The Activity and Osmotic Coefficients of Aqueous Calcium Chloride at 298.15 K

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A critical evaluation of the mean activity, $\gamma_\pm$, and osmotic coefficients, ϕ, of aqueous calcium chloride at 298.15 K is presented for the concentration range of 0 to 10 mol·kg^{-1}. Osmotic coefficients were calculated from direct vapor pressure measurements, from isopiestic measurements or from freezing point depression measurements. Activity coefficients were calculated from electromotive force measurements of galvanic cells, both without liquid-junction and with transference, and from diffusion data. A non-linear least-squares program was used to fit data from all sources using both ϕ and $\ln \gamma_\pm$ as a function of molality. An eight-parameter extended Debye-Huckel equation describes the osmotic coefficient, the mean activity coefficient, and the excess free energy as a function of molality. The scientific literature has been covered through July, 1976.

Keywords: Activity coefficient; calcium chloride; critical evaluation; electrolyte; excess free energy; osmotic coefficient; solutions; thermodynamic properties.

Contents

1. Introduction

The purpose of this paper is twofold. First, a table and equations giving recommended values of mean activity and osmotic coefficients for calcium chloride in aqueous solution at 25°C will be presented. The table and equations result from an evaluation and correlation of the experimental data published in the past seventy years. Literature through July, 1976 has been considered. Second, the procedure used in the critical evaluation and correlation of data on activity and osmotic coefficients of electrolyte solutions will be detailed. This will serve as a guide for future data evaluations for the remaining polyvalent salts.

Thermodynamic expressions will be described as well as data treatment methods for each experimental technique. Fine details of the critical evaluation procedure will be explained and the results of this critical evaluation will be presented for the activity and osmotic coefficients of aqueous calcium chloride solutions at 25°C, over a range of molalities from 0.0001 to 10.0 mol·kg^{-1}.

The basis of the present evaluation is the work begun by Wu and Hamer [1][1] a number of years ago. Preliminary values of osmotic and mean activity coefficients were published by them in 1968. We have adopted their correlating equations and have used a modified version of their non-linear least squares method to obtain parameters that best fit the experimental data.

Critical evaluations of activity and osmotic coefficient data were begun in the 1930–1940 period by Harned and Owen and by Robinson and Stokes. Their results were included in books published by Harned and Owen in 1943 and by Robinson and Stokes in 1955. The most recent revised editions of these books [2, 3] were published in 1958 and 1965 respectively. Wu and Hamer [1] evaluated activity and osmotic coefficient data for a series of electrolytes in 1968 but their work on polyvalent electrolytes was not completed. Their work on the 1:1 electrolytes [4] was published in 1972. The

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[1] Figures in brackets indicate literature references at the end of this paper.

evaluation of polyvalent electrolyte data is continuing in the Electrolyte Data Center, at the National Bureau of Standards.

2. Thermodynamic Relations

The first and second laws of thermodynamics can be represented by the equation:

$$dU = TdS - PdV + \sum_i \mu_i dn_i + \frac{\partial U}{\partial e}\, de, \tag{1}$$

where U is the energy of a system, S is the entropy, T the thermodynamic temperature, P the pressure, V the volume, μ_i is the chemical potential of the ith component of the system $\mu_i = (\partial U/\partial n_i)_{S,v,n_j(j\neq i)}$, and n_i the number of moles of the ith component. The last term, $(\partial U/\partial e)\,de$, is the electrical work in terms of the charge, e. The Gibbs energy, G, is defined by

$$G = U - TS + PV. \tag{2}$$

Its differential can then be written as

$$dG = -SdT + VdP + \sum_i \mu_i dn_i + (\partial G/\partial e)de, \tag{3}$$

and

$$\mu_i = (\partial G/\partial n_i)_{P,T,n_j(j\neq i),e}. \tag{4}$$

The activity function used in solution thermodynamics is defined for a component of the solution in terms of the chemical potential of that component by

$$\mu_i - \mu_i^\circ = RT\ln a_i, \tag{5}$$

where a_i is the activity of the ith component, μ_i° is the chemical potential of the ith component in an arbitrary standard state.

The activity coefficient of a component of a solution is defined as the ratio of the activity of the component to the relative amount of the component in the solution. The three commonly used measures of the solution composition which will also be used here are: molality, m, in moles per kilogram of solvent; concentration (molarity), c, moles per liter of solution; mole fraction, x, moles per total moles of solution. The corresponding activity coefficients are then defined by

$$a_i = \gamma_i m_i \text{ or } y_i c_i \text{ or } f_i x_i. \tag{6}$$

The numerical values of a_i and μ_i° will depend on the choice of standard state and will differ with the different units of composition.

Equation (5) is a general definition of the activity function and applies to the solvent as well as the solutes in a solution. We will denote the properties of the solvent by subscript 1. Its activity is thus a_1. The subscript 2 will denote a solute. The solute activity is thus a_2.

The standard states of unit activity generally used in electrolyte solutions are chosen as follows. For the solvent the standard state is the pure solvent with $a_1 = 1$ and $a_1/x_1 = 1$ when $x_1 = 1$. The standard state of a solute will depend on the composition units used. Two alternatives, mole fraction and molality are used. Unless otherwise noted we will use the standard state defined on the molality scale. For the molality scale the standard state is chosen so that $a_2/m = 1$ as $m \to 0$. A hypothetical ideal solution is defined as one in which $a_2/m = 1$ at all concentrations. The standard state is chosen as this hypothetical ideal solution at unit activity. Similarly on the mole fraction scale $a_2/x_2 = 1$ as $x_2 \to 0$ and the standard state is the hypothetical ideal solution in which $a_2/x_2 = 1$ at unit activity.

For an electrolyte solute that dissociates completely into ν_+ cations and ν_- anions the activity can be expressed as

$$a_2 = (a_+)^{\nu_+}(a_-)^{\nu_-} = a^{\nu}_{\pm}, \tag{7}$$

where a_+ and a_- are "single ion" activities and $\nu = (\nu_+ + \nu_-)$. So $a_\pm$ is called the mean activity and is related to the chemical potential of the electrolyte solute by

$$\mu_2 = \mu_2^\circ + \nu RT\ln a_\pm. \tag{8}$$

In a similar way is defined a mean ionic molality

$$m_\pm = m(\nu_+^{\nu_+}\nu_-^{\nu_-})^{1/\nu}, \tag{9}$$

and a mean activity coefficient

$$\gamma_\pm = (\gamma_+^{\nu_+}\gamma_-^{\nu_-})^{1/\nu}, \tag{10}$$

so that

$$a_\pm = \gamma_\pm m_\pm. \tag{11}$$

For the remainder of this paper the term γ will denote the mean activity coefficient, $\gamma_\pm$.

The activity coefficients for the different units of composition are related by

$$y_\pm = d_o(m/c)\gamma, \tag{12}$$

$$f_\pm = \gamma(1 + 0.001\,\nu m M_1), \tag{13}$$

$$f_\pm = y_\pm\,(d - 0.001\,M_2 c + 0.001\,M_1 c\nu)/d_o. \tag{14}$$

where d = density of solution, d_o = density of solvent, M_2 = molar mass of the solute and M_1 = molar mass of the solvent. The formula masses used in this evaluation were $M_2 = 110.986\ \mathrm{g\cdot mol^{-1}}$ $CaCl_2$, and $M_1 = 18.0154\ \mathrm{g\cdot mol^{-1}}$ H_2O.

A relation between the solute and solvent activities is given by the Gibbs-Duhem equation, which for a binary solution can be written in terms of activities by

$$d\ln a_2 = (-x_1/x_2)d\ln a_1 \tag{15}$$

Because the activity coefficient of the solvent in dilute solutions is a very insensitive measure of solution non-ideality, Bjerrum [5] introduced a function called the practical osmotic coefficient, ϕ, defined by

$$\mu_1-\mu_1^\circ=\frac{-\phi RTM_1\sum_i m_i}{1000}RT\ln a_1, \qquad (16)$$

where m_i is the molality of the ith ion. For a single electrolyte $\sum_i m_i=\nu m$

and
$$\mu_1-\mu_1^\circ=-\nu\phi RTmM_1/1000=RT\ln a_1, \qquad (17)$$

or
$$\phi=-(1000/\nu mM_1)\ln a_1. \qquad (18)$$

The osmotic coefficient, ϕ, and the solute mean activity coefficient, γ, are related through eqs (18), (15), (11), and (7), to give

$$d\ln\gamma=(\phi-1)dm/m+d\phi, \qquad (19)$$

which can be integrated to give

$$\ln\gamma=(\phi-1)+\int_0^m(\phi-1)dm/m, \qquad (20)$$

or alternatively

$$\phi=1+\frac{1}{m}\int_{m=0}^{m} m\,d\ln\gamma. \qquad (21)$$

The Gibbs energy of a binary solution, at constant temperature and pressure, containing 1 kg of solvent and m moles of solute can be written as

$$G=n_1\mu_1+n_2\mu_2, \qquad (22)$$

and

$$G=\frac{1000}{M_1}\mu_1+m\mu_2. \qquad (23)$$

From the definitions of activity, a, osmotic coefficient, ϕ, and mean activity coefficient, $\gamma_\pm$, for an electrolyte solution we obtain

$$G=\frac{1000}{M_1}(\mu_1^\circ+RT\ln a_1)+m\,(\mu_2^\circ+RT\ln a_2), \qquad (24)$$

and

$$G=\frac{1000}{M_1}\left[\mu_1^\circ-\frac{\nu m\phi RTM_1}{1000}\right]+m\left[\mu_2^\circ+\nu RT\ln(m_\pm\,\nu_\pm)\right]. \qquad (25)$$

For an ideal solution defined by $\gamma_\pm=1$, eq (21) gives $\phi=1$, so that

$$G_{\text{ideal}}=\frac{1000}{M_1}\left(\mu_1^\circ-\frac{\nu mRTM_1}{1000}\right)+m(\mu_2^\circ+\nu RT\ln m_\pm). \qquad (26)$$

Defining the non-ideality of a solution in terms of the excess Gibbs energy,

$$\Delta G^{ex}=G-G_{\text{ideal}}, \qquad (27)$$

and subtracting eq (26) from eq (25) we obtain the relation between the excess Gibbs energy and the osmotic and mean activity coefficients

$$\Delta G^{ex}=\nu mRT\,(1-\phi+\ln\gamma). \qquad (28)$$

2.1. Expressions for Activity and Osmotic Coefficients

In dilute solutions of electrolytes the main effect causing deviations from ideality is that of electrostatic attraction between ions of opposite charge. Debye and Huckel [6], assuming that ions are point charges, derived their limiting law equation for a salt dissociating into two kinds of ions

$$\ln y_\pm=-\,|z_+z_-|\,A_cI_c^{1/2}, \qquad (29)$$

where z_+ and z_- are the charges of the cation and anion, respectively. I_c is the ional concentration equal to $\frac{1}{2}\sum_i c_iz_i^2$; A_c, a constant at given temperature and solvent properties, is given by

$$A_c=(2\pi N)^{1/2}\frac{e^3}{(4\pi\varepsilon_\circ)^{3/2}k^{3/2}}\left(\frac{1}{T^{3/2}\varepsilon^{3/2}}\right), \qquad (30)$$

where

N = Avogadro constant = 6.022045×10^{26} kmol^{-1}

e = elementary charge = 1.6021892×10^{-19} C

$\varepsilon_\circ$ = permittivity of free space = $8.854187818\times10^{-12}$ C^2 J^{-1}m^{-1}

k = Boltzmann constant = 1.380662×10^{-23} J·K^{-1}

T = temperature = 298.15 K at 25 °C

ε = dielectric constant of the solvent = 78.30 for water at 25 °C.

The values given above for the general physical constants are from Cohen and Taylor [7] and the dielectric constant from Malmberg and Maryott [8].

The subscript c denotes that compositions are measured on the concentration basis. The unit of concentration is kmol·m^{-3} which is numerically equal to mol·l^{-1}.

The constant A_m on the molality scale is given by

$$A_m=A_cd_o^{1/2}, \qquad (31)$$

where d_o is the density of the solvent.

For aqueous solutions at 25 °C:

$$A_c=1.1780\ \text{kmol}^{-1/2}m^{3/2}, \qquad (32)$$

$$A_m=1.17625\ \text{kg}^{1/2}\text{mol}^{-1/2}. \qquad (33)$$

When the ions are considered as hard spheres of diameter s, the Debye-Huckel equation becomes

$$\ln y_\pm=\frac{-|z_+z_-|A_cI_c^{1/2}}{1+B_csI_c^{1/2}}, \qquad (34)$$

where B_c is given by

$$B_c=(8\pi N)^{1/2}\frac{e}{(4\pi\varepsilon xT\varepsilon_\circ)^{1/2}}. \qquad (35)$$

In aqueous solutions at 25 °C

$$B_c = 0.32914 \times 10^{10} (\mathrm{m}^3/\mathrm{kmol})^{1/2} \mathrm{m}^{-1}. \tag{36}$$

On the molality scale

$$B_m = 0.32866 \times 10^{10} (\mathrm{kg/mol})^{1/2} \mathrm{m}^{-1}. \tag{37}$$

The Debye-Huckel limiting law, eq (29), was derived to apply only at very low concentrations. The limiting form of this theory can be derived in several ways which should also give correct results at moderate concentrations [9, 10, 11, 12, 13]. The mathematics involved in proceeding beyond the limiting law stage are so formidable that the theories have been of very limited usefulness in the experimental range of concentrations.

Friedman [13] has used the cluster theory of Mayer [12] to derive an apparently rigorous theory which gives the thermodynamic properties of electrolyte solutions as the sum of convergent series. The first term in these series is identical to and thus confirms the Debye-Huckel limiting law. The second term is a $I \ln I$ term whose coefficient is, like the coefficient in the Debye-Huckel limiting law equation, a function of the charge type of the salt and the properties of the solvent. Higher terms involve direct potentials corresponding to the forces between sets of ions and become mathematically very difficult. We do get from this theory, as well as from others referred to above, a higher order limiting law which can be written as

$$\ln \gamma = - |z_+ z_-| A_m I^{1/2} - \frac{(\sum_i \nu_i z_i^3)^2}{3\nu \sum_i (\nu_i z_i^2)} A_m^2 \, I \ln I. \tag{38}$$

For symmetrical electrolytes the coefficient of the $I \ln I$ term is zero.

