Activity and Osmotic Coefficients of Aqueous Sulfuric Acid at 298.15 K

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A critical evaluation of the mean activity coefficient, $\gamma_{\pm}$, and osmotic coefficient, ϕ, of aqueous sulfuric acid at 298.15 K is presented for the molality range of 0 to 28 $\mathrm{mol{\cdot}kg^{-1}}$. 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. A least-squares program was used to fit data from all sources using both ϕ and ln $\gamma_{\pm}$ as functions of molality. A nine parameter equation describes the osmotic coefficient, the mean activity coefficient, and the excess Gibbs energy as a function of the one-half power of molality. The scientific literature has been covered through January, 1980.

Key words: Activity coefficients; aqueous; critical evaluation; electrolytes; excess free energy; free energy; ionic; osmotic coefficients; solutions; sulfuric acid; standard reference data; thermodynamic properties.

Contents

1. Introduction

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 were published in 1958 and 1965, respectively. Wu and Hamer (1969) evaluated activity and osmotic coefficient data for a series of electrolytes in that year but their work on polyvalent electrolytes was not completed. Their results for the 1:1 electrolytes were published in 1972 (Hamer and Wu). The evaluation of polyvalent electrolyte data is continuing in the Electrolyte Data Center at the National Bureau of Standards.

The results for sulfuric acid solutions presented here form a basis of reference for further evaluations, along with NaCl and KCl, (Hamer and Wu, 1972) and $CaCl_2$ (Staples and Nuttall, 1977). This completes the critical evaluation for the four most common reference electrolytes. The recommended values of mean activity and osmotic coefficients for sulfuric acid in aqueous solution at 298.15 K are presented in both tabular form and as equations as functions of molality. The table and equations result from an evaluation and correlation of the experimental data published in the past one hundred and thirty years. Literature through January, 1980 has been considered.

The procedures used in this critical evaluation and correlation of data on activity and osmotic coefficients of sulfuric acid solutions have been detailed in preceding publications (Staples and Nuttall, 1977, 1976 and Goldberg and Nuttall, 1978).

Thermodynamic expressions as well as data treatment methods for each experimental technique have been described in the last three above-mentioned references. The results of this critical evaluation are presented for the activity and osmotic coefficients of aqueous sulfuric acid solutions at 298.15 K, over a range of molalities from 0.001 to 30.0 $\mathrm{mol{\cdot}kg^{-1}}$. Data for more concentrated solutions, greater than 75 weight-percent H_2SO_4 (31 $\mathrm{mol{\cdot}kg^{-1}}$), have not been included in this evaluation due to a larger uncertainty in the experimental results and the small amount of H_2O present compared to H_2SO_4. At 75 weight-percent H_2SO_4 there are 1.8 moles of water per mole of acid.

2. Evaluation Procedure

As a thorough discussion of the entire evaluation procedure has already been referenced, it will only be touched on briefly, here.

0047-2689/81/030779-20/$5.00

First, a compilation 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 files of the NBS Chemical Thermodynamics Data Center (up to 1977), the files of Wu and Hamer (up to 1967), and a computer search of Chemical Abstracts and National Technical Information Services through January, 1980.

The data selected for consideration in this correlation are given in tables 1–39. Reasons for the rejection of certain data are discussed in section 5.

It should be noted that only 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; for isopiestic vapor pressure measurements, the observed isopiestic molalities of H_2SO_4 and the reference salt are the primary data.

All the data were converted to the ^{12}C scale of atomic weights (1971) to be consistent with the NBS Tech. Note 270 series. Where necessary, data corrected to the most recent recommended values of the physical constants (Cohen and Taylor, 1973) with the exception that the "chemically" determined Faraday, 96486.54 C·mol^{-1} was used. It is felt that this value is probably more accurate than the electrically derived value of 1973 (Bower, 1977), though the difference is insignificant for the present application. The 1971 molecular weight that was used for H_2SO_4 in the present review is 98.0776; this has not varied over a hundred-year period by more than about $\pm$ 0.005. Thus, no corrections were considered in the calculation of molalities. A more recent value (1975) is 98.0734, where the atomic weight of sulfur was rounded to 32.06, due to uncertainties in isotopic distribution.

3. Activity of the Solvent

3.1. 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

$$\ln a_1 = \ln (P/P_0) + \frac{B_T(P-P_0)}{RT}, \tag{1}$$

and

$$\phi = -\frac{1000}{\nu m M_1} \ln a_1. \tag{2}$$

where P is the pressure of the water vapor over the solution and P_0 is that over pure water. At 25°C, we take $P_0 = 3168.1$ Pa (23.767 Torr) (Stimson, 1969), and B_T, the second virial coefficient for water, vapor, -922 cm^3·mol^{-1} from the Steam Tables (Keenan et al., 1969). Corrections for nonideality of water vapor are given by the second term on the right of eq (1). The gas constant, R, value of 8.31441 J·mol^{-1}K^{-1} was used. The molecular weight of the solvent, M_1, and the sum of cations and anions, ν, were referenced previously (Staples and Nuttall, 1977).

