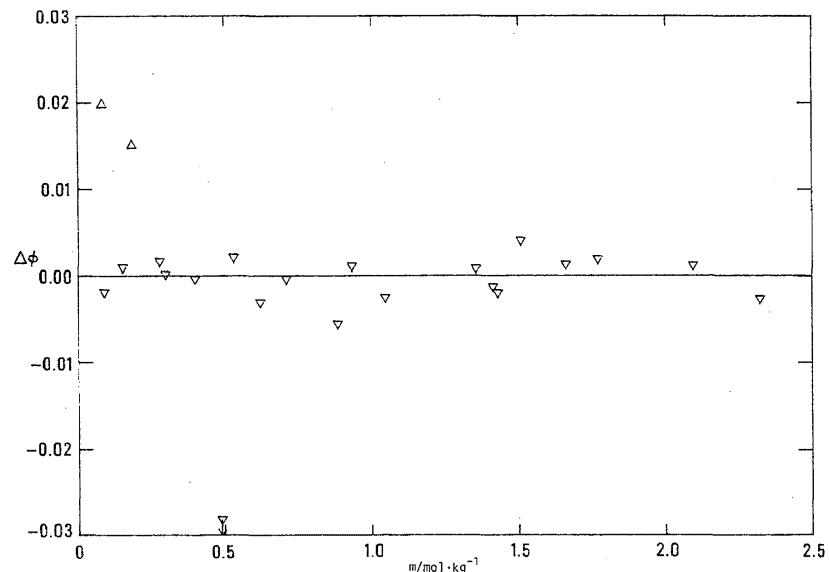
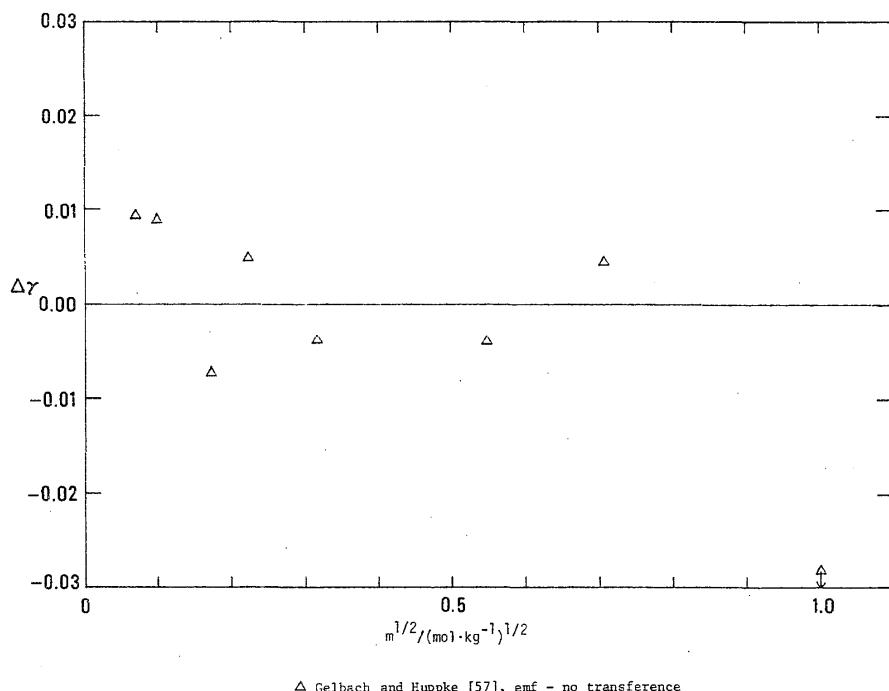