One report [14] has been published that claims experimental verification of the validity of the $I \ln I$ term, for $LaCl_3$ in the range 10^{-4} to 10^{-3} mol·kg^{-1}.

A comparison of limiting law equations with experimental data at low concentrations is given in figure 1. Following Friedman (13), a plot of (log γ-DHLL)/I is given in figure 2; the abbreviation, DHLL, represents the Debye-Huckel limiting law. This plot shows little evidence of the experimental data for calcium chloride approaching the theoretical slope in the concentration range within which measurements are available.

Equations selected for correlating the data should apply over the entire range of measurements. Not only should they reproduce the data well, but they should take into account the very dilute region because they are used to evaluate the integral in equations (20) and (21). Thus the Debye-Huckel limiting law was included as the first term. What is appropriate at slightly higher concentrations is difficult to determine. We have made a choice of the empirical form of an equation used previously by Hamer and Wu [4] and others, and have not included the $I \ln I$ term indicated by theory. This is because inclusion of the $I \ln I$ term does not appear to make a significant difference in the results but, at higher concentration it makes the fitting much more difficult, requiring more terms with larger coefficients in the polynomial extension, than with the form of the equation selected.

Several other correlating equations were considered. Two of these are given in the appendix, and are compared with our equations (39,40).

In this paper we have followed Hamer and Wu [4] and others and have used the equation

$$\ln \gamma = \frac{- |z_+ z_-| A_m I_m^{1/2}}{1 + B I_m^{1/2}} + Cm + Dm^2 + Em^3 + \ldots \tag{39}$$

to correlate the experimental data. The ionic strength I_m is given by $I_m = \frac{1}{2} \sum_i m_i z_i^2$, and B is used to denote B_m's. The constants B, C, D, E, etc. are empirical.

Through the use of eqs (21), (28), and (39) the osmotic coefficient and excess Gibbs energy can be expressed in terms of the same parameters by

$$\phi = 1 + \left\{ \frac{|z_+ z_-| A_m}{B^3 I} [-(1 + B I^{1/2}) + 2 \ln (1 + B I^{1/2}) + 1/(1 + B I^{1/2}] + \tfrac{1}{2} Cm + \tfrac{2}{3} Dm^2 + \tfrac{3}{4} Em^3 + \ldots \right\}, \tag{40}$$

and

$$\Delta G^{ex} = \nu m R T \left\{ \frac{|z_+ z_-| A_m}{B^3 I} [(2 - B I^{1/2}) B I^{1/2} - 2 \ln (1 + B I^{1/2})] + \tfrac{1}{2} Cm + \tfrac{1}{3} Dm^2 + \tfrac{1}{4} Em^3 + \ldots \right\}, \tag{41}$$

where I is used to represent I_m.

Values for the parameters are determined by a least squares fit of experimental data using eq (39) for experiments such as galvanic cell measurements that measure solute activity and thus γ values, and eq (40) for experiments such as vapor pressure measurements that measure solvent activity and thus ϕ values. All the original data are used in a single fitting program to determine the best values for the parameters.

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

Most determinations of activity and osmotic coefficients of an electrolyte solution are based on these experimental techniques:

(1) electromotive force (emfs) of galvanic cells without liquid junction
(2) emfs of galvanic cells with transference
(3) diffusion
(4) isopiestic or vapor pressure equilibration
(5) vapor pressure lowering
(6) freezing-point depression
(7) boiling-point elevation

The first three measure the activity of the solute and the last four measure the activity of the solvent.

In the analysis of data for $CaCl_2$ in aqueous solution at 25 °C we have considered data determined by methods 1 through 6. Due to the apparent lack of data, the boiling point method has not been considered.

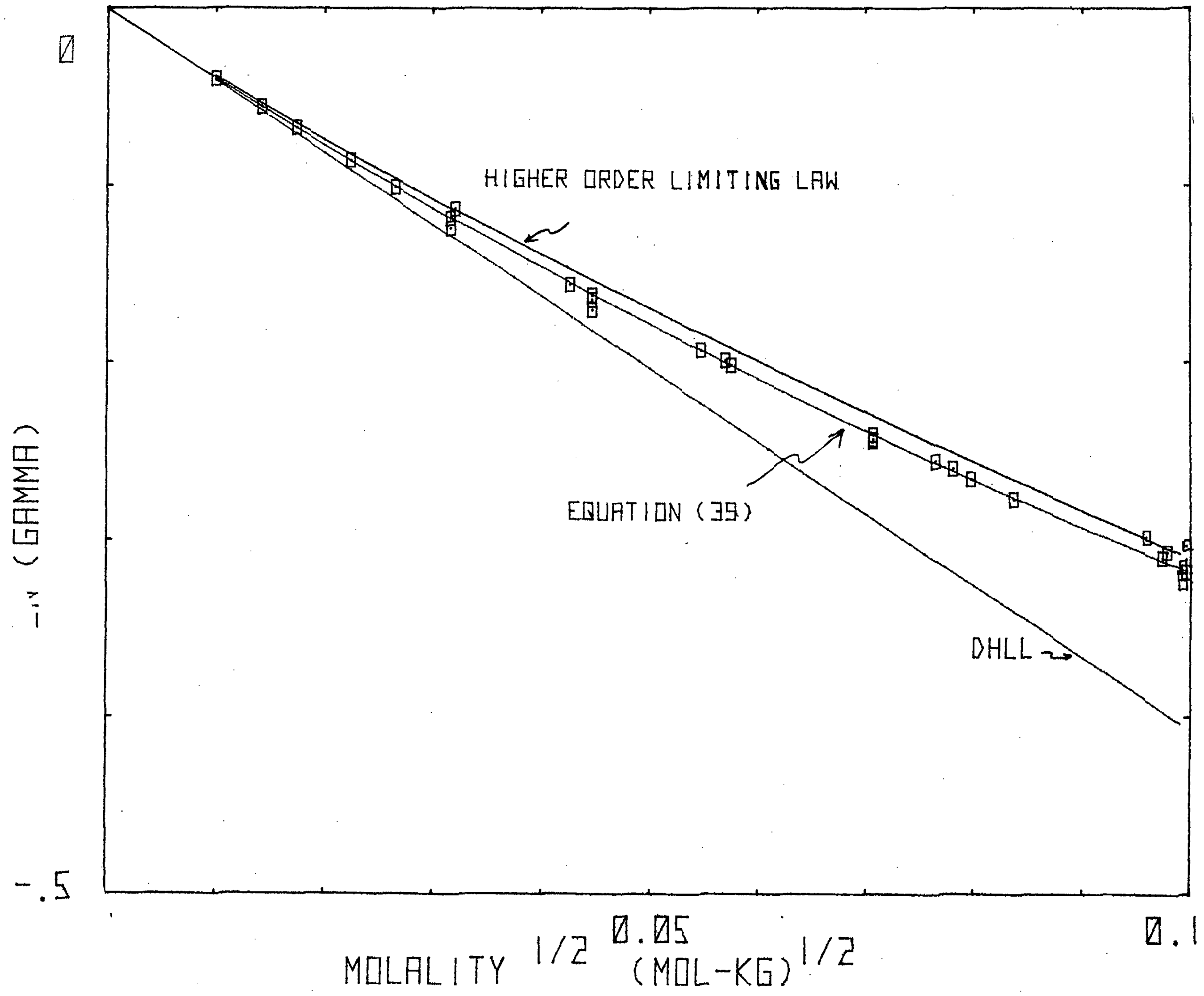

FIGURE 1. Comparison of limiting laws with experimental activity coefficients.

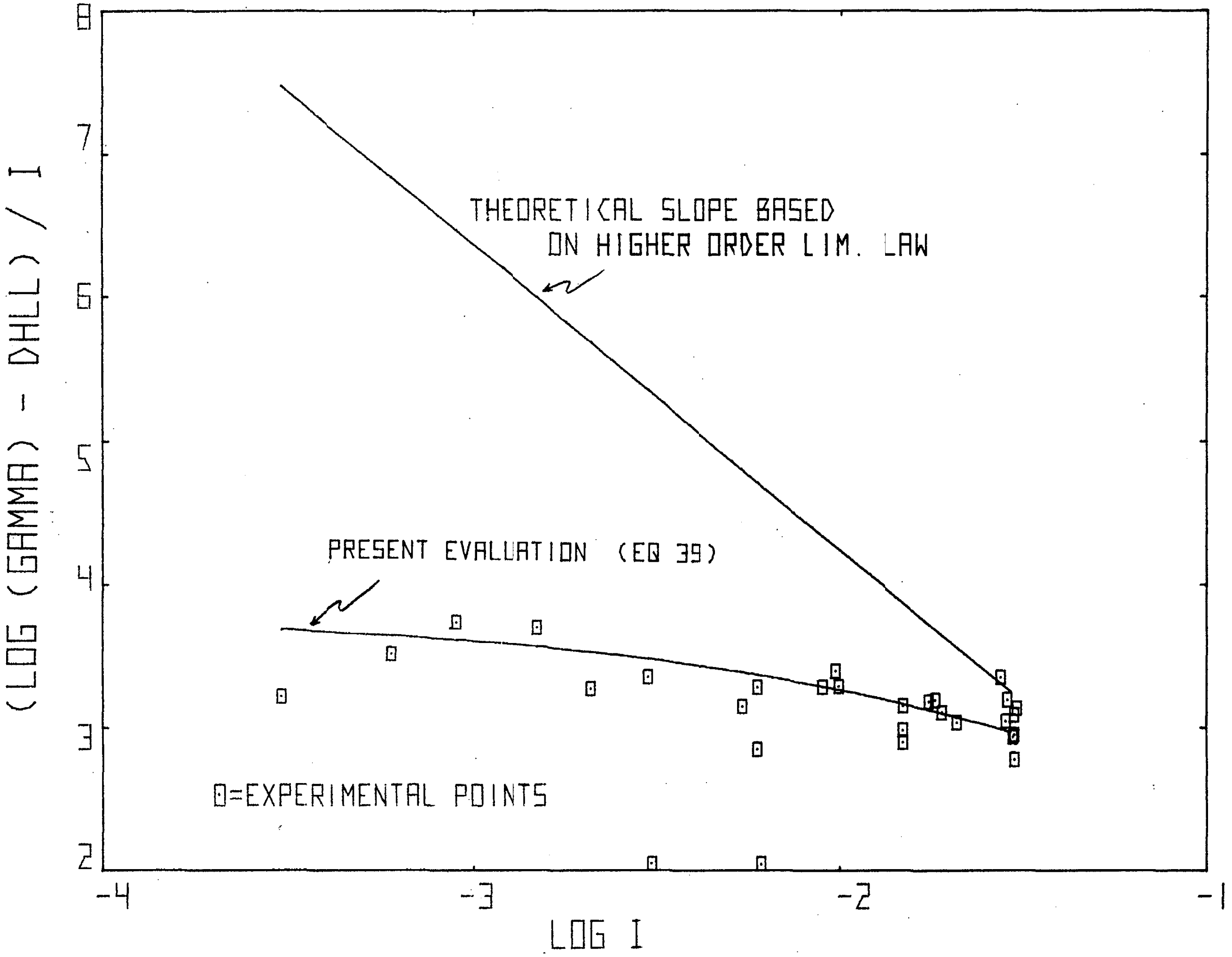

FIGURE 2. Comparison of theoretical slopes with experimental activity coefficients.

4. Evaluation Procedure

A discussion of the evaluation procedure used with $CaCl_2$ solutions will be given. Although the procedures are quite general the details will pertain to $CaCl_2$ solutions in water at 25 °C.

4.1. Preliminary Procedure

First an overview of all available data was necessary before a critical evaluation could be accomplished. All available reprints of original articles were assembled through a combination of the inhouse files of the Chemical Thermodynamics Data Center (up to 1976), the files of Wu and Hamer (up to 1967) and a computer search of Chemical Abstracts and National Technical Information Services through July, 1976.

The data selected for consideration in this correlation are given in tables 1–24. It should be noted that, in general, experimentally observed data are used as a starting point rather than smoothed or recalculated data. Thus for emf data the observed compositions and cell voltages are the primary data and for isopiestic vapor pressure measurements the observed isopiestic molalities of $CaCl_2$ and the reference salt are the primary data.

All the data were made consistent with the ^{12}C scale of atomic weights, and where necessary were corrected to the most recent recommended values of the physical constants [7].

4.2. Osmotic Coefficients

Osmotic coefficients for $CaCl_2$ solutions are derived from vapor pressure measurements. The methods used are all relative in that they measure the vapor pressure of water over the solution relative to that over pure water (in the dynamic vapor pressure, bithermal equilibration and dew point methods) or to that over a reference solution of a different electrolyte (isopiestic equilibration method).

a. Isopiestic Measurements

Three references solutions have been used for the isopiestic experiments. Robinson [15] used KCl, Stokes [16] NaCl and H_2SO_4. The osmotic coefficients of NaCl and KCl were calculated at the experimental molalities by use of the equations and parameters given by Hamer and Wu [4]. Osmotic coefficients of H_2SO_4 solutions were calculated by use of the equation

$$\begin{aligned}\phi = 0.802771 - 0.681325m^{1/2} + 1.22418m \\ - 1.120911m^{3/2} + 0.690683m^2 - 0.236908m^{5/2} \\ + 4.34707\times10^{-2}m^3 - 3.97733\times10^{-3}m^{7/2} \\ + 1.40099\times10^{-4}m^4 \quad (42)\end{aligned}$$

which was obtained by fitting the available data on the activity of H_2SO_4 solutions. About 150 experimental points were used to obtain the equation. The first term would be unity if eq (42) fit the data to infinite dilution, but the equation is only valid from about 0.1 to 20 mol · kg^{-1}

A very recent evaluation by Rard, Habenschuss, and Spedding [17] shows agreement with eq (42) to within 0.25% in ϕ over the wide range of molalities from 0.1 to 20 mol · kg^{-1}. As this is within the experimental error it lends some degree of confidence to the use of this tentative equation. Rard [17a] has measured isopiestic ratios of 60 solutions using H_2SO_4 as a reference and Spedding et al. [17b], 78 solutions, where KCl was the reference electrolyte.