Early measurements of activities of sulfuric acid solutions included Regnault (1845), Helmholtz (1886), Sorel (1890), Dieterici (1899), Briggs, (1903), Burt (1904),Bronsted (1910) and Hacker (1912). Most of these investigations concerned themselves with vapor pressure measurements on more concentrated solutions, from about 2 to 50 mol·kg^{-1}, over a temperature range of about 0–100°C. None of these results were included in the present evaluation, due to the wide variation of results and a substantial lack of data at 25°C.

Wilson (1921) calculated relative vapor pressures at 25°C from many of the above authors. The calculations produced widely scattered results and are not of the highest order of accuracy. They were not included in the present evaluation.

Daudt (1923) measured vapor pressures at very low temperatures for compositions of 20–60 mol·kg^{-1} H_2SO_4; these data were not considered further, because of the low temperatures. An enlightening discussion of the reliability of all previous data was presented by Greenewalt (1925). He also reports an equation for log p as a function of temperature over the entire composition range of H_2SO_4.

One of the first reliable vapor pressure measurements at 25°C appears in Grollman and Frazer (1925). Thirteen values of the osmotic coefficient, ϕ, have been calcuated from these data and are presented in table 1. The molalities range from 0.1 to 3 mol·kg^{-1}.

McHaffie (1927) determined vapor pressures for high molalities (above 20 mol·kg^{-1}) using a vapor condensation method. These data are represented in table 2.

Hepburn's (1928) results, using a dew point method for 9 solutions from 7 to 12.5 mol·kg^{-1}, are shown as Table 3. These appear to be in some agreement with Bronsted (1910), Dieterici (1897) and Burt (1904) for the composition range of 4–15 mol·kg^{-1}. Hepburn points out that good agreement between McHaffie (1927), Daudt (1923) and Briggs (1903) exists at the higher compositions of 18–60 mol·kg^{-1}.

Approximate vapor pressure measurements on 3 molalities by von Meyeren (1932) were not included in this evaluation due to the large uncertainty in the results.

Vapor pressures of 7 compositions of H_2SO_4 from 4 to 18 mol·kg^{-1} were measured by Collins (1933), between 24–125°C. The results were calculated from relative vapor pressures at 25° and appear in table 4.

Direct vapor pressure measurements were made by Shankman and Gordon (1939) for 20 compositions from 2–23 mol·kg^{-1} and these results appear in table 5.

Abel (1946) presents vapor pressures of H_2SO_4 from 2.5 to over 90 mol·kg^{-1}. The data for these 11 points are shown in table 6.

An absorption method was employed by Jones (1951) to calculate the vapor pressure of H_2SO_4 at rounded molalities from 0.5 to 55 mol·kg^{-1}. His results are tabulated in table 7.

Deno and Taft (1954) used the Hammett relation to calculate the activity of water in aqueous H_2SO_4, but the measurements have not been included in the present evaluation because all molalities exceeded 30 mol·kg^{-1}.

Another set of direct vapor pressure measurements were performed by Hornung and Giauque (1955) on 3 solutions (14–28 mol·kg^{-1}) as a function of temperature. The resulting osmotic coefficients appear in table 8.

3.2. Isopiestic Measurements

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

$$\phi = \frac{(\nu m\phi)_r}{\nu m}. \tag{3}$$

Scatchard, Hamer, and Wood (1938) determined the isopiestic ratios of H_2SO_4 and both NaCl (32 points) and KCl (23 points), from 01. to 4.5 mol·kg^{-1}. These results are presented in tables 9 and 10, respectively.

Sheffer, Janis, and Ferguson (1939) also employed the isopiestic method to determine the activities of 19 pairs of solutions of H_2SO_4 using NaCl as reference. The average values for each pair of 19 compositions from 0.02 to 4.4 mol·kg^{-1} are presented in table 11.

Robinson (1939) has used KCl as a reference to determine the isopiestic ratios of 53 solutions from 0.2 to 3 mol·kg^{-1}. Agreement with Scatchard, Hamer, and Wood (1938) was reported. Robinson's results are tabulated in table 12. Robinson (1945) also has determined isopiestic ratios of H_2SO_4/NaCl and the resulting osmotic coefficients are calculated in table 13.

Stokes (1945a) measured the isopiestic molalities of H_2SO_4 and $CaCl_2$. His results appear in table 14. The 32 molalities of H_2SO_4 ranged from 4.3 to 15.4 mol·kg^{-1}.

Sodium hydroxide was used as a reference by Stokes (1945b) in the isopiestic determinations for 33 data sets of H_2SO_4 from 1.6 to 21.6 mol·kg^{-1}. Table 15 contains the recalculated osmotic coefficients based on the Hamer-Wu (1972) evaluation of NaOH. A set of standard values for water activity in H_2SO_4 was proposed by Stokes (1947) but these values were based on previous works and were not included in this present evaluation.

Rard and Spedding (1977) have carefully determined the isopiestic molalities of 60 solutions of H_2SO_4 using $CaCl_2$ as a reference. Their equilibration times of 4 days or more were generally double those used by previous investigators, and a higher degree of precision was observed. The molalities range from 3.8 to 13.3 mol·kg^{-1}; those data are presented in table 16.