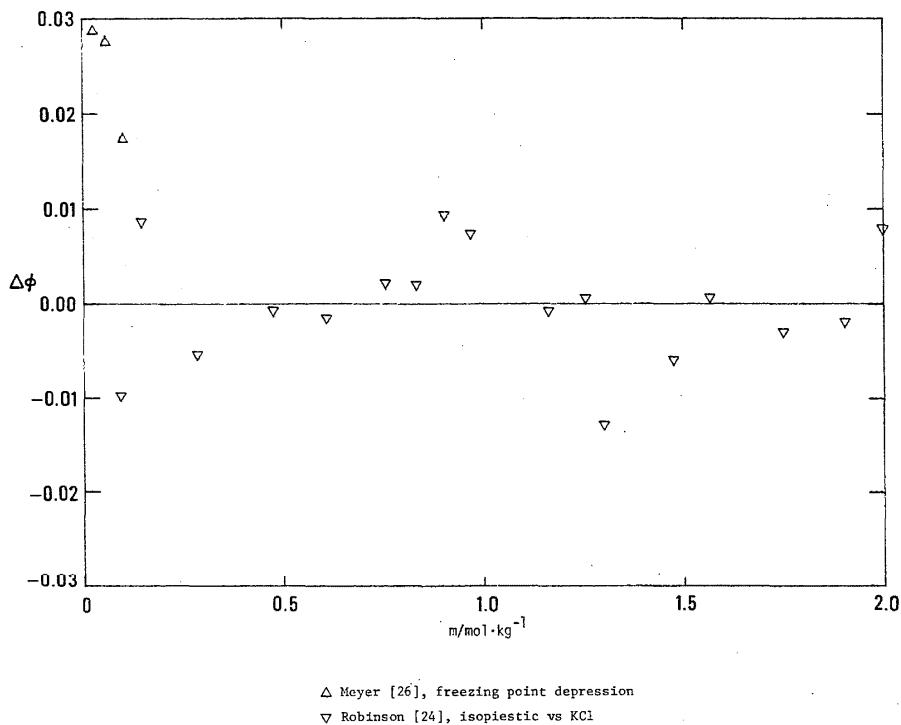
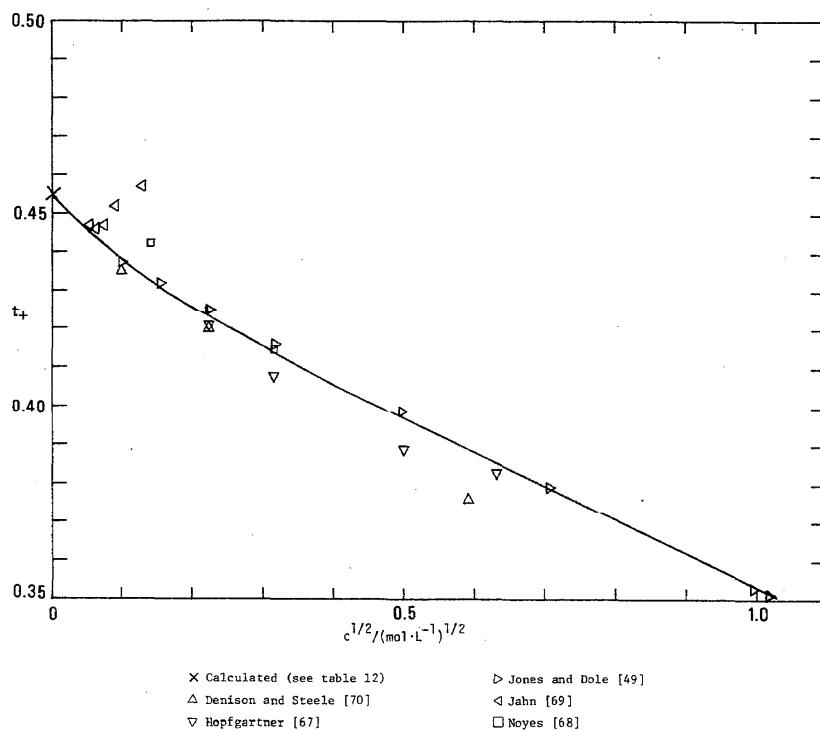
Figure 5.  $\text{CaBr}_2$ :  $\Delta\phi$  vs molalityFigure 6.  $\text{CaI}_2$ :  $\Delta\phi$  vs molality