Osmotic coefficients for the data of Robinson [15] are presented in table 1 and, those of Stokes [16], appear in tables 2 and 3. Table 2 gives values of ϕ calculated from isopiestic molalities using NaCl as the reference salt and table 3 gives the values of ϕ at high molalities, measured with H_2SO_4 as reference.

The data of Rard et al. [17a,b] are shown in table 22, where the reference electrolyte was H_2SO_4 and in table 23, where the reference salt was KCl.

Platford [65] tabulates 4 isopiestic molalities of NaCl and $CaCl_2$ from 1 to 3 mol · kg^{-1}, but these data were discovered after the correlation had been completed. Inclusion of Platford's data does not alter the final results. They are listed as table 24.

The values of osmotic coefficients at each experimental point were calculated by

$$\phi = \frac{(\nu m\phi)_r}{\nu m} \quad (43)$$

Platford [18] has used H_2SO_4 as an isopiestic standard for several salts at 0 °C. He used the ϕ for H_2SO_4 at 25 °C and enthalpy data to obtain the osmotic coefficient at 0 °C and then used the H_2SO_4 as a reference to obtain ϕ for $CaCl_2$ at 0 °C, so there is no advantage in reversing the calculations to redetermine ϕ at 25 °C for $CaCl_2$ from the 0 °C data.

Jakli and van Hook [19] have determined ϕ over a temperature range of 0–90 °C but only 3 points were determined near 25 °C. All points were omitted from the final fit of data.

b. Dynamic Vapor Pressure Measurements

For the data using water as reference, the water activity, a_1, and the osmotic coefficient, ϕ, were calculated for each experimental point by

$$\ln a_1 = \ln(P/P_o) + \frac{B_T(P - P_o)}{RT}, \quad (44)$$

and

$$\phi = -\frac{1000}{\nu m M_1}\ln a_1. \quad (45)$$

where P is the pressure of the water vapor over the solution and P_o is that over pure water. At 25 °C, we take $P_o = 3168.6$ Pa (23.766_5 Torr) [20], and B_T, the second virial coefficient for water vapor, -992 cm^3 · mol^{-1} from the Steam Tables [21]. Corrections for non-ideality of water vapor are given by the second term on the right of eq (44). These corrections are about 0.1% of ϕ over the entire composition range. This correction was applied to the direct vapor pressure measurements discussed here and in section c. and d. below. The correction was not applied to the isopiestic measurements because the ϕ values of the reference salts have effectively been corrected by referencing them to emf data in previous evaluations.

A reputedly accurate set of dynamic vapor pressure measurements were reported in 1940 by Bechtold and Newton [22]. The activity of water and the osmotic coefficient calculated at each of 3 molalities is presented in table 4. Each value is the average of 4, 6, or 7 runs, respectively.

c. Dew Point Measurements

A paper by Hepburn [23] reported vapor pressures from dew point measurements for 14 molalities from 0.2 to 7.3 (saturation) mol·kg^{-1}. Table 5 gives these recalculated results but 9 of the points were given zero weight in the least squares fit because of gross deviations (about 0.1 in ϕ) from smoothed values using data points from all sources. Hepburn and Garside [24] recalculated their data in 1941 but only the original data [23] were included in our evaluation. The complete reference to these data include references [23 a,b,c,].

Reasonably accurate vapor pressure measurements were reported by Petit [25] in 1965 for 13 molalities from 0.25 to 6 mol·kg^{-1}. The calculated results appear in table 6. All of our a_1 values agree well with those reported.

An equation for calculating log P over $CaCl_2$ solutions in the range 225–270 K was reported by Klimenki. Mogil'nyi, and Krynkov [26] but no reasonable values of log P could be obtained by us using their equation. Thus, the data were not used but the reference is cited for completeness of the bibliography on aqueous $CaCl_2$ solutions.

d. Bithermal Equilibration Measurement

Stokes [27] reported measurements at one composition of vapor pressure from bithermal equilibration through the vapor phase. His results are shown in table 7.

e. Freezing Point Depression Measurements

Some data derived form the depression of the freezing point method, by extrapolation to 298.15 K using heat of dilution data, have been presented in the Landolt-Bornstein tables [52]. References to the original freezing point data and the heats of dilution have been cited on page 2141 of reference [52]. The values of the activity coefficients are reported at rounded molalities over a range of 0.001 to 1 mol·kg^{-1}. These data are presented in table 18 but have not been used in the evaluation due to the availability of original freezing point data. These data agree well with the activity coefficients calculated from eq [39], and are apparently based on the results of Loomis [53].

The freezing point compilation for $CaCl_2$ given in the International Critical Tables [54] is also based on the measurements of Loomis [53], as well as Rodebush [55], and Ponsot [56].

Recent and careful freezing point measurements by Gibbard and Fong [57] include 10 molalities from 0.02 to 0.7 mol·kg^{-1}. These results are shown in table 19. Similarly reliable results were obtained by Loomis [53], and both of these sets of data were used in the evaluation. The data of Loomis are presented in table 20.

Rodebush [55] measured freezing points of six solutions from about 1 to 4 mol·kg^{-1}. All but the lowest molalities were given zero weight due to the apparent large errors at higher molalities. These data are illustrated in table 21. Ponsot's [56] data only included one molality and could not be used due to the very large deviation of ϕ from eq [40].

The freezing point depression measurements were used to calculate osmotic coefficients, first at 0 °C, then thermochemical data was used to obtain a temperature correction and ϕ at 25 °C was calculated. The ϕ at 0 °C was calculated from the freezing point depression according to Pitzer and Brewer [58].

The relative apparent molal enthalpy, ϕ_L data taken from thermodynamic properties evaluated by the National Bureau of Standards [59] was fitted as a function of $m^{1/2}$. From the slope at experimental molalities, a value of the relative partial molal enthalpy, $\bar{L}_1$, was obtained. The relative partial molal heat capacity, $\bar{J}_1$, was calculated from the fit of the apparent molal heat capacity, ϕ_C, as function of $m^{1/2}$ taken from the combined data of Perron, Desnoyers, and Millero [60] and Pitzer and Brewer [58].

f. Boiling Point Elevation Measurements

Plake [64] has measured the boiling point elevation of 9 solutions from 0.001 to 0.3 mol·kg^{-1} but these data were not considered due to the large and uncertain temperature correction necessary.

4.3. Activity Coefficients

Activity coefficients, $\gamma_\pm$, considered in this correlation were derived from two types of measurements: galvanic cell electromotive force (emf) measurements and diffusion measurements.

a. Galvanic Cell Measurements

Three types of cells were used for the emf measurements: 1. single fluid cells without transference; 2. two fluids cells without transference; and 3. concentration cells with transference.

All electrical units were converted to those of 1969. Where necessary, the data were corrected to the presently accepted values for the physical constants [7] such that $RT/F=0.0256926$ and for $CaCl_2$ $3RT/2F=0.0385389$, where $R=8.31441$ J·mol^{-1}·K^{-1}, and other constants are as previously noted.

(1) *Cells without Transference*

(a). Single Fluid Cell. Single fluid cells

$$Pb(s), PbC_2O_4(s), CaC_2O_4(s); CaCl_2(m); AgCl(s), Ag(s);$$

were used by Sahay [21] and cells of the type

$$Ca(Hg)_x(\ell)|CaCl_2(m);\ AgCl(s),\ Ag(s),$$

were used by Mussini and Pagella [29].

The emf of these cells is given by

$$E=E^\circ-\frac{3RT}{2F}\ln\left(m\cdot\gamma\cdot 4^{1/3}\right),\qquad(46)$$

and E° was eliminated by selecting the most dilute experimental point as a reference so that

$$E-E_r=-\frac{3RT}{2F}\ln\left[\frac{m\gamma}{(m\gamma)_r}\right],\qquad(47)$$

from which ln γ and γ can be calculated. The subscript r refers to a reference value. This reference value was selected as described in section 5, Correlation of Results. The results are presented in table 8 (Sahay) and table 9 (Mussini and Pagella).

(b). Two fluid cells. The two-fluid cell, used by Lucasse [30], Fosbinder [31], and Scatchard and Tefft [32, 33], was

$$Ag(s),\ AgCl(s);\ CaCl_2(m)|Ca_xHg(\ell)|CaCl_2(m_r);\ AgCl(s),\ Ag(s).$$

The emf of this cell is

$$E=\frac{3RT}{2F}\ln\left[\frac{m\gamma}{(m\gamma)_r}\right]\qquad(48)$$

Early measurements on calcium amalgam electrodes were investigated by Tamele [34] and Drucker and Luft [35]. Measurements of the calcium amalgam cell were made in 1925 by Lucasse [30] where m_r=0.01 mol·kg^{-1} with the thirteen molalities extending from 0.01 to 3.5 mol·kg^{-1}. The original tabulated emfs corrected as described, were used in recalculating his data (see table 10 where γ_r was taken as 0.7295 instead of the value 0.716 that Lucasse originally used.

In 1929, Fosbinder [31] performed similar emf measurements on $CaCl_2$ solutions of eleven molalities from m = 0.0099 to 3.3 mol·kg^{-1}. Here again, recalculations were based on corrected emf measurements and γ_r = 0.7304. These data are shown in table 11.

Scatchard and Tefft [33], reported smoothed values of γ for nineteen molalities, 0.001 to 1 mol·kg^{-1}. These were based on emf measurements reported in their preceding article [32]. The original emf data were recalculated for the nine molalities from 0.01 to 1 mol·kg^{-1}. The reference γ_r values used are presented in table 12, for each reference molality.

Harned [36] recalculated the data of Lucasse, but only the original data were used in the present evaluation.

Data from these cells at the higher concentrations are questionable. Robinson [3, 15] did not include the activity data obtained from methods employing calcium-amalgam electrodes in his data evaluation because of suspected reversibility problems with the calcium-amalgam electrode. However, more recent investigations by Butler [37], Mussini and Pagella [29] and Sahay [28] indicate that the activity data at the lower molalities of $CaCl_2$ are acceptable.

Butler, using data from Drucker and Luft [35], Tamele [36], Shibata [38], and Fosbinder[31], has determined a standard E° for the calcium-amalgam electrode which is in agreement within 1 mV of the value reported by Mussini and Pagella [29] in 1971. This agreement combined with Butler's observation of a lack of trend of E° with amalgam composition and, therefore, substantiation of the assumption γ_{Ca}=1 in the amalgam, lends more credence to activity measurements employing a calcium-amalgam electrode where the molality of $CaCl_2$ does not exceed about 0.1 mol·kg^{-1}. A very recent determination of standard potentials of the calcium amalgam electrode [61] may prove useful in explaining uncertainties in such activity measurements.

Activities of $CaCl_2$ solutions were also measured by means of a calcium ion-selective electrode by Huston and Butler [39]:

$$Ag(s),\ AgCl(s);\ CaCl_2(m)|\text{organic phase }(\ell)|CaCl_2(m_r);\ AgCl(s),\ Ag(s).$$

Most data points fell on a line which had a slope of 88.7 mV over a molality range of about 0.01 to 5 mol·kg^{-1}. Unfortunately insufficient data were available to allow calculation of activity coefficients (i.e. no emfs were tabulated).

Briggs and Lilley [40] also determined relative activities of $CaCl_2$ solutions with the calcium ion-selective electrode, from 0.001 to 0.1 mol·kg^{-1}. There results appear in table 15.

(2) *Cells with Transference*

Cells with transference were measured by Shedlovsky and MacInnes [41] and McLeod and Gordon [42]. Shedlovsky [43] recalculated his results thirteen years later, but only the original data were used in our evaluation. Lucasse [30] also derived transference numbers from cell data, reporting 11 data points which included 0.01 to 2.6 mol·kg^{-1}.

Eleven molalities were reported at 25 °C by McLeod and Gordon, over the range of 0.003 to 0.08 mol·kg^{-1}. Other measurements included 15 and 35 °C. Shedlovsky reported 6 molalities ranging from 0.002 to 0.1 mol·kg^{-1}.

The cell with transference

$$Ag(s),\ AgCl(s);\ CaCl_2(m_r)|CaCl_2(m);\ AgCl(s),\ Ag(s)$$

was used by Shedlovsky and MacInnes [41]and by McLeod and Gordon[42].

The emf is given by

$$E=-\frac{3RT}{2F}\int_{m_r}^{m}t_+\,d\ln m\gamma,\qquad(49)$$

where t_+ is the cation transference number. Shedlovsky and MacInnes used transference numbers from Longsworth [44] and McLeod and Gordon used transference numbers from Keenan, McLeod and Gordon [45].

The two sets of emf data seem to agree well but the two sets of transference numbers differ consistently by about 0.001. It was not possible to choose a preferred set of transference numbers based on deviations of each set of data from calculated activity coefficients, so the activity coefficients were calculated by using transference numbers calculated from

$$t_+ = 0.4392 - 0.4392\, c^{1/2} + 0.1620\, c - 0.1660\, c^{3/2}, \qquad (50)$$

where c is in equiv. l^{-1}. This eq was obtained by smoothing the combined data from both sources of transference numbers [44, 45]. The data of Shedlovsky and MacInnes [41] are listed in table 13, and those of McLeod and Gordon [42], in table 14. Data of Lucasse [30] are tabulated in table 16. These data were not included in the evaluation.