Recently Rard and Miller (1977, 1978) have made available unpublished isopiestic data using KCl as a reference. Their results agree well with the values calculated by eq (11), see table 17, in the range 0.1 to 3 mol·kg^{-1} for the 17 points.

Glueckauf and Kitt (1956) used a bithermal isopiestic method to determine osmotic coefficients between 20 and 65 mol·kg^{-1}. These authors added a constant correction of 0.08 in the values of $(m_2 - m_1)$ to bring their results into agreement with others. The Clausius-Clapeyron relationship was used to construct a curve of osmotic coefficient values at 25°C. Because of the necessity of the inexplicable correction, the uncertainties in the thermal data, the quoted uncertainty of 1 percent in the activty data and the smoothing of the data reported, these results were not used.

3.3. Freezing Point and Other Measurements

The solvent activities of each of the six sets of freezing point data were calculated at the reference temperature 273.15 K and then corrected to 298.15 K by the method detailed in the previous publications, (Goldberg and Nuttall, 1978 and Staples and Nuttall, 1977). The relative apparent molal enthalpy, ϕ_L, was calculated from the heats of dilution tabulated in NBS Tech Note 270-3 (Wagman et al., 1968). These data can be described over the range of 0.0002–2.8 mol·kg^{-1} as a function of $m^{1/2}$ by the two equations

$$\phi_L = \sum_{i=1}^{8} B_i m^{i/2} \tag{4}$$

Table 1. Vapor Pressure Measurements
Grollman & Frazer (1925)

m/ mol·kg^{-1}	a_w	Φ
0.0730*	0.99748	0.6400
0.2410	0.99155	0.6513
0.3150	0.98890	0.6554
0.5490	0.98029	0.6710
0.6360	0.97701	0.6767
0.8920	0.96675	0.7014
1.0970	0.95818	0.7206
1.2820	0.94986	0.7425
1.6710	0.93006	0.8029
1.7720	0.92493	0.8149
2.0090	0.91232	0.8452
2.4680	0.88659	0.9025
2.8710	0.85972	0.9741

Table 2. Vapor Pressure Measurements
McHaffie (1927)

m/ mol·kg^{-1}	a_w	Φ
19.7043*	0.07596	2.4203
19.7043*	0.07537	2.4276
32.2874*	0.01268	2.5029
32.2874*	0.01243	2.5144
32.2874*	0.01239	2.5163
39.2992*	0.00666	2.3597
51.5980*	0.00346	2.0325

Table 3. Vapor Pressure Measurements
Hepburn (1928)

m/ mol·kg^{-1}	a_w	Φ
7.3259*	0.52130	1.6453
7.9431	0.48385	1.6911
8.3557	0.45481	1.7447
8.5432	0.44176	1.7694
9.2102*	0.39841	1.8488
9.9741*	0.35547	1.9197
10.8050	0.32305	1.9349
11.6090	0.28263	2.0140
12.5732	0.24389	2.0765

Table 4. Vapor Pressure Measurements
Collins (1933)

m/ mol·kg^{-1}	a_w	Φ
1.1329	0.95605	0.7340
2.5490	0.88013	0.9268
3.3987	0.82518	1.0461
4.3697	0.75224	1.2055
5.4902	0.66328	1.3836
6.7973	0.56531	1.5526
8.3422	0.46132	1.7160
10.1960	0.35729	1.8677
12.4618	0.25824	2.0101
15.2940	0.16618	2.1712
18.9354	0.09711	2.2786
23.7907	0.03705	2.5631

Table 5. Vapor Pressure Measurements
Shankman & Gordon (1939)

m/ mol·kg^{-1}	a_w	Φ
1.9190	0.91750	0.8307
2.2390	0.89961	0.8742
3.6590	0.80500	1.0969
3.7760	0.79661	1.1143
4.2180	0.76293	1.1870
4.2790	0.75383	1.1933
4.3390	0.75414	1.2033
4.9470	0.70545	1.2997
5.4540	0.66818	1.3678
5.8330	0.63819	1.4246
6.6710	0.57461	1.5368
7.5400	0.51132	1.6450
8.3330	0.45451	1.7404
9.4000	0.39370	1.8342
10.1350	0.35390	1.8959
11.2350	0.29957	1.9852
12.7200	0.24063	2.0721
15.1200	0.15593	2.1911
20.6500	0.07208	2.3554
22.6300	0.05385	2.3885

Table 6. Vapor Pressure Measurements
Abel (1946)

m/ mol·kg^{-1}	a_w	Φ
12.4618 *	0.25989	2.0007
15.2940 *	0.16851	2.1544
17.3608 *	0.08426	2.6365
18.9354 *	0.09479	2.3022
23.7907 *	0.04171	2.4708
30.5880 *	0.01854	2.4123
40.7840 *	0.00590	2.3287
57.7774 *	0.00164	2.0531
91.7641 *	0.00032	1.6211
193.7242 *	0.00003	1.0110