Figure 7.  $\text{SrCl}_2$ :  $\Delta\psi$  vs molalityFigure 8.  $\text{SrCl}_2$ :  $\Delta\gamma$  vs molality  $^{1/2}$

Figure 9.  $\text{SrBr}_2$ :  $\Delta\phi$  vs molalityFigure 10.  $\text{SrI}_2$ :  $\Delta\phi$  vs molality



Figure 13.  $\text{BaBr}_2$ :  $\Delta\Phi$  vs molalityFigure 14.  $\text{BaBr}_2$ :  $\Delta\gamma$  vs molality<sup>1/2</sup>

Figure 15.  $\text{BaI}_2$ :  $\Delta\phi$  vs molalityFigure 16. Transference number of  $\text{Ba}^{2+}$  in  $\text{BaCl}_2$  as a function of the square root concentration (molarity) $^{1/2}$ .

#### 4. Evaluated Activity and Osmotic Coefficients

The coefficients of eqs (1), (2), and (3) with their standard deviations are given in tables 13 to 15. We have retained ten digits for the coefficients of eqs (1), (2), and (3). We have chosen not to round off these coefficients further because to do so would be a loss of information which might be useful for some applications in which the derivative of the activity coefficient with respect to the molality is of interest. The digits in excess of those required to ensure a precision of 0.001 or better in the calculation of  $\phi$  or  $\ln \gamma$  have been subscripted. The standard deviations for observations of unit weight are given in table 16 for the three equations.

In tables 17 to 28 are values of the activity and osmotic coefficients, the activity of water, and the excess Gibbs energy tabulated at regular intervals up to the highest concentrations at which measurements have been reported. For those cases, where the experimental investigations go to saturation or supersaturation, we have also given the values of these properties at saturation. For  $\text{CaCl}_2$ ,  $\text{CaBr}_2$ ,  $\text{SrCl}_2$ , and  $\text{BaCl}_2$ , we have taken the solubilities from tables of Linke and Seidell [58]; for  $\text{MgCl}_2$  and  $\text{MgBr}_2$ , the solubilities are from Stokes [9].

We have also included at the bottom of tables 17 and 28 values for the standard deviations ( $\sigma$ ) of the calculated values of the osmotic coefficient, the activity coefficient, and the logarithm of the activity coefficient.

We note that, for a given system, there are systematic differences in the values of the activity and osmotic coefficients calculated from eqs (1), (2), and (3). Typically these differences are less than one percent in  $\gamma$  and less than 0.010 in  $\phi$ . However, these differences become larger at the highest molalities for which data exists and these differences range as high as ten percent in  $\gamma$  and 0.015 in  $\phi$ .

For several systems ( $\text{CaI}_2$ ,  $\text{SrBr}_2$ ,  $\text{SrI}_2$ ,  $\text{BaBr}_2$ , and  $\text{BaI}_2$ ) the isopiestic data stop at a concentration far short of saturation; isopiestic investigations that fill this gap would be useful. Also of value would be reliable freezing point data and calorimetrically determined  $\phi_L$  and  $\phi_C$  data that could be used to obtain activity and osmotic coefficient data in the dilute range of concentrations.

##### 4.1. Comparison With Other Compilations

The appendices in the book by Robinson and Stokes [58a] contain tables of the mean activity and osmotic coefficients in aqueous solution for the alkaline earth metal halides. Their tables are based entirely on their own isopiestic measurements (see ref. [23] and the papers cited therein). The tables given by Harned and Owen [65] are also based on the isopiestic measurements by Robinson and Stokes [23], although they do give some comparisons with activity coefficients for aqueous barium chloride and strontium chloride that were ob-

tained from emf and direct vapor pressure measurements. Since both these treatises [58a,65] were prepared in the precomputer era, there are no coefficients given in them for correlating equations and there is little statistical analysis.