Masaki [46] reported emf measurements for 5 molalities, 0.001 to 0.01 mol·kg^{-1}, at 30 °C on cells with liquid junction, but only a few activity coefficients could be calculated, all with an error too large in include in the least squares fit.

Haas and Jellinek [47] also reported emf measurements on the cell

$$\mathrm{Ag(s); AgCl(s), CaCl_2}(m)|\mathrm{KCl\ (sat'd)}|\mathrm{KCl\ (0.1N), Hg_2Cl_2; Hg}(\ell)$$

for 7 molalities from 0.003 to 3.9 mol·kg^{-1} but activity coefficients cannot be calculated from the data, because of the unknown liquid-junction potentials.

b. Diffusion Coefficient Measurements

The theory of Onsager and Fuoss [48] for the diffusion of a binary electrolyte may be represented by equations:

$$D = \nu(1000RT)(\overline{M}/c)\left(1 + c\,\frac{\partial \ln y_\pm}{\partial c}\right), \qquad (51)$$

where D is the diffusion coefficient, and $\overline{M}/c$ is given by:

$$\frac{\overline{M}}{c} = \Bigg[\frac{\lambda_+^\circ \lambda_-^\circ}{1000\nu_+ F^2 |z_+| \Lambda_\circ} - \frac{(|z_-|\lambda_+^\circ - |z_+|\lambda_-^\circ)^2 (1 + \varkappa s)^{-1}\varkappa}{1000|z_+ z_-|(\nu_+ + \nu_-)\Lambda_\circ^2 (6\pi N \eta^\circ)} + \left(\frac{z_-^2\lambda_+^\circ + z_+^2\lambda_-^\circ}{(|z_+ z_-|\nu_+ + \nu_-)\Lambda_\circ}\right)^2 \frac{\varkappa^4 \phi(\varkappa s)}{48\pi^2 N^2 \eta^\circ c}\Bigg], \qquad (52)$$

and where $\phi(\varkappa s)$ is given by:

$$\phi(\varkappa s) = e^{2\varkappa s} Ei(2\varkappa s)/(1 + \varkappa s)^2, \qquad (53)$$

where Ei denotes the exponential integral functions, in which the distance of closest approach, s, is used. Here λ_+ and λ_- are the limiting equivalent conductances, respectively, of the positive and negative ions, $\Lambda_\circ$ the limiting equivalent conductance of the solution. $\eta_\circ$ is the viscosity of the solvent and $\varkappa$ is the Debye-Huckel quantity given by:

$$\varkappa = \left(\frac{2Ne^2}{\varepsilon^\circ \varepsilon k T}\right)^{1/2} I_c^{1/2}, \qquad (54)$$

where N, ε, ε°, k, e, and T have the significance given earlier. Rearrangement of eq (51) yields

$$\frac{\mathfrak{D}'}{\nu(1000\,RT)(\overline{M}/c)} - 1 \equiv \mathfrak{D}' = \frac{c\,\partial \ln y_\pm}{\partial c}. \qquad (55)$$

Accordingly,

$$\ln y_\pm = \int_0^c \frac{2\mathfrak{D}' dc^{1/2}}{c^{1/2}}. \qquad (56)$$

At the lower limit of concentration

$$\lim_{c\to 0}\left[\frac{\mathfrak{D}'}{c^{1/2}}\right] = \frac{\partial \ln y_\pm}{2\partial c^{1/2}} = -\tfrac{1}{2}A_c. \qquad (57)$$

By plotting $\mathfrak{D}'/c^{1/2}$ versus $c^{1/2}$ to the limiting value, the integral of eq (56) may be evaluated and thus log $y_\pm$ and $y_\pm$, and hence γ can be obtained. This method is applicable only to very dilute solutions. Harned [49, 2] had calculated activity coefficients for $\mathrm{CaCl_2}$ solutions from the diffusion data of Harned and Levy [50] and Harned and Parker [51]. We have used his values of γ without recalculation, and these values are listed for rounded molalities in table 17.

TABLE 1. OSMOTIC COEFFICIENTS FROM ISOPIESTIC MEASUREMENTS: ROBINSON, 1940 [15] REFERENCE SALT: KCl

m_r/mol·kg^{-1}	ϕ_r^a	ϕ/ϕ_r	m/mol·kg^{-1}	ϕ
.1234	.9224	.92747	.0887	.8555
.2127	.9121	.93783	.1512	.8554
.2304	.9107	.94349	.1628	.8593
.2780	.9076	.94413	.1963	.8569
.4534	.9010	.96974	.3117	.8738
.5453	.8993	.98465	.3692	.8855
.7667	.8976	1.02043	.5009	.9160
.7890	.8976	1.01958	.5159	.9152
.8476	.8976	1.03096	.5481	.9254
1.3610	.9015	1.10087	.8242	.9925
1.4170	.9023	1.10981	.8512	1.0013
1.5540	.9042	1.12682	.9194	1.0189
1.7810	.9080	1.15612	1.0270	1.0497
1.9580	.9113	1.18130	1.1050	1.0765
2.0100	.9123	1.18270	1.1330	1.0790
2.1670	.9156	1.20189	1.2020	1.1004
2.5230	.9237	1.24133	1.3550	1.1466
2.6160	.9260	1.25377	1.3910	1.1609
2.8430	.9317	1.27632	1.4850	1.1891
2.9340	.9341	1.28769	1.5190	1.2028
3.0980	.9385	1.30470	1.5830	1.2245
3.2240	.9420	1.31780	1.6310	1.2413
3.5320	.9508	1.34399	1.7520	1.2779
3.5800	.9522	1.35222	1.7650	1.2876
4.0140	.9653	1.39302	1.9210	1.3447
4.0210	.9655	1.38679	1.9330	1.3390
4.5340	.9817	1.43458	2.1070	1.4083
4.7470	.9885	1.45301	2.1780	1.4364
4.8100	.9906	1.45625	2.2020	1.4425

[a] Reference ϕ_r calculated from equations and parameters for the reference salt taken from Hamer and Wu [4]

TABLE 2. OSMOTIC COEFFICIENTS FROM ISOPIESTIC MEASUREMENTS: STOKES, 1945 [16] REFERENCE SALT: NaCl

m_r /mol·kg^{-1}	ϕ_r^a	ϕ/ϕ_r	m/mol·kg^{-1}	ϕ
.1255	.9294	.92144	.0908	.8564
.1586	.9263	.92102	.1148	.8532
.3034	.9207	.93816	.2156	.8637
.3901	.9202	.94846	.2742	.8728
.5617	.9223	.96637	.3875	.8913
.7366	.9266	.98846	.4968	.9159
.9232	.9327	1.01062	.6090	.9426
1.0460	.9374	1.02429	.6808	.9601
1.3250	.9492	1.05385	.8382	1.0003
1.3500	.9504	1.05845	.8503	1.0059
1.6830	.9666	1.09144	1.0280	1.0550
1.9630	.9816	1.11852	1.1700	1.0980
2.2440	.9977	1.14461	1.3070	1.1420
2.6110	1.0200	1.17454	1.4820	1.1981
2.6120	1.0201	1.17420	1.4830	1.1978
2.6220	1.0207	1.17552	1.4870	1.1999
2.7240	1.0272	1.18306	1.5350	1.2153
2.9880	1.0444	1.20217	1.6570	1.2556
3.2410	1.0615	1.21934	1.7720	1.2943
3.3020	1.0657	1.22432	1.7980	1.3048
3.9370	1.1109	1.26368	2.0770	1.4039
4.0840	1.1218	1.27227	2.1400	1.4272
4.8650	1.1810	1.31469	2.4670	1.5527
5.3420	1.2182	1.33985	2.6580	1.6322
5.3840	1.2215	1.34131	2.6760	1.6384
6.0080	1.2706	1.37122	2.9210	1.7423
6.0280	1.2722	1.37250	2.9280	1.7461
6.1470	1.2815	1.37609	2.9780	1.7635
6.1660	1.2830	1.37896	2.9810	1.7693

[a] Reference ϕ_r calculated from equations and parameters for the reference salt taken from Hamer and Wu [4].

TABLE 3. OSMOTIC COEFFICIENTS FROM ISOPIESTIC MEASUREMENTS: STOKES, 1940 [16] REFERENCE: H_2SO_4

m_r/mol·kg^{-1}	ϕ_r^a	ϕ/ϕ_r	m/mol·kg^{-1}	ϕ
4.3290	1.1996	1.46696	2.9510	1.7597
4.5200	1.2290	1.47135	3.0720	1.8082
4.9850	1.2994	1.48275	3.3620	1.9268
5.5610	1.3841	1.49690	3.7150	2.0719
5.8990	1.4322	1.50140	3.9290	2.1502
6.2370	1.4788	1.51163	4.1260	2.2354
6.7420	1.5458	1.52465	4.4220	2.3567
6.9160	1.5680	1.52840	4.5250	2.3966
7.1160	1.5931	1.53528	4.6350	2.4458
7.6110	1.6527	1.54444	4.9280	2.5525
7.6870	1.6616	1.54761	4.9670	2.5715
8.3810	1.7385	1.56187	5.3660	2.7153
8.5570	1.7569	1.56349	5.4730	2.7469
8.6220	1.7636	1.56451	5.5110	2.7592
8.8010	1.7817	1.56853	5.6110	2.7947
9.5470	1.8526	1.57437	6.0640	2.9166
10.0910	1.8996	1.57820	6.3940	2.9979
10.1360	1.9033	1.57759	6.4250	3.0026
10.4560	1.9290	1.57470	6.6400	3.0376
10.7860	1.9543	1.57207	6.8610	3.0723
10.7800	1.9538	1.57097	6.8620	3.0694
10.8130	1.9563	1.57303	6.8740	3.0773
11.1150	1.9783	1.56726	7.0920	3.1004
11.3150	1.9922	1.56436	7.2330	3.1166
11.3830	1.9969	1.56231	7.2860	3.1198
11.4340	2.0004	1.56074	7.3260	3.1221
11.4560	2.0019	1.56055	7.3410	3.1240
11.4830	2.0037	1.56146	7.3540	3.1287
11.5820	2.0103	1.55882	7.4300	3.1336
11.5750	2.0098	1.55766	7.4310	3.1306
11.7150	2.0190	1.55681	7.5250	3.1432
12.0410	2.0396	1.54868	7.7750	3.1587
12.1990	2.0492	1.54145	7.9140	3.1588
12.3310	2.0571	1.53696	8.0230	3.1617
12.5520	2.0700	1.53204	8.1930	3.1713
13.2090	2.1058	1.50977	8.7490	3.1793
13.4580	2.1186	1.50151	8.9630	3.1810
14.3710	2.1618	1.46868	9.7850	3.1750
14.7010	2.1763	1.45974	10.0710	3.1768
14.8000	2.1805	1.45684	10.1590	3.1766
15.4290	2.2063	1.43526	10.7500	3.1666
15.4420	2.2068	1.43366	10.7710	3.1638

(a) Reference ϕ_r calculated from eq (42).

TABLE 4. OSMOTIC COEFFICIENTS FROM VAPOR PRESSURE MEASUREMENTS: BECHTOLD AND NEWTON, 1940 [22]

m/mol·kg^{-1}	a_{H_2O}	ϕ
0.3043	0.98635	0.8359
3.0335	.74607	1.7867
7.0310	.3099	3.0828

TABLE 5. OSMOTIC COEFFICIENTS FROM VAPOR PRESSURE MEASUREMENTS: HEPBURN, 1932 [23]

m/mol·kg^{-1}	a_{H_2O}	ϕ
.1990 (d)	.98896	1.0323
.2840 (d)	.98602	.9175
.3440 (d)	.98602	.7574
.4940 (d)	.97971	.7677
.6350 (d)	.97299	.7979
.7960 (d)	.96290	.8788
1.0000 (d)	.95155	.9189
1.5040 (d)	.90951	1.1668
1.9850	.86159	1.3887
2.4950	.81071	1.5562
2.9900	.75183	1.7651
4.0040	.62018	2.2077
5.8260 (d)	.39925	2.9160
7.2780	.29484	3.1049

(d) given zero weight in fitting equation.

TABLE 6. OSMOTIC COEFFICIENTS FROM VAPOR PRESSURE MEASUREMENTS: PETIT, 1965 [25]

m/mol·kg^{-1}	a_{H_2O}	ϕ
.2500	.98812	.8847
.5000 (d)	.97652	.8793
.7500 (d)	.95916	1.0287
1.0000 (d)	.94176	1.1103
1.5000 (d)	.90321	1.2558
2.0000	.86062	1.3887
2.5000	.80747	1.5827
3.0000	.74994	1.7748
3.5000	.68525	1.9981
4.0000	.62371	2.1836
4.5000	.55980	2.3855
5.0000	.49841	2.5768
6.0000	.39049	2.8998

TABLE 7. OSMOTIC COEFFICIENTS FROM BITHERMAL EQUILIBRATION: STOKES, 1947 [27]

m/mol·kg^{-1}	a_{H_2O}	ϕ
3.024	0.7473	1.7823
3.024	.7473	1.7823
3.019	.7473	1.7853
3.036	.7457	1.7884

TABLE 8. ACTIVITY COEFFICIENTS FROM EMF MEASUREMENTS: SAHAY, 1959 [28]

REFERENCE MOLALITY = 0.001 mol·kg^{-1} REFERENCE GAMMA = 0.8886_0

Pb(s), PbC_2O_4(s), CaC_2O_4(s); $CaCl_2$(m); AgCl(s), Ag(s)

m/mol·kg^{-1})	Emf /(V)	γ/γ_r	γ
.002000	.02490	.95404	.8478
.005000	.05720	.88230	.7840
.010000	.08080	.81383	.7232
.020000	.10380	.73908	.6568
.050000	.13350	.63891	.5677
.060000 (d)	.13740	.58912	.5235
.080000 (d)	.21520	3.32655	2.9560 (?)

(d) given zero weight in fitting equation.