Table 7. Vapor Pressure Measurements
Jones (1951)

m/ mol·kg^{-1}	a_w	Φ
1.1329 *	0.95805	0.6999
2.5490	0.88213	0.9104
4.3697	0.74924	1.2224
6.7973	0.56331	1.5622
8.3422	0.45931	1.7256
10.1960	0.35229	1.8933
12.4618	0.24724	2.0748
15.2940	0.15817	2.2310
18.9354	0.09311	2.3198
23.7907	0.04505	2.4109
30.5880 *	0.01702	2.4639
40.7840 *	0.00401	2.5044

Table 8. Vapor Pressure Measurements
Hornung & Giauque (1955)

m/ mol·kg^{-1}	a_w	Φ
13.8800	0.20199	2.1323
18.5089	0.09918	2.3101
27.7400	0.02604	2.4333

Table 9. Isopiestic Vapor Pressure Measurements
Scatchard, Hamer & Wood (1935) Ref. salt : NaCl

m_r	$Φ_r$	$Φ/Φ_r$	m/ mol·kg^{-1}	Φ
0.09918	0.9329	0.72699	0.09095*	0.6782
0.09930	0.9329	0.72891	0.09082*	0.6800
0.10014	0.9328	0.73532	0.09079*	0.6859
0.10288	0.9324	0.72926	0.09405*	0.6799
0.20120	0.9237	0.72204	0.18577*	0.6669
0.20432	0.9235	0.72101	0.18892*	0.6659
0.20603	0.9234	0.72268	0.19006*	0.6674
0.21275	0.9231	0.72165	0.19654*	0.6662
0.30303	0.9207	0.72367	0.27916*	0.6663
0.30922	0.9206	0.72426	0.28463*	0.6668
0.40034	0.9203	0.72884	0.36619	0.6707
0.40846	0.9203	0.72772	0.37419	0.6697
0.50503	0.9213	0.73182	0.46089	0.6742
0.51709	0.9215	0.73274	0.47046	0.6752
0.68788	0.9252	0.73705	0.62219	0.6819
0.99954	0.9356	0.75154	0.88666	0.7031
1.00100	0.9356	0.75049	0.88920	0.7022
1.16140	0.9421	0.76592	1.01090	0.7215
1.62200	0.9635	0.79213	1.36510	0.7632
2.08450	0.9884	0.81434	1.70650	0.8049
2.41350	1.0078	0.83148	1.93510	0.8380
2.50220	1.0133	0.83415	1.99980	0.8452
3.39110	1.0719	0.86874	2.60230	0.9312
3.73900	1.0966	0.88086	2.82980	0.9659
4.25850	1.1348	0.89649	3.16680	1.0173
4.60130	1.1608	0.90514	3.38900	1.0506
5.45930	1.2274	0.92635	3.92890	1.1370
6.07810	1.2761	0.93917	4.31450	1.1985
6.14610	1.2815	0.93672	4.37420	1.2004
6.14290	1.2812	0.93660	4.37250	1.2000
6.14510	1.2814	0.93627	4.37560	1.1997
6.14300	1.2812	0.93629	4.37400	1.1996

Table 10. Isopiestic Vapor Pressure Measurements
Scatchard, Hamer & Wood (1935) Ref. salt : KCl

m_r	$Φ_r$	$Φ/Φ_r$	m/ mol·kg^{-1}	Φ
0.10098	0.9264	0.74019	0.09095*	0.6857
0.10027	0.9266	0.73603	0.09082*	0.6820
0.10059	0.9265	0.73863	0.09079*	0.6843
0.10380	0.9259	0.73578	0.09405*	0.6812
0.20444	0.9128	0.73367	0.18577*	0.6697
0.20715	0.9126	0.73100	0.18892*	0.6671
0.20893	0.9125	0.73286	0.19006*	0.6687
0.21584	0.9119	0.73213	0.19654*	0.6676
0.30896	0.9060	0.73783	0.27916*	0.6685
0.31486	0.9057	0.73747	0.28463*	0.6680
0.40838	0.9022	0.74348	0.36619	0.6708
0.41783	0.9020	0.74442	0.37419	0.6714
0.51923	0.8997	0.75105	0.46089	0.6757
0.53045	0.8995	0.75168	0.47046	0.6762
0.70998	0.8978	0.76073	0.62219	0.6830
1.03990	0.8984	0.78189	0.88666	0.7024
1.04270	0.8984	0.78175	0.88920	0.7023
1.72280	0.9070	0.84135	1.36510	0.7631
2.24600	0.9173	0.87743	1.70650	0.8049
2.62320	0.9261	0.90373	1.93510	0.8370
2.72730	0.9287	0.90919	1.99980	0.8444
3.79160	0.9585	0.97135	2.60230	0.9310
4.22100	0.9717	0.99442	2.82980	0.9663