The more recent paper by Pitzer and Mayorga [58b] gives a correlating equation different than the three selected in this paper. The coefficients of their correlating equations are based on a fit to the osmotic coefficients tabulated by Robinson and Stokes [58a]. A preliminary progress report by Wu and Hamer [58c] give both tables of activity and osmotic coefficients for the systems contained herein and values of the coefficients for an equation essentially identical to eq (1a) in this paper; i.e., it differs in that  $\log_{10} \gamma$  is calculated rather than  $\ln \gamma$ . Wu and Hamer [58c] also give an extensive bibliography of the sources of experimental data for these systems and their tabulated activity and osmotic coefficients are based entirely on the available isopiestic data and on electrochemical cells without transference [58d].

A comparison of our tables of recommended values with the tables of Robinson and Stokes [58a] indicates that the activity and osmotic coefficients are in reasonable agreement with each other, the largest apparent difference in the osmotic coefficient being equal to 0.041 for aqueous barium iodide, and the largest apparent differences in the activity coefficient being equal to 3.5% for aqueous magnesium chloride. However, there are larger than expected difference between our tabulated values and those given by Wu and Hamer [58c] for several of the systems, namely, aqueous  $\text{MgCl}_2$ ,  $\text{MgI}_2$ ,  $\text{SrI}_2$ ,  $\text{BaBr}_2$ , and  $\text{BaI}_2$ . These differences are probably attributable to the fact that we have considered a larger set of experimental data in the performance of our evaluations.

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<b>Glossary of Symbols</b>	
$a_w$	activity of water
$\Delta b$	$(\partial \Delta \bar{C}_p / \partial T)_p$
$c_B$ or $c$	concentration of solute substance B
$m_B$ or $m$	molality of solute substance B
$t_B$	transport or transference number of ion B
$x_B$ or $x$	mole fraction of substance B
$z_B$	charge number of an ion B
$A$	constant in Debye-Hückel limiting law
$A_1$	$ z_+ z_-  A$
$A_2$	$\frac{\left( \sum_i \nu_i z_i^3 \right)^2}{\nu \sum_i (\nu_i z_i^2)} A^2$
$A_i$	coefficients in a specified equation
$B, C, D, E, \dots$	coefficients in eqs (1)
$B_i$	coefficients in a specified equation
$B_T$	the second virial coefficient for water vapor
$\Delta C_{fus}^\circ$	the heat capacity change accompanying the fusion of the pure solvent at the freezing temperature of the pure solvent
$\Delta \bar{C}_p$	the difference between the partial molal heat capacity of the solvent in a solution and the molal heat capacity of the solid solvent at the freezing temperature of the solution
$\Delta G^{\text{ex}}$	the excess Gibbs energy of a solution containing one kilogram of solvent
$\Delta H_{fus}^\circ$	the enthalpy of fusion of the pure solvent at the freezing temperature of the pure solvent
$I_m$ or $I$	ionic strength: $(I_m = \frac{1}{2} \sum_i m_i z_i^2)$
	$\bar{J}_1$ relative partial molal heat capacity of the solvent in a solution
	$\bar{L}_1$ relative partial molal enthalpy of the solvent in a solution
	$M_1$ molecular weight of solvent
	$P$ vapor pressure of a solution
	$P^\circ$ vapor pressure of pure solvent
	$R$ molar gas constant
	$T$ thermodynamic or absolute temperature
	$T_{fus}$ absolute temperature of fusion of pure solvent
	$\alpha_i$ coefficients in a specified equation
	$\beta_i$ coefficients in a specified equation
	$\gamma_\pm$ or $\gamma$ activity coefficient, molality basis
	$\Theta$ freezing point depression of a given solution
	$\nu_i$ number of ions of species $i$ formed from one molecule of solute assuming complete dissociation
	$\nu$ total number of ions formed from one molecule of solute assuming complete dissociation: $[\nu = \sum_i \nu_i]$
	$\rho_B$ or $\rho$ mass concentration or density of a given system
	$\rho^\circ$ mass concentration or density of pure solvent
	$\phi$ osmotic coefficient
	$\Phi_C$ apparent molal heat capacity
	$\Phi_L$ relative apparent molal enthalpy
	$\Lambda$ molar conductivity of electrolyte solution
	$\Lambda^\circ$ limiting value of the molar conductivity of a solution as the solute concentration approach zero.