TABLE 9. ACTIVITY COEFFICIENTS FROM EMF MEASUREMENTS: MUSSINI AND PAGELLA, 1971 [29]

REFERENCE MOLALITY = 0.005828 $mol \cdot kg^{-1}$ REFERENCE GAMMA = 0.7752_2

$Ca(Hg)_x | CaCl_2(m); AgCl(s), Ag(s)$

$m/mol \cdot kg^{-1}$	Emf/(V)	γ/γ_r	γ
.009197	.01590	.95730	.7421
.014720	.03110	.88731	.6879
.019320	.03920	.83417	.6467
.024360	.04750	.82058	.6361
.034030	.05910	.79370	.6153
.038830	.06360	.78173	.6060
.048300	.07050	.75168	.5827
.058480	.07680	.73109	.5668
.072360	.08320	.69759	.5408
.096800	.09260	.66551	.5159

TABLE 10. ACTIVITY COEFFICIENTS FROM EMF MEASUREMENTS: LUCASSE, 1925 [30]

REFERENCE MOLALITY = 0.0100 $mol \cdot kg^{-1}$ REFERENCE GAMMA = 0.7294_6

$Ag(s), AgCl(s); CaCl_2(m) | Ca_xHg(\ell) | CaCl_2(m_r); AgCl(s), Ag(s)$

$m/mol \cdot kg^{-1}$	Emf/(V)	ν/ν_r	ν
.035040	.04107	.82851	.6044
.062940	.06062	.76600	.5588
.103200	.07720	.71819	.5239
.206600 (d)	.10139	.67217	.4903
.371300 (d)	.12351	.66394	.4843
.465500 (d)	.13354	.68689	.5011
.662200 (d)	.15431	.82785	.6039
.960800 (d)	.17505	.97722	.7128
1.003000 (d)	.17737	.99421	.7252
1.606000 (d)	.21057	1.46953	1.0720
1.960000 (d)	.23138	2.06605	1.5071
3.167000 (d)	.28567	5.23026	3.8153
3.502000 (d)	.30057	6.96338	5.0795

(d) given zero weight in fitting equation.

TABLE 11. ACTIVITY COEFFICIENTS FROM EMF MEASUREMENTS: FOSBINDER, 1929 [31]

REFERENCE MOLALITY = 0.0099 $mol \cdot kg^{-1}$ REFERENCE GAMMA = 0.7303_5

$Ag(s), AgCl(s); CaCl_2(m) | Ca_xHg(\ell) | CaCl_2(m_r); AgCl(s), Ag(s)$

$m/mol \cdot kg^{-1}$	Emf /(V)	γ/γ_r	γ
.043500	.04872	.80562	.5884
.062800	.06072	.76196	.5565
.078100	.06887	.75704	.5529
.089700 (d)	.06687	.62579	.4570
.141100 (d)	.08943	.71433	.5217
.306900 (d)	.11739	.67842	.4955
.715800 (d)	.15610	.79426	.5801
1.208100 (d)	.18295	.94453	.6898
1.537800 (d)	.20239	1.22870	.8974
1.983300 (d)	.21709	1.39530	1.0191
3.502000 (d)	.30057	6.89375	5.0348

TABLE 12. ACTIVITY COEFFICIENTS FROM EMF MEASUREMENTS: SCATCHARD AND TEFFT, 1930 [32]

$Ag(s), AgCl(s); CaCl_2(m) | Ca_xHg(\ell) | CaCl_2(m_r); AgCl(s), Ag(s)$

$m_r/mol \cdot kg^{-1}$	γ_r	$m/mol \cdot kg^{-1}$	Emf(meas.)/V	γ/γ_r	γ
.099890	.52080	.009921	-.07613	1.39646	.7273
.099780	.52090	.010510	-.07423	1.38329	.7206
.100410	.52040	.025940	-.04391	1.23871	.6446
.099830	.52080	.027580	-.04121	1.24238	.6470
.099890	.52080	.041130	-.02893	1.14641	.5971
.099930	.52070	.126340	.00789	.97067	.5054
.100290	.52050	.442000 (d)	.05582	.96581	.5027
.099680	.52090	.658900 (d)	.07683	1.11075	.5786
.100560	.52030	.930100 (d)	.09618	1.31155	.6824

(d) given zero weight in fitting equation.

TABLE 13. ACTIVITY COEFFICIENTS FROM EMF MEASUREMENTS: SHEDLOVSKY AND MACINNES, 1937 [41]

REFERENCE MOLALITY = 0.050196 $mol \cdot kg^{-1}$ REFERENCE GAMMA = 0.5790_8

$Ag(s), AgCl(s); CaCl_2(m_r) | CaCl_2(m); AgCl(s), Ag(s)$

$m/mol \cdot kg^{-1}$	Emf/V	$t_+^{(a)}$	γ/γ_r	γ
.0018207	.047561	.43147	1.47682	.8552
.0061101	.029273	.42577	1.33155	.7711
.0095685	.022705	.42286	1.27059	.7358
.0242493	.009754	.41504	1.11820	.6475
.0376638	.003820	.41028	1.04556	.6055
.0970105	-.008610	.39598	.90294	.5229

TABLE 14. ACTIVITY COEFFICIENTS FROM EMF MEASUREMENTS: MCLEOD AND GORDON, 1946 [42]

REFERENCE MOLALITY = 0.025270 $mol \cdot kg^{-1}$ REFERENCE GAMMA = 0.6434_5

$Ag(s), AgCl(s); CaCl_2(m_r) | CaCl_2(m); AgCl(s), Ag(s)$

$m/mol \cdot kg^{-1}$	Emf/V	$t_+^{(a)}$	γ/γ_r	γ
.0033155	.029196	.42900	1.26998	.8172
.0058595	.020703	.42602	1.20324	.7742
.0063695	.019496	.42552	1.19139	.7666
.0094820	.013715	.42293	1.13980	.7334
.0113420	.011160	.42162	1.11484	.7174
.0148830	.007326	.41947	1.07636	.6926
.0348040	-.004316	.41119	.95228	.6127
.0479460	-.008577	.40728	.90571	.5828
.0600840	-.011848	.40415	.89089	.5732
.0645300	-.012479	.40308	.86383	.5558
.0749290	-.014439	.40069	.84431	.5433

(a) The activity coefficients were calculated from eq (49) using transference numbers calculated from eq (50).

Table 15. ACTIVITY COEFFICIENTS FROM ION-SELECTIVE ELECTRODE DATA: BRIGGS AND LILLEY, 1974 [40]

REFERENCE MOLALITY = 0.0010275 $mol \cdot kg^{-1}$ REFERENCE GAMMA = 0.8872_8

$Ag, AgCl; CaCl_2(m_r) \parallel CaCl_2(m); AgCl, Ag$

$m/mol \cdot kg^{-1}$	Emf/(V)	γ/γ_r	γ
0.0032519	-0.04109	0.91767	0.8142
.010165	-0.08045	0.81520	0.7233
.033081	-0.11950	0.69000	0.6122
.099104	-0.15518	0.58131	0.5158
.295890	-0.19215	0.50814	0.4509

TABLE 16. ACTIVITY COEFFICIENTS FROM EMF MEASUREMENTS: LUCASSE, 1925 {30}

REFERENCE MOLALITY = 0.0100 $mol\cdot kg^{-1}$ REFERENCE GAMMA = 0.7293

$Ag(s), AgCl(s); CaCl_2(m_r) | CaCl_2(m) ; AgCl(s), Ag(s)$

$m/mol\cdot kg^{-1}$ (d)	Emf/V	t_+		γ/γ_r	γ (d)
.01547	.00601	.41915	a	.93648	.6830
.02006	.00974	.41686	a	.91045	.6640
.03955	.01898	.40969	a	.82509	.6017
.04966	.02198	.40681	a	.79521	.5800
.08053	.02841	.39946	a	.74191	.5411
.16120	.03683	.367	b	.64806	.4726
.32080	.04600	.321	b	.62514	.4559
.61620	.05487	.277	b	.70205	.5120
1.01300	.06264	.259	b	1.63402	1.1917
1.60000	.07164	.254	b	1.74162	1.2702
2.58600	.08357	.251	b	.41139	0.3000

(a) The activity coefficients were calculated from eq (49) using transference numbers calculated from eq (50).

(b) Transference numbers given by Lucasse {30}.

(d) These values were not included in the evaluation procedure

TABLE 17. ACTIVITY COEFFICIENTS FROM DIFFUSION COEFFICIENT DATA: HARNED, 1959 [49, 2]

$m/mol\cdot kg^{-1}$	γ
.0001	.961
.0002	.946
.0003	.935
.0005	.918
.0007	.904
.001	.888
.002	.850
.003	.824
.005	.786
.007	.758
.01	.727
.03	.624
.05	.576
.07	.547
.1	.518

TABLE 18. ACTIVITY COEFFICIENTS FROM FREEZING POINT DATA: LANDOLT-BORNSTEIN, 1936 [52]
(Extrapolation to 25°C)

$m/mol\cdot kg^{-1}$	γ (d)
0.001	0.883
.002	.843
.005	.783
.01	.730
.02	.670
.05	.589
.1	.531
.2	.478
.5	.447
1.0	.505

(d) These values were not included in the evaluation procedure.

Table 19. OSMOTIC COEFFICIENTS FROM FREEZING POINT MEASUREMENTS:

Gibbard and Fong, 1975 [57]

$m/mol\cdot kg^{-1}$	F.P. Depression/K	$\phi_{(273)}$	$a_{w(298)}$	$\phi_{(298)}$
.02755	.1362	.8860	.99869	.8816
.04930	.2394	.8703	.99770	.8655
.11290	.5406	.8583	.99481	.8533
.14445	.6913	.8579	.99336	.8529
.17385	.8342	.8602	.99200	.8552
.29190	1.4272	.8767	.98635	.8712
.36465	1.8097	.8901	.98273	.8841
.44830	2.2674	.9073	.97841	.9007
.52900	2.7323	.9267	.97405	.9195
.72735	3.9541	.9758	.96271	.9669

Table 20. OSMOTIC COEFFICIENTS FROM FREEZING POINT MEASUREMENTS:

Loomis, 1897 [54]

$m/mol\cdot kg^{-1}$	F.P. Depression/K	$\phi_{(273)}$	$a_{w(298)}$	$\phi_{(298)}$
.01000	.0513	.9193	.99951	.9159
.02010	.1013	.9032	.99902	.8990
.05020	.2437	.8700	.99766	.8653
.10040	.4823	.8610	.99537	.8561
.20080	.9718	.8676	.99068	.8625
.50210	2.6050	.9308	.97524	.9238

Table 21. OSMOTIC COEFFICIENTS FROM FREEZING POINT MEASUREMENTS:

Rodebush, 1918 [55]

$m/mol\cdot kg^{-1}$	F.P. Depression/K	$\phi_{(273)}$	$a_{w(298)}$	$\phi_{(298)}$
.76676	4.2100	.9857	.96035	.9763
1.33620	8.6300	1.1605	.92066	1.1447
1.98403 (d)	15.2300	1.3768	.86538	1.3484
3.14184 (d)	29.8300	1.6589	.76368	1.5877
3.24726 (d)	31.2500	1.6737	.75550	1.5976
4.32487 (d)	51.0000	1.9141	.65893	1.7846

(d) given zero weight in fitting equation.

TABLE 22. OSMOTIC COEFFICIENTS FROM ISOPIESTIC MEASUREMENTS:
Rard and Spedding, 1976 [17a] REFERENCE SALT: H_2SO_4

m_r/mol·kg^{-1}	ϕ_r^a	ϕ/ϕ_r	m/mol·kg^{-1}	ϕ
3.8135	1.1193	1.44774	2.6341	1.6205
4.0329	1.1534	1.45340	2.7748	1.6764
4.3210	1.1980	1.46073	2.9581	1.7500
4.6645	1.2507	1.46932	3.1746	1.8376
4.9087	1.2876	1.47572	3.3263	1.9001
5.2915	1.3444	1.48583	3.5613	1.9976
5.5427	1.3809	1.49190	3.7152	2.0602
5.8672	1.4270	1.50037	3.9105	2.1411
6.1892	1.4715	1.50875	4.1022	2.2202
6.4495	1.5065	1.51546	4.2558	2.2831
6.7945	1.5516	1.52435	4.4573	2.3651
7.1360	1.5945	1.53284	4.6554	2.4441
7.4182	1.6287	1.54020	4.8164	2.5085
7.7500	1.6675	1.54740	5.0084	2.5803
8.1238	1.7093	1.55554	5.2225	2.6589
8.3817	1.7370	1.55971	5.3739	2.7091
8.7002	1.7698	1.56501	5.5592	2.7698
8.7043	1.7702	1.56468	5.5630	2.7698
8.7166	1.7715	1.56483	5.5703	2.7720
8.7390	1.7737	1.56540	5.5826	2.7766
8.8855	1.7883	1.56774	5.6677	2.8035
9.0406	1.8033	1.56930	5.7609	2.8300
9.1765	1.8163	1.57073	5.8422	2.8529
9.3449	1.8320	1.57221	5.9438	2.8803
9.5049	1.8465	1.57324	6.0416	2.9050
9.6885	1.8628	1.57375	6.1563	2.9316
9.8271	1.8748	1.57420	6.2426	2.9513
10.0300	1.8919	1.57482	6.3690	2.9794
10.2030	1.9061	1.57386	6.4828	2.9999
10.3690	1.9194	1.57282	6.5926	3.0188
10.4820	1.9282	1.57241	6.6662	3.0319
10.5880	1.9364	1.57150	6.7375	3.0430
10.7140	1.9459	1.56991	6.8246	3.0549
10.8190	1.9537	1.56897	6.8956	3.0653
10.9230	1.9613	1.56732	6.9692	3.0739
11.0560	1.9708	1.56667	7.0570	3.0876
11.0740	1.9721	1.56596	7.0717	3.0882
11.1920	1.9803	1.56300	7.1606	3.0953
11.2370	1.9835	1.56343	7.1874	3.1010
11.3010	1.9878	1.56212	7.2344	3.1053
11.3490	1.9911	1.56105	7.2701	3.1082
11.3480	1.9910	1.56051	7.2720	3.1070
11.4800	1.9999	1.55913	7.3631	3.1181
11.5560	2.0049	1.55620	7.4258	3.1200
11.6380	2.0103	1.55430	7.4876	3.1246
11.7630	2.0183	1.55228	7.5779	3.1329
11.8440	2.0234	1.55053	7.6387	3.1373
11.9390	2.0293	1.54817	7.7117	3.1417
12.0360	2.0353	1.54502	7.7902	3.1445
12.1110	2.0398	1.54288	7.8496	3.1472
12.1850	2.0443	1.54203	7.9019	3.1523
12.2060	2.0455	1.54050	7.9234	3.1511
12.3760	2.0555	1.53556	8.0596	3.1563
12.4500	2.0597	1.53333	8.1196	3.1582
12.5670	2.0663	1.53056	8.2107	3.1627
12.7400	2.0759	1.52471	8.3557	3.1652
12.8800	2.0835	1.52002	8.4736	3.1670
12.9920	2.0895	1.51730	8.5626	3.1704
13.0520	2.0926	1.51371	8.6225	3.1677
13.2880	2.1048	1.50565	8.8254	3.1690

[a] Reference ϕ_r calculated from eq (42).