Table 11. Isopiestic Vapor Pressure Measurements
Scheffer, Janis & Ferguson (1939) Ref. salt : NaCl

m_r	$Φ_r$	$Φ/Φ_r$	m/ mol·kg^{-1}	Φ
0.02423	0.9557	0.86105	0.01876*	0.8229
0.05095	0.9437	0.74636	0.04551	0.7043
0.10415	0.9322	0.72515	0.09575*	0.6760
0.20315	0.9236	0.72001	0.18810*	0.6650
0.30890	0.9206	0.71841	0.28665	0.6614
0.41600	0.9203	0.72185	0.38420	0.6643
0.56750	0.9224	0.72805	0.51965	0.6716
0.70655	0.9257	0.73593	0.64005	0.6813
0.81700	0.9291	0.74261	0.73345	0.6899
0.99590	0.9354	0.75276	0.88200	0.7041
1.20100	0.9437	0.76582	1.04550	0.7227
1.48700	0.9568	0.78212	1.26750	0.7484
1.85900	0.9759	0.80268	1.54400	0.7834
2.77000	1.0302	0.84593	2.18300	0.8715
3.72900	1.0958	0.87360	2.82950	0.9623
4.23000	1.1327	0.89363	3.15550	1.0122
5.25500	1.2114	0.91843	3.81450	1.1126
6.14440	1.2813	0.94200	4.34850	1.2070

Table 12. Isopiestic Vapor Pressure Measurements
Robinson (1939) Ref. salt : KCl

m_r	Φ_r	Φ/Φ_r	$m/\ \mathrm{mol\cdot kg^{-1}}$	Φ
0.21400	0.9120	0.73313	0.19460*	0.6686
0.24340	0.9098	0.73324	0.22130*	0.6671
0.33850	0.9028	0.74106	0.34950	0.6691
0.40360	0.9024	0.89689	0.30000	0.8093
0.40360	0.9024	0.74451	0.36140	0.6718
0.54460	0.8993	0.75138	0.48320	0.6757
0.66470	0.8981	0.75970	0.58330	0.6823
0.72680	0.8977	0.75993	0.63760	0.6822
0.82000	0.8976	0.76984	0.71010	0.6910
0.92450	0.8978	0.77938	0.79080	0.6997
1.02200	0.8983	0.78621	0.86660	0.7062
1.07500	0.8986	0.79032	0.90690	0.7102
1.17600	0.8995	0.80098	0.97880	0.7205
1.22600	0.9000	0.80525	1.01500	0.7247
1.23800	0.9001	0.80599	1.02400	0.7255
1.27500	0.9005	0.80875	1.05100	0.7283
1.41300	0.9022	0.81842	1.15100	0.7384
1.46800	0.9030	0.82588	1.18500	0.7457
1.65400	0.9058	0.83789	1.31600	0.7590
1.72800	0.9071	0.84211	1.36800	0.7638
1.85800	0.9094	0.85073	1.45600	0.7737
2.04300	0.9131	0.86688	1.57500	0.7916
2.11900	0.9146	0.86826	1.62700	0.7941
2.36700	0.9200	0.88851	1.77600	0.8175
2.52200	0.9237	0.89767	1.87300	0.8291
2.52400	0.9237	0.89838	1.87300	0.8298
2.65200	0.9268	0.90620	1.95100	0.8399
2.91600	0.9336	0.92220	2.10800	0.8610
2.93700	0.9342	0.92055	2.12700	0.8599
3.06600	0.9376	0.92783	2.20300	0.8700
3.22100	0.9419	0.94058	2.28300	0.8859
3.25200	0.9428	0.94179	2.30200	0.8879
3.27000	0.9433	0.94454	2.30800	0.8910
3.45000	0.9484	0.95357	2.41200	0.9044
3.45100	0.9484	0.95384	2.41200	0.9047
3.55700	0.9515	0.95773	2.47600	0.9113
3.62300	0.9535	0.95923	2.51800	0.9146
3.67800	0.9551	0.96384	2.54400	0.9206
3.84600	0.9602	0.97528	2.62900	0.9364
3.86300	0.9607	0.97587	2.63900	0.9375
3.86400	0.9607	0.97539	2.64100	0.9371
3.92500	0.9626	0.98250	2.66300	0.9459
3.98900	0.9645	0.98640	2.69600	0.9514
4.01000	0.9652	0.98611	2.71100	0.9518
4.08700	0.9676	0.98827	2.75700	0.9562
4.11600	0.9685	0.98812	2.77700	0.9570
4.17100	0.9702	0.99310	2.80000	0.9635
4.29300	0.9740	0.99860	2.86600	0.9727
4.31000	0.9746	1.00221	2.86700	0.9767
4.61000	0.9841	1.01631	3.02400	1.0002
4.62900	0.9847	0.98594	3.13000	0.9709
4.62900	0.9847	1.01781	3.03200	1.0023
4.81000	0.9906	1.02778	3.12000	1.0181
4.84100	0.9916	1.02912	3.13600	1.0205