TABLE 23. OSMOTIC COEFFICIENTS FROM ISOPIESTIC MEASUREMENTS:
Spedding, et al 1976 [17b] REFERENCE SALT: KCl

$m_r/\text{mol}\cdot\text{kg}^{-1}$	ϕ_r^a	ϕ/ϕ_r	$m/\text{mol}\cdot\text{kg}^{-1}$	ϕ
.7292	.8977	1.01320	.4798	.9096
.8245	.8976	1.02761	.5349	.9224
.8521	.8976	1.03285	.5500	.9271
.9252	.8978	1.04207	.5919	.9356
1.1069	.8989	1.06838	.6907	.9603
1.1279	.8990	1.07083	.7022	.9627
1.2691	.9004	1.09114	.7754	.9825
1.3553	.9015	1.10470	.8179	.9958
1.3733	.9017	1.10545	.8282	.9968
1.4121	.9022	1.11067	.8476	1.0020
1.4553	.9028	1.11581	.8695	1.0073
1.5284	.9038	1.12751	.9037	1.0191
1.5333	.9039	1.12801	.9062	1.0196
1.5367	.9040	1.12789	.9083	1.0196
1.5560	.9043	1.13073	.9174	1.0225
1.5728	.9045	1.13233	.9260	1.0242
1.6297	.9054	1.14113	.9521	1.0332
1.6321	.9055	1.14161	.9531	1.0337
1.7145	.9068	1.15002	.9939	1.0429
1.8751	.9097	1.17004	1.0684	1.0644
1.8967	.9101	1.17330	1.0777	1.0679
1.9239	.9107	1.17637	1.0903	1.0713
1.9589	.9113	1.18002	1.1067	1.0754
1.9835	.9118	1.18330	1.1175	1.0790
2.2513	.9174	1.21469	1.2356	1.1144
2.3347	.9193	1.22489	1.2707	1.1261
2.5585	.9246	1.24893	1.3657	1.1547
3.1969	.9413	1.31730	1.6179	1.2399
3.2179	.9419	1.31992	1.6253	1.2432
3.2655	.9432	1.32348	1.6449	1.2483
3.2955	.9440	1.32629	1.6565	1.2521
3.3345	.9452	1.32986	1.6716	1.2569
3.3405	.9453	1.33027	1.6741	1.2575
3.3450	.9454	1.33079	1.6757	1.2582
3.3559	.9458	1.33171	1.6800	1.2595
3.4950	.9498	1.34729	1.7294	1.2796
3.5388	.9511	1.35105	1.7462	1.2849
3.5927	.9526	1.35479	1.7679	1.2906
3.6171	.9534	1.35876	1.7747	1.2954
3.6264	.9536	1.35782	1.7805	1.2949
3.6401	.9540	1.36005	1.7843	1.2976
3.6532	.9544	1.36082	1.7897	1.2988
3.6851	.9554	1.36387	1.8013	1.3030
3.7661	.9578	1.37086	1.8315	1.3130
3.7829	.9583	1.37338	1.8363	1.3161
3.9116	.9622	1.38451	1.8835	1.3322
3.9483	.9634	1.38734	1.8973	1.3365
4.0066	.9652	1.39467	1.9152	1.3461
4.0835	.9676	1.40247	1.9411	1.3570
4.1503	.9696	1.40636	1.9674	1.3637
4.1512	.9697	1.40659	1.9675	1.3639
4.2051	.9714	1.41137	1.9863	1.3709
4.2460	.9726	1.41456	2.0011	1.3759
4.3007	.9744	1.41930	2.0201	1.3829
2.6203	.9261	1.25773	1.3889	1.1648
2.7064	.9282	1.26597	1.4252	1.1751
2.7249	.9287	1.26875	1.4318	1.1783
2.7361	.9290	1.26953	1.4368	1.1794
2.8209	.9312	1.27628	1.4735	1.1884
2.8393	.9316	1.27819	1.4809	1.1908
2.8724	.9325	1.28312	1.4924	1.1965
2.9017	.9333	1.28587	1.5044	1.2001
2.9195	.9337	1.28777	1.5114	1.2024
2.9443	.9344	1.29085	1.5206	1.2062
3.0206	.9364	1.29876	1.5505	1.2162
3.1406	.9397	1.31203	1.5958	1.2329
4.3152	.9748	1.42261	2.0222	1.3868
4.3211	.9750	1.42251	2.0251	1.3870
4.3637	.9764	1.42591	2.0402	1.3922
4.3793	.9769	1.42785	2.0447	1.3948
4.5782	.9832	1.44370	2.1141	1.4195
4.6072	.9842	1.44669	2.1231	1.4238
4.6202	.9846	1.44852	2.1264	1.4262
4.6660	.9861	1.45162	2.1429	1.4314
4.6789	.9865	1.45265	2.1473	1.4330
4.6893	.9868	1.45303	2.1515	1.4339
4.7195	.9878	1.45556	2.1616	1.4378
4.7520	.9889	1.46031	2.1694	1.4440

[a] Reference ϕ_r calculated from equations and parameters for the reference salt taken from Hamer and Wu [4].

TABLE 24. OSMOTIC COEFFICIENTS FROM ISOPIESTIC MEASUREMENTS: Platford, 1975 [65] REFERENCE SALT: KCl

m_r/mol·kg^{-1}	ϕ_r^a	ϕ/ϕ_r	m/mol·kg^{-1}	ϕ
1.918	0.9791	1.11673	1.145	1.0934
2.476	1.0116	1.16080	1.422	1.1743
4.404	1.1457	1.29168	2.273	1.4799
6.085	1.2767	1.37654	2.947	1.7574

[a] Reference ϕ_r calculated from equations and parameters for the reference salt taken from Hamer and Wu [4].

5. Correlation of Results

In order to obtain values of ln γ and γ from the cell measurement it is necessary to know a value for γ_r at a $CaCl_2$ composition of m_r for each experiment. We have arrived at the values of γ_r by an iteration technique. Initial values for γ_r were calculated by eq (39) using parameters given by Wu and Hamer [1]. Using these reference values a pair of values of m, γ was obtained at each experimental point. These data were then combined with the pairs of m, γ values from the diffusion data, m, ϕ values from the freezing point data, and the vapor pressure methods and a new set of parameters for eq (39) was calculated by a non-linear least-squares fit to minimize $\Sigma w_i[f_i - f_{(calc)_i}]^2$ where the function, $f=\ln\gamma$, or $f=\phi$, and f_{calc} was obtained from eq (39) or (40), respectively. The summation is over the number of experimental points. Using the new parameters a new set of γ_r was calculated and the fitting procedure repeated. This process continued until the parameters remained essentially unchanged. The procedure is outlined in figure 3. All computer programs have been documented in a Nat. Bur. Stand. Technical Note [62].

Initially all the experimental data were weighted equally and included in the fitting procedure. The data were divided into sets according to source and an estimate of the standard deviation of each set was made by equating it to the root-mean-square deviation of the points in the set from the curve obtained in the initial fit. Using weights corresponding to these estimates of standard deviations a second fit of the data was made. The results of these calculations together with subjective evaluation of experimental procedures were used to weight the experimental points. Zero weight was given to emf data at concentrations greater than 0.1 mol·kg^{-1} measured with cells using a calcium amalgam electrode.

After the first iteration, experimental points with deviations from calculated values of greater than 0.1 in ϕ or γ, were given zero weight, these points have been marked in the tables of data.

The selected weighting factors used for each set of experimental data are shown in table 25. Of the vapor pressure data, Robinson [15] was weighted the highest and Stokes (vs NaCl) [16] slightly less, based on the internal consistency of their experimental data. The data based on H_2SO_4, Stokes [16] and Rard [17a], were weighted lower because of the tentative nature of the evaluated osmotic coefficients of H_2SO_4, as well as a larger scatter of data points. Spedding's [17b] data based on KCl was given high weight. Hepburn [23], in view of the apparent unreliability of the experimental results, was given the lowest weight. Bechtold [22] and Stokes [27] were weighted equally at 0.5. Although Bechtold's measurements are considered to be quite reliable, the lowest molality has a much larger uncertainty than the more concentrated points, as is expected from these vapor pressure measurements. They were given a lower than anticipated weight in order to include all of the 3 data points.

Petit [25] was assigned a weight intermediate between Bechtold and Hepburn; again the higher molalities are more reliable.

Freezing point results of Loomis [53], Rodebush [55], and Gibbard [57] were given a weight of 0.5, due to the necessary correction to 25 °C.

The emf data of Mussini [29], McLeod [42], Shedlovsky [41], Briggs [40], and the data from Harned [49, 2] were weighted equally high. Fosbinder [31] and Lucasse [30] were assigned lowest weights because of the uncertainty in the behavior of calcium amalgam electrodes above 0.1 mol·kg^{-1}. Scatchard [32] and Sahay [28] were weighted equally at 0.5 since some data points in each experiment had to be assigned zero weights.

With all the experimental values weighted as discussed, an analysis of variance indicated that 8 parameters were needed to fit the data.

The estimates of standard deviation of ϕ and ln γ are shown in the last column of table 25.

By repeating the fitting process with the weighted data a final set of parameters for eqs (39, 40, and 41) was obtained. The values for eqs (39, 40, and 41) are

			$\sigma\times10^3$
$B =$	1.60002	(kg·mol^{-1})$^{1/2}$	8.7
$C =$	0.256690	(kg·mol^{-1})	10.8
$D =$	0.151052	(kg·mol^{-1})^2	10.7
$E =$	-3.77055×10^{-2}	(kg·mol^{-1})^3	5.3
$F =$	9.90578×10^{-3}	(kg·mol^{-1})^4	1.4
$G =$	-1.69480×10^{-3}	(kg·mol^{-1})^5	0.2
$H =$	1.34960×10^{-4}	(kg·mol^{-1})^6	0.01
$I =$	-3.94208×10^{-6}	(kg·mol^{-1})^7	0.0003

It should be noted that the form of the Hamer-Wu [4] equation has been modified for eq (39), to calculate ln γ rather than log γ. The constants A, C, D, E, F, G, H, and I differ by a factor of ln (10) from those used in Hamer and Wu's equation.

There were 290 experimental data points considered which were based on vapor pressure methods, of which, 277 were assigned non-zero weights. Of the 101 experimental points considered which yielded γ values, 64 were given non-zero weights. Thus 341 data points were used in the final calculation.

FLOW DIAGRAM OF EVALUATION PROCEDURE

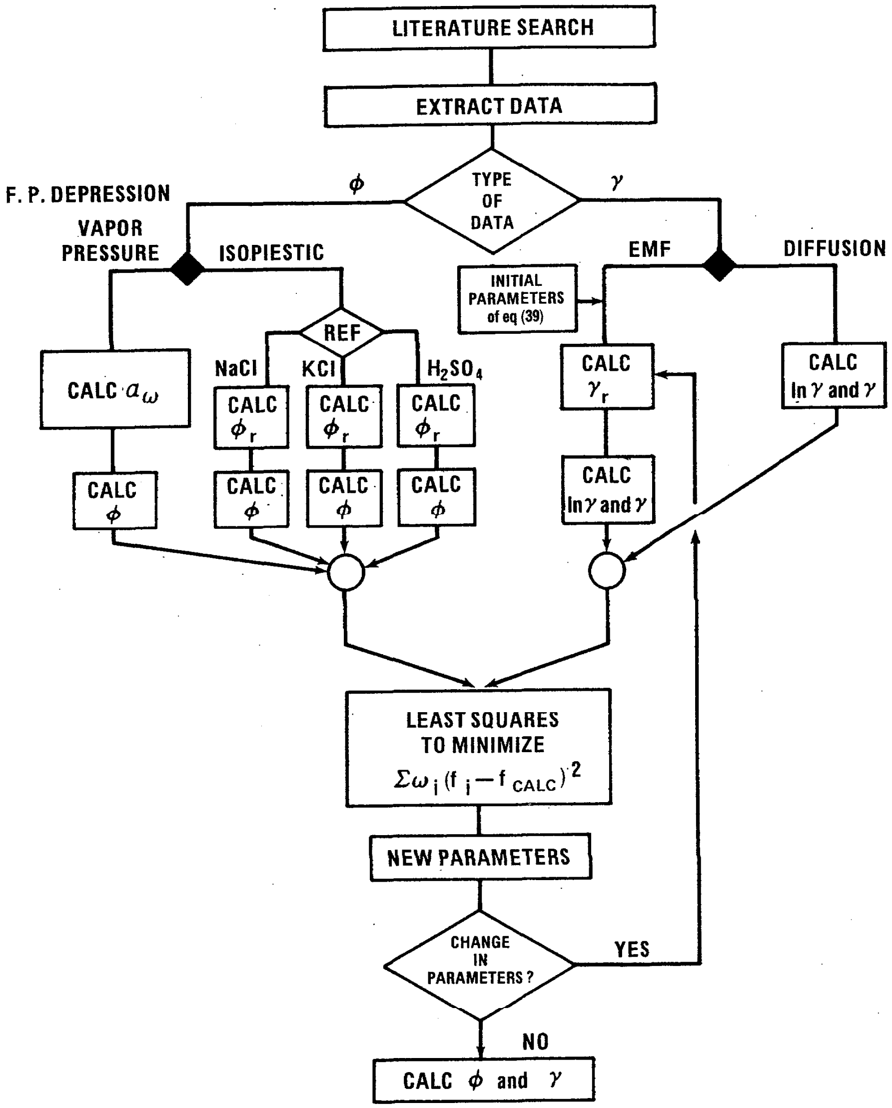

FIGURE 3. Flow diagram of evaluation procedures.

Table 25. Weighting Factors Used for Experimental Data

Type of Measurement	Reference	No. of Points/Weight		σ
Isopiestic				
	Robinson vs KCl [15]	29	1.0	.0046
	Stokes vs NaCl [16]	29	0.9	.0048
	Stokes vs H_2SO_4 [16]	42	0.5	.0065
	Spedding vs KCl [17b]	78	1.0	.0046
	Rard vs H_2SO_4 [17a)	60	0.5	.0065
Vapor Pressure				
	Bechtold [22]	3	0.5	.0065
	Hepburn [23]	5	0.05	.0205
	Petit [25]	9	0.1	.0144
Bithermal equilibration				
	Stokes [27]	4	0.5	.0065
Freezing Point				
	Loomis [53]	6	0.5	.0065
	Gibbard [57]	10	0.5	.0065
	Rodebush [55]	2	0.5	.0065
Emf				
	Sahay [28]	5	0.5	.0065
	Mussini [29]	10	1.0	.0046
	Scatchard [32]	6	0.5	.0065
	Fosbinder [31]	3	0.05	.0205
	Lucasse [30]	3	0.05	.0205
	Shedlovsky [41]	6	1.0	.0046
	McLeod [42]	11	1.0	.0046
	Briggs [40]	5	1.0	.0046
Diffusion				
	Harned [49, 2]	15	1.0	.0046

Table 26. RECOMMENDED VALUES FOR MEAN ACTIVITY COEFFICIENT AND OSMOTIC COEFFICIENT OF $CaCl_2$ IN H_2O AT 298.15 K.

$m/mol\cdot kg^{-1}$	γ	ϕ	a_w	$\Delta G^{ex}/J\cdot kg^{-1}$
.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.
1.500	.6070	1.2004	.907271	-7805.
2.000	.7842	1.3754	.861853	-9199.
2.500	1.0529	1.5660	.809293	-9565.
3.000	1.4550	1.7685	.750702	-8780.
3.500	2.052	1.9781	.6879	-6752.
4.000	2.926	2.1885	.6231	-3422.
4.500	4.176	2.3926	.5588	1233.
5.000	5.907	2.5826	.4976	7197.
5.500	8.199	2.7515	.4414	14419.
6.000	11.072	2.8932	.3913	22810.
6.500	14.461	3.0041	.3481	32258.
7.000	18.215	3.0833	.3115	42632.
7.500	22.149	3.1332	.2808	53798.
8.000	26.112	3.1592	.2551	65631.
8.500	30.07	3.169	.2332	78031.
9.000	34.11	3.171	.2138	90924.
9.500	38.43	3.173	.1961	104272.
10.000	43.12	3.176	.1796	118055.

TABLE 27. STANDARD DEVIATION OF CALCULATED VALUES AT SELECTED MOLALITIES

m	γ	$\sigma(\gamma)$	ϕ	$\sigma(\phi)$	$\ln\gamma$	$\sigma(\ln\gamma)$
.001	.889	0.000	.962	0.000	-.118	0.000
.010	.729	0.000	.908	0.000	-.316	0.000
.100	.517	.001	.852	0.000	-.668	.001
1.000	.496	.002	1.044	.001	-.702	.004
3.000	1.455	.008	1.769	.001	0.375	.005
5.000	5.907	.036	2.583	.002	1.776	.006
7.000	18.21	.108	3.083	.001	2.902	.006
9.000	34.11	.228	3.171	.002	3.530	.007
10.000	43.12	.290	3.177	.003	3.764	.007

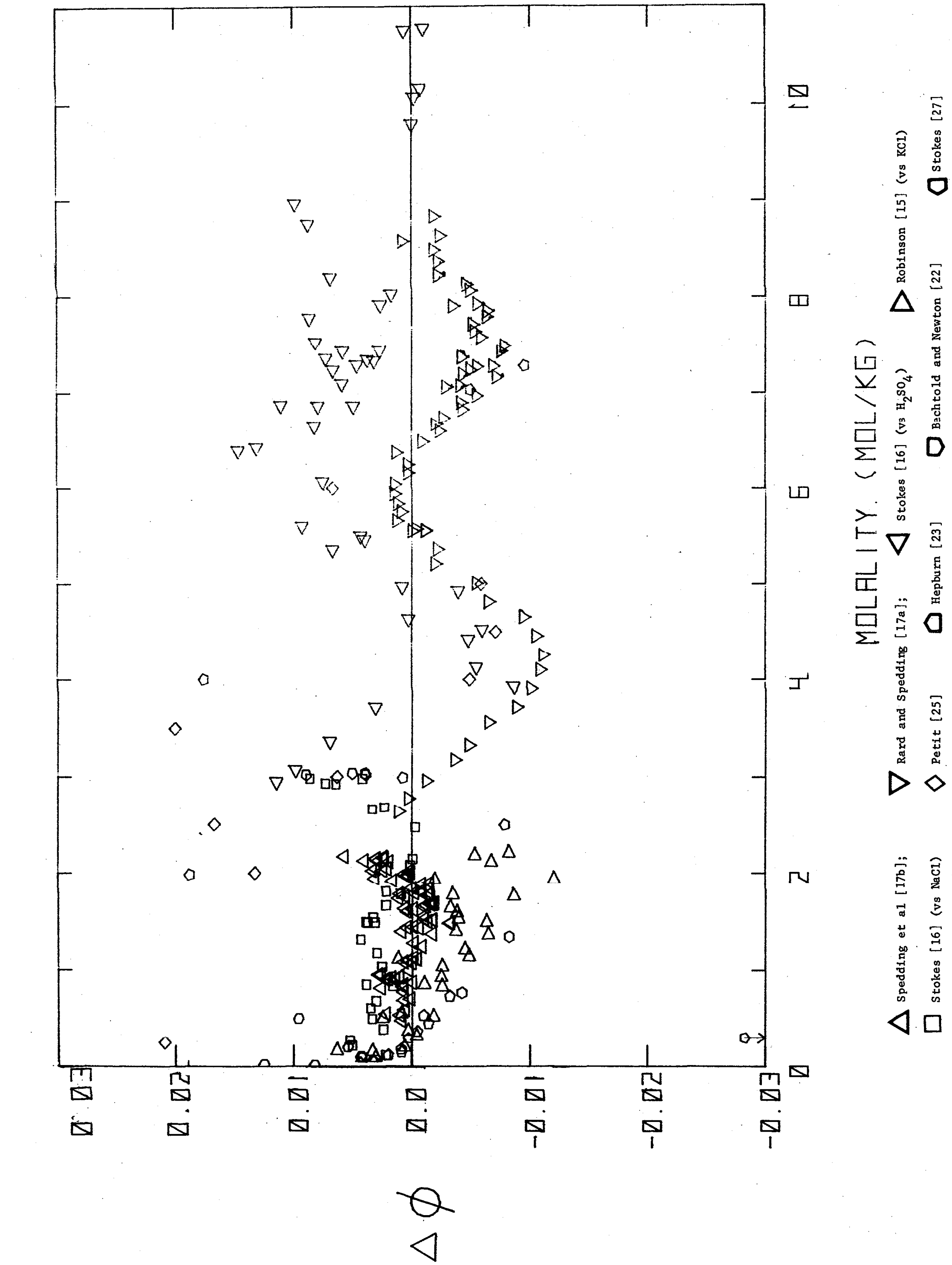

FIGURE 4. Δφ vs molality.

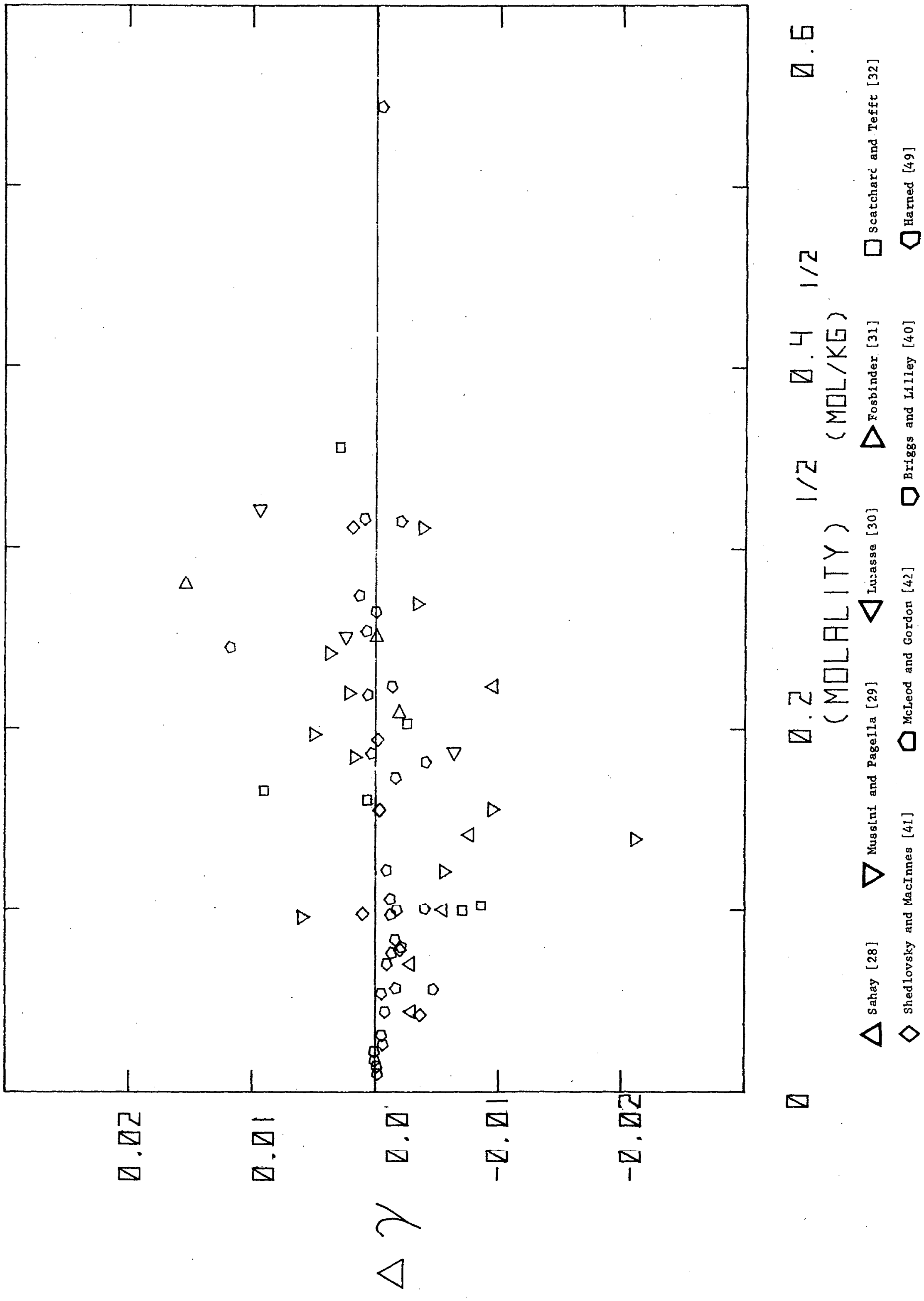

FIGURE 5. Δγ vs molality.$^{1/2}$

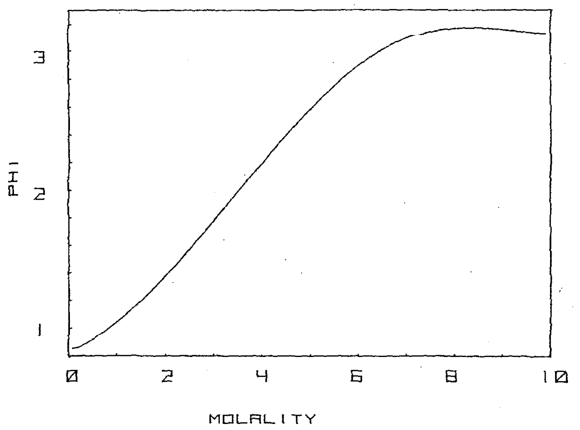

FIGURE 6. Osmotic coefficient vs molality.

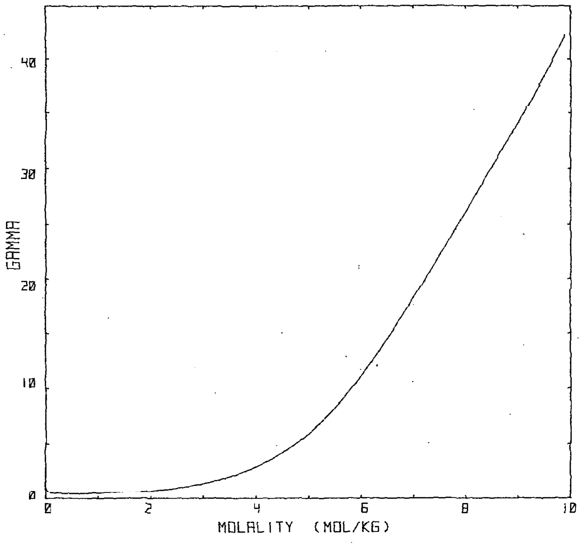

FIGURE 7. Mean activity coefficient vs molality.