Table 13. Isopiestic Vapor Pressure Measurements
Robinson (1945) Ref. salt : NaCl

m_r	Φ_r	Φ/Φ_r	$m/\ \mathrm{mol\cdot kg^{-1}}$	Φ
2.62158	1.0207	0.83900	2.08310	0.8564
4.00610	1.1160	0.88873	3.00510	0.9919
4.22946	1.1326	0.89527	3.14950	1.0140
4.62753	1.1628	0.90573	3.40610	1.0531
4.86450	1.1810	0.91180	3.55670	1.0768
4.88860	1.1829	0.91193	3.57380	1.0787
5.41799	1.2242	0.92603	3.90050	1.1336
5.48069	1.2291	0.92607	3.94550	1.1382
5.64446	1.2420	0.92993	4.04650	1.1549
6.09928	1.2778	0.94033	4.32420	1.2015
6.12865	1.2801	0.93967	4.34810	1.2029
6.14655	1.2915	0.94120	4.35370	1.2062

Table 14. Isopiestic Vapor Pressure Measurements
Stokes (1945a) Ref. salt : $CaCl_2$

m_r	Φ_r	Φ/Φ_r	$m/\ \mathrm{mol\cdot kg^{-1}}$	Φ
2.95100	1.7483	0.68168	4.32900	1.1918
3.07200	1.7984	0.67965	4.52000	1.2223
3.36200	1.9199	0.67442	4.98500	1.2948
3.71500	2.0689	0.66805	5.56100	1.3821
3.92900	2.1588	0.66605	5.89900	1.4379
4.12600	2.2408	0.66154	6.23700	1.4824
4.42200	2.3615	0.65589	6.74200	1.5489
4.52500	2.4025	0.65428	6.91600	1.5719
4.63500	2.4456	0.65135	7.11600	1.5929
4.92300	2.5564	0.64748	7.61100	1.6552
4.96700	2.5707	0.64616	7.68700	1.6611
5.36600	2.7087	0.64026	8.30100	1.7343
5.47300	2.7430	0.63959	8.55700	1.7544
5.51100	2.7549	0.63918	8.62200	1.7609
5.61100	2.7355	0.63754	8.80100	1.7758
6.06400	2.9092	0.63517	9.54700	1.8478
6.39400	2.9832	0.63363	10.09100	1.8903
6.42500	2.9895	0.63388	10.13600	1.8950
6.64000	3.0294	0.63504	10.45600	1.9238
6.86100	3.0644	0.63610	10.78600	1.9493
6.86200	3.0645	0.63655	10.78000	1.9507
6.87400	3.0663	0.63572	10.81300	1.9493
7.09200	3.0946	0.63806	11.11500	1.9745
7.23300	3.1100	0.63924	11.31500	1.9880
7.28600	3.1152	0.64008	11.38300	1.9940
7.32600	3.1189	0.64072	11.43400	1.9984
7.34100	3.1203	0.64080	11.45600	1.9995
7.35400	3.1214	0.64042	11.48300	1.9990
7.43000	3.1278	0.64151	11.58200	2.0065
7.43100	3.1279	0.64199	11.57500	2.0081
7.52500	3.1350	0.64234	11.71500	2.0139
7.77500	3.1500	0.64571	12.04100	2.0340
7.91400	3.1561	0.64874	12.19900	2.0475
8.02300	3.1600	0.65064	12.33100	2.0560
8.19300	3.1644	0.65272	12.55200	2.0655
8.74900	3.1706	0.66235	13.20900	2.1000
8.96300	3.1711	0.66600	13.45300	2.1120
9.78500	3.1749	0.68039	14.37100	2.1617
10.07100	3.1769	0.68506	14.70100	2.1763
10.15900	3.1772	0.68642	14.80000	2.1809
10.75000	3.1653	0.69674	15.42900	2.2057
10.77100	3.1646	0.69751	15.44200	2.2074

Table 15. Isopiestic Vapor Pressure Measurements
Stokes (1945b) Ref. salt : NaOH

m_r	Φ_r	Φ/Φ_r	$m/\ \mathrm{mol\cdot kg^{-1}}$	Φ
1.98800	1.0223	0.79219	1.67300	0.8099
2.11500	1.0320	0.79571	1.77200	0.8212
2.32200	1.0481	0.80290	1.92800	0.8415
3.24000	1.1264	0.83430	2.58900	0.9397
3.86500	1.1865	0.84759	3.04000	1.0057
4.00000	1.2002	0.84899	3.14100	1.0190
4.38200	1.2405	0.85294	3.42500	1.0581
4.64700	1.2698	0.85604	3.61900	1.0870
5.68200	1.3931	0.86563	4.37600	1.2059
6.35800	1.4807	0.86840	4.88100	1.2858
6.50900	1.5009	0.86752	5.00200	1.3021
6.69300	1.5258	0.86742	5.14400	1.3235
7.83800	1.6866	0.86284	6.05600	1.4553
8.80300	1.8264	0.85487	6.86500	1.5614
10.03700	2.0045	0.84306	7.93700	1.6899
10.92700	2.1283	0.83310	8.74400	1.7731
12.55100	2.3346	0.81808	10.22800	1.9099
13.62100	2.4514	0.80789	11.24000	1.9805
15.60100	2.6189	0.79827	13.02900	2.0906
18.14000	2.7388	0.80184	15.08200	2.1960
19.59600	2.7667	0.80722	16.18400	2.2334
19.64200	2.7673	0.80861	16.19400	2.2376
21.98600	2.7722	0.82201	17.83100	2.2788
23.87200	2.7607	0.83806	18.99000	2.3136
23.89600	2.7605	0.83793	19.01200	2.3131
25.82600	2.7434	0.85646	20.10300	2.3496
26.31600	2.7372	0.86228	20.34600	2.3602
26.69300	2.7312	0.86583	20.55300	2.3648
26.80200	2.7293	0.86734	20.60100	2.3672
26.91200	2.7272	0.86715	20.69000	2.3649
27.26200	2.7195	0.87043	20.88000	2.3672
27.44700	2.7149	0.87341	20.95000	2.3712
28.74500	2.6629	0.88514	21.65000	2.3571

Table 16. Isopiestic Vapor Pressure Measurements
Rard & Spedding (1976) Ref. salt : $CaCl_2$

m_r	Φ_r	Φ/Φ_r	m/ mol·kg^{-1}	Φ
8.82540	3.1708	0.66416	13.28800	2.1059
8.62250	3.1699	0.66063	13.05200	2.0941
8.56260	3.1695	0.65907	12.99200	2.0889
8.47360	3.1688	0.65789	12.88000	2.0847
8.35570	3.1673	0.65586	12.74000	2.0773
8.21070	3.1648	0.65335	12.56700	2.0678
8.11960	3.1627	0.65218	12.45000	2.0626
8.05960	3.1611	0.65123	12.37600	2.0586
7.92340	3.1565	0.64914	12.20600	2.0490
7.90190	3.1557	0.64849	12.18500	2.0464
7.84960	3.1535	0.64814	12.11100	2.0439
7.79020	3.1508	0.64724	12.03600	2.0393
7.71170	3.1467	0.64593	11.93900	2.0326
7.63870	3.1425	0.64494	11.84400	2.0268
7.57790	3.1387	0.64421	11.76300	2.0220
7.48760	3.1323	0.64338	11.63800	2.0153
7.42580	3.1275	0.64259	11.55600	2.0097
7.36310	3.1222	0.64139	11.48000	2.0025
7.27200	3.1138	0.64082	11.34800	1.9954
7.27010	3.1136	0.64059	11.34900	1.9946
7.23440	3.1101	0.64016	11.30100	1.9910
7.18740	3.1052	0.63962	11.23700	1.9862
7.16060	3.1023	0.63980	11.19200	1.9849
7.07170	3.0922	0.63859	11.07400	1.9746
7.05700	3.0904	0.63830	11.05600	1.9726
6.96920	3.0793	0.63803	10.92300	1.9647
6.89560	3.0693	0.63736	10.81900	1.9563
6.82460	3.0591	0.63698	10.71400	1.9486
6.73750	3.0456	0.63633	10.58800	1.9380
6.66620	3.0339	0.63597	10.48200	1.9295
6.59260	3.0211	0.63580	10.36900	1.9208
6.48280	3.0008	0.63538	10.20300	1.9067
6.36900	2.9781	0.63500	10.03000	1.8911
6.24260	2.9510	0.63524	9.82710	1.8746
6.15630	2.9313	0.63542	9.68850	1.8626
6.04160	2.9036	0.63563	9.50490	1.8456
5.94380	2.8788	0.63605	9.34490	1.8310
5.84220	2.8517	0.63665	9.17650	1.8155
5.76090	2.8291	0.63723	9.04060	1.8028
5.66770	2.8023	0.63786	8.88550	1.7875
5.58260	2.7769	0.63881	8.73900	1.7739
5.57030	2.7732	0.63905	8.71660	1.7722
5.56300	2.7709	0.63911	8.70430	1.7709
5.55920	2.7698	0.63897	8.70020	1.7698
5.37390	2.7113	0.64115	8.38170	1.7383
5.22250	2.6608	0.64286	8.12380	1.7105
5.00840	2.5857	0.64625	7.75000	1.6710
4.81640	2.5149	0.64927	7.41820	1.6329
4.65540	2.4535	0.65238	7.13600	1.6006
4.45730	2.3756	0.65602	6.79450	1.5584
4.25580	2.2942	0.65987	6.44950	1.5138
4.10220	2.2310	0.66280	6.18920	1.4787
3.91050	2.1511	0.66650	5.86720	1.4337
3.71520	2.0689	0.67029	5.54270	1.3868
3.56130	2.0040	0.67302	5.29150	1.3487
3.32630	1.9048	0.67763	4.90870	1.2908
3.17460	1.8412	0.68059	4.66450	1.2531
2.95810	1.7512	0.68459	4.32100	1.1989
2.77480	1.6761	0.68804	4.03290	1.1532
2.63410	1.6193	0.69073	3.81350	1.1185