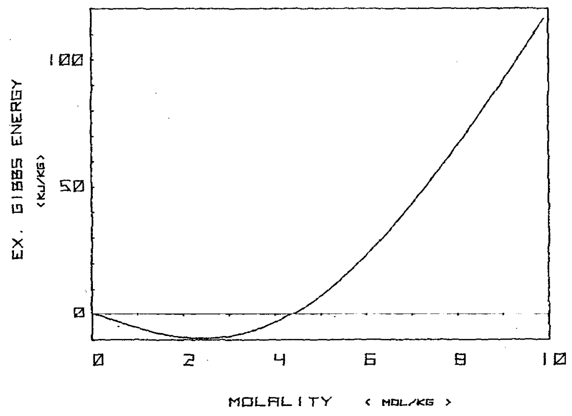

FIGURE 8. Excess Gibbs energy vs molality.

6. Final Recommended Values for the Mean Activity and Osmotic Coefficients of $CaCl_2$ in Water at 298.15 K

Table 26 presents recommended values for ϕ, γ, and ΔG^{ex} at rounded molalities up to 10 mol·kg^{-1}. It should be noted that saturation occurs at 7.28 mol·kg^{-1} [23].

Figures 4 and 5 show a plot of the deviations of the observed values of ϕ and γ, respectively, from the values calculated for the observed concentrations (experimental—calculated).

The osmotic and mean activity coefficients as a function of molality, are illustrated in figs 6 and 7, respectively, and the excess Gibbs energy as a function of molality is shown in fig 8.

The set of mean activity and osmotic coefficients as well as the activities of water given in table 26, together with the equation from which they were calculated; were derived from this present correlation and are recommended for use as a reference source up to a molality of 10 mol·kg^{-1}. The values of the mean activity coefficient, osmotic coefficient, activity of water, and the excess Gibbs energy may be calculated at any molality (0—10 mol·kg^{-1}) from eqs (39, 40, 41) and the parameters *B, C, D, E, F, G, H, I* given in section 5.

Estimates of the standard deviations of the values of the osmotic coefficient calculated from eq (40) and of the mean activity coefficients calculated from eq (39) are illustrated in table 27.

Previously published tabulations of Robinson and Stokes [3], Harned and Owen [2], Pitzer and Brewer [58], Conway [63], and others are in reasonable agreement with table 26, but do not give correlating equations for use in interpolation. Such an equation is especially useful where computer calculations are possible. A data base larger than any of the previous tabulations was used, including available literature through July, 1976.

Such a set of standard values can serve to place all future experimental determinations of activity or osmotic coefficients for polyvalent electrolytes on a single, consistent reference base. Also most theoretical treatments of polyvalent electrolyte data can be tested using this single data source.

Appendix

Several forms of correlating equations, other than that of eqs (39 and 40), give comparable fits to the experimental data. Two of these are given here. The first uses the higher order limiting law, eq (38), followed by an empirical polynomial in the square-root of molality. Here, A_1 and A_2 are calculated coefficients from eq (38) and B_i are adjustable parameters:

$$\ln \gamma = -A_1 I^{1/2} - A_2 I \ln I + \sum_{i=1}^{9} B_i m^{(i+1)/2}, \quad (59)$$

and

$$\phi = 1 - \frac{A_1 I^{1/2}}{3} - \frac{A_2 I}{2}[\ln I + 1/2] + \sum_{i=1}^{9} B_i \frac{(i+1)}{(i+3)} m^{(i+1)/2}; \quad (60)$$

The parameters for eqs (59, 60) are listed below:

Term	Parameters	Standard deviation
$B1$	−1.398192476	0.08
$B2$	21.29097223	0.50
$B3$	−33.10951856	1.2
$B4$	36.59996012	1.6
$B5$	−25.67758601	1.3
$B6$	11.33499774	0.58
$B8$	−3.0486152	0.16
$B8$	0.4550893192	0.025
$B9$	$-2.883352369\times10^{-2}$	0.002

The second uses the Debye-Huckel limiting law followed by an empirical polynomial in square-root of molality:

$$\ln\gamma = -A_1 I^{1/2} + \sum_{i=1}^{8} B_i m^{(i+1)/2} \tag{61}$$

and

$$\phi = 1 - \frac{A_1 I^{1/2}}{3} + \sum_{i=1}^{8} B_i \frac{(i+1)}{(i+3)} m^{(i+1)/2} \tag{62}$$

Parameters for eqs (61,62) are:

Term	Parameters	Standard deviation
$B1$	10.26430765	0.047
$B2$	−18.05044031	0.23
$B3$	21.8426561	0.45
$B4$	−16.79968441	0.46
$B5$	8.13967344	0.27
$B6$	−2.377190479	0.09
$B7$	0.3783336173	0.02
$B8$	$-2.506441862\times10^{-2}$	0.001

In eqs (59, 60) nine parameters were necessary to fit the experimental data. Eight were needed with eqs (61, 62) and eqs (39, 40). The standard deviation for an observation of unit weight for Y (ϕ or $\ln\gamma$) in each set of fitting equations is $\sigma = 0.0045$ for eqs (39, 40), $\sigma = 0.0054$ for eqs (59, 60), and $\sigma = 0.0048$ for eqs (61, 62).

Agreement with Pitzer's equations for predicting ϕ and γ was good.

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7. References

[1] Wu, Y.-C., and Hamer, W. J., Osmotic Coefficients and Mean Activity Coefficients of a Series of Uni-Bivalent and Bi-Univalent Electrolytes in Aqueous Solutions at 25°C, National Bureau of Standards Report (NBSIR) 10052, Part XIV, 1969, 83 p.

[2] Harned, H. S., and Owen, B. B., "The Physical Chemistry of Electrolytic Solutions, "3rd ed., Reinhold Pub. Corp., N. Y., (1958).

[3] Robinson, R. A., and Stokes, R. H., "Electrolyte Solutions," 2nd ed., revised Butterworth and Co., London, (5th impression, 1970).

[4] Hamer, W. J., and Wu, Y.-C., J. Phys. Chem. Reference Data, **1**, 1047 (1972).

[5] Bjerrum, N., Z. Elektrochem, **24**, 321 (1918); Proc. 7th Int. Congr. App. Chem., Sect. X. London, (1909).

[6] Debye, P., and Huckel, E., Physik. Z., **24**, 185 (1923).

[7] Cohen, E. R., and Taylor, B. N., J. Phys. Chem. Reference Data, **2**, 663 (1973).

[8] Malmberg, C. G., and Maryott, A. A., J. Res. Nat. Bur. Stand., **56**, 1 (1956).

[9] Kramers, H. A., Proc. Roy. Acad. (Amsterdam) XXX, 145 (1927).

[10] Kirkwood, J. G., Chem. Rev. **19**,275 (1936).

[11] Kirkwood, J. G., and Poirier, J. C., J. Phys. Chem. **58**, 591 (1954).

[12] Mayer, J. E., J. Chem. Phys. **18**,1426 (1950).

[13] Friedman, H. L., "Ionic Solution Theory" Interscience publishers, N.Y., (1962).

[14] Gibbard, H. F., and Wilson, M. J., J. Phys. Chem. **80**, 89 (1976).

[15] Robinson, R. A., Trans. Faraday Soc., **36**, 735 (1940).

[16] Stokes, R. H., Trans. Faraday Soc., **41**, 637 (1945) and recomputed values in: Stokes, R. H., Trans. Faraday Soc., **44**, 295 (1948).

[17] Rard, J. A., Habenschuss, A., and Spedding, F. H., J. Chem. Eng. Data, **21**, 374 (1976).

[17a] Rard, J. A., and F. H. Spedding, J. Chem. Eng. Data, **22**, 56 (1977).

[17b] Spedding, F. H., H. O. Weber, V. W. Saeger., H. H. Petheram, J. A. Rard, and A. Habenschuss, J. Chem. Eng. Data, **21**, 341 (1976).

[18] Platford, R. F., J. Chem. Eng. Data, **18**, 215 (1973).

[19] Jakli, G., and van Hook, W. A., J. Chem. Eng. Data, **17**, 348 (1972).

[20] Stimson, H. F., J. Res. Nat. Bur. Stand, **73A**, 493 (1969).

[21] Keenan, J. H., Keyes, F. G., Hill, P. G., and Moore, J. G., "Steam Tables", Int'l ed.—Metric Units, John Wiley & Sons, Inc., New York (1969) p. 148.

[22] Bechtold, M. F., and Newton, R. F., J. Am. Chem. Soc., **62**, 1390 (1940).

[23] Hepburn, J. R. I., Pt. IV, J. Chem. Soc., 1284 (1932). a) ibid., Pt. I, p. 550. b) ibid., Pt. II, p. 566. c) ibid., Pt. III, p. 575.

[24] Hepburn, J. R. I., and Garside, J. E., Trans.Faraday Soc., **37**, 473 (1941).

[25] Petit, M. C., J. Chim. Phys. **62**,1119 (1965).

[26] Klimenko, A. P., Mogel'nyi, V. I., and Kryukov, V. A., Chim. Ind., Genie Chim. **103** (5), 591 (1970).

[27] Stokes, R. H., J. Am. Chem. Soc., **69**, 1291 (1947).

[28] Sahay, J. N., Current Sci. (India), **28**, 148 (1959).

[29] Mussini, T., and Pagella, A., J. Chem. Eng. Data, **16**, 49 (1971).

[30] Lucasse, W. W., J. Am. Chem. Soc., **47**, 743 (1925).

[31] Fosbinder, R. J., J. Am. Chem. Soc., **51**, 1345 (1929).

[32] Scatchard, G., and Tefft, R. F., J. Am. Chem. Soc., **52**, 2265 (1930).

[33] Scatchard, G., and Tefft, R. F., J. Am. Chem. Soc., **52**, 2272 (1930).

[34] Tamele, M., J. Phys. Chem., **28**, 502 (1924).

[35] Drucker, C., and Luft, F., Z. phys. Chem., **121**, 307 (1926).

[36] Harned, H. S., J. Am. Chem. Soc., **48**, 326 (1926).

[37] Butler, J. N., unpublished data cited in Interim Report to Office of Saline Water, U. S. Department of the Interior, by Tyco Laboratories, Inc. Waltham, Mass. 02154, June 1, 1965-July 31, 1968, 175 p.

[38] Shibata, F. L. E., J. Sci. Hiroshima Univ., **A1**, 147 (1931).

[39] Huston, R., and Butler, J. N., Anal. Chem. **41**, 200 (1969).

[40] Briggs, C. C., and Lilley, T. H., J. Chem. Thermodynamics, **6**, 599 (1974).

[41] Shedlovsky, T., and MacInnes, D. A., J. Am. Chem. Soc., **59**, 503 (1937).

[42] McLeod, H. G., and Gordon, A. R., J. Am. Chem. Soc., **68**, 58 (1946).

[43] Shedlovsky, T., J. Am. Chem. Soc., **72**, 3680 (1950).

[44] Longsworth, L. G., J. Am. Chem. Soc., **57**, 1185 (1935).

[45] Keenan, A. G., McLeod, H. G., and Gordon, A. R., J. Chem. Phys., **13**, 466 (1945).

[46[Masaki, K., Bull. Chem. Soc. Japan, **7**, 35 (1932).

[47] Haas, K., and Jellinek, K., Z. physik. Chem., **A162**, 153 (1932).

[48] Onsager, L., and Fuoss, R. M., J. Phys. Chem., **36**, 2689 (1932).
[49] Harned, H. S., "The Structure of Electrolyte Solutions", edited by W. J. Hamer, Chap. 10, Wiley & Sons, Inc., N. Y., (1959).
[50] Harned, H. S., and Levy, A. L., J. Am. Chem. Soc., **71**, 2781 (1949).
[51] Harned, H. S., and Parker, H. W., J. Am. Chem. Soc., **77**, 265 (1955).
[52] Roth, W. A., and Scheel, K., ed., Landolt-Bornstein "Physikalisch-Chemische Tabellen," Dritter Erganzungband, Dritter Teil, J. Springer, Berlin, p. 2141, (1936).
[53] Loomis, E. H., Ann. Physik. **60**, 523 (1897).
[54] Washburn, E. W., ed., "International Critical Tables", vol. IV, p. 257, McGraw Hill Book Co, New York, NY (1928).
[55] Rodebush, W. H., J. Am. Chem. Soc., **40**, 1204 (1918).
[56] Ponsot, A., C. R. Hebd. Seances Acad. Sci, **122**, 668 (1896).
[57] Gibbard, H. F., and Fong, S.-L.; J. Solution Chem., **4**, 863 (1975).
[58] Pitzer, K. S., and Brewer, L., "Lewis and Randall, Thermodynamics," 2nd ed., McGraw Hill Book Co., Inc., New York, New York, (1961).
[59] Parker, V. B., Wagman., D. D.; and Evans, W. H., "Selected Values of Chemical Thermodynamic Properties—Tables for the Alkaline Earth Elements", Nat. Bur. Stand. Tech. Note 270-6, U. S. Government Printing Office, Washington, D. C. 20402 (1971).
[60] Perron, G., Desnoyers, J. E., and Millero, F. J., Can. J. Chem., **52**, 3738 (1974).
[61] Longhi, P., Mussini, T., and Vaghi, E., Chim. Ind. (Milan), **57**, 169 (1975).
[62] Staples, B. R. and Nuttall, R. L., "Computer Programs for the Evaluation of Activity and Osmotic Coefficients", Nat. Bur. Stand. Tech. Note 928, U. S. Government Printing Office, Washington, D. C. 20402 (1976).
[63] Conway, B. E., "Electrochemical Data," Greenwood Press Publishers, Westport, Connecticut, lst reprinting (1969).
[64] Plake, E., Z. physik. Chem, **A172**, 113 (1935).
[65] Platford, R. F., J. Solution Chem. **4**, 591 (1975).