Table 17. Isopiestic Vapor Pressure Measurements
Rard & Miller (1977,1978) Ref. salt : KCl

m_r	Φ_r	Φ/Φ_r	m/ mol·kg^{-1}	Φ
0.15337	0.9182	0.72758	0.14053	0.6681
0.16182	0.9172	0.72803	0.14817	0.6678
0.17348	0.9159	0.72912	0.15862	0.6678
0.18574	0.9146	0.73041	0.16953	0.6680
3.63300	0.9538	0.96199	2.51770	0.9175
3.70360	0.9559	0.96599	2.55600	0.9234
3.93970	0.9630	0.97875	2.68350	0.9426
4.03250	0.9659	0.98308	2.73460	0.9495
4.14390	0.9693	0.98912	2.79300	0.9588
4.20140	0.9711	0.99127	2.82560	0.9627
4.32180	0.9749	0.99713	2.88950	0.9721
4.33520	0.9754	0.99828	2.89510	0.9737
4.39310	0.9772	1.00046	2.92740	0.9776
4.42540	0.9782	1.00220	2.94380	0.9804
4.48820	0.9802	1.00701	2.97130	0.9871
4.53830	0.9818	1.00915	2.99810	0.9908
4.78920	0.9899	1.01954	3.13160	1.0093

The values of the parameters for eq (4) for ϕ_L for in J·mol^{-1} are:

Molality range:	0.14 – 2.78 mol·kg^{-1}	2×10^{-4} – 0.14 mol·kg^{-1}
Term	Parameter	Parameter
B1	$1.586369\cdot10^5$	$1.539690\cdot10^4$
B2	$-6.124691\cdot10^5$	$0.0416204\cdot10^8$
B3	$14.478857\cdot10^5$	$-0.645883\cdot10^8$
B4	$-21.389212\cdot10^5$	$4.866484\cdot10^8$
B5	$19.721989\cdot10^5$	$-20.856582\cdot10^8$
B6	$-10.987938\cdot10^5$	$51.486445\cdot10^8$
B7	$3.376785\cdot10^5$	$-68.087565\cdot10^8$
B8	$-0.4387609\cdot10^5$	$37.331143\cdot10^8$
	($\sigma = 32$ J·mol^{-1}, about 0.2%)	($\sigma = 28$ J·mol^{-1}, about 0.5%)

The relative apparent molal heat capacity, ϕ_C, in $J{\cdot}K^{-1}{\cdot}mol^{-1}$, taken from Craig and Vinal (1940) and Giauque, Hornung, Kunzler, and Rubin (1960) over the range from about 0.03 to 2.5 $mol{\cdot}kg^{-1}$ is described by the equation

$$\phi_C = \phi^{\circ}_C + Am^{1/2} + Bm$$
$$= -52.95 + 150.51m^{1/2} - 38.11m \qquad (5)$$

Here, $\sigma = 1.9$ J or about 1–2 percent.

The derivatives of eqs (4) and (5) are then used to calculate $\bar{L}_1$ and $\bar{J}_1$ values. The osmotic coefficients, obtained at 273.15 K, are used to calculate values at 298.15 K, using the integrated form of the Gibbs-Helmholtz equation:

$$\phi_{25^{\circ}C} = \phi_{0^{\circ}C} - \frac{1000}{\nu m M_1}\left[\frac{-25\bar{L}_1}{R\,(298.15)(273.15)} + \frac{J_1(25)}{R\,(273.15)} - \frac{\bar{J}_1}{R}\ln\frac{298.15}{273.15}\right] \qquad (6)$$

which is derived on the assumption that $\bar{J}_1$ is constant over the temperature range of interest (Goldberg and Nuttall, 1978).

The above authors emphasize that both accurately measured freezing point depressions and thermal data, Φ_L and Φ_C, are required to obtain accurate values of the osmotic coefficient at both 273.15 and 298.15 K. The error in the calculated values of the osmotic coefficients due to any error in the thermal data becomes larger as the concentrations of the solutions increases.

Jones et al. (1907) has reported freezing point measurements for 16 molalities between 0.1 and 6.4 $mol{\cdot}kg^{-1}$. The results are presented in table 18 up to 3 $mol{\cdot}kg^{-1}$, as the thermal properties eqs (4,5) are only useful below this molality. Jones has reported similar results in 1902 for 9 concentrations (0.1 to 2.8 $mol{\cdot}kg^{-1}$) and in 1893 for 11 more dilute solutions, 0.001 to 0.1 $mol{\cdot}kg^{-1}$, tables 19 to 20, respectively.

The freezing points of Barnes (1892) for 7 solutions (0.01–0.3 $mol{\cdot}kg^{-1}$) were also quoted by Jones but these results are identical to those of Jones (1893).

Five freezing points were reported by Loomis (1893). These data are listed in table 21 for the molalities 0.01 to 0.2 $mol{\cdot}kg^{-1}$. Loomis also reported identical data in articles appearing in 1894 (*a* and *b*).

Roth and Knothe have determined freezing point depressions at 3 molalities below 0.1 $mol{\cdot}kg^{-1}$, and table 22 shows the resulting osmotic coefficients from their unpublished data quoted in Landolt-Börnstein Tabellen (1960).

About 90 measurements of freezing points of H_2SO_4 solutions ranging from 5×10^{-4} to 0.4 $mol{\cdot}kg^{-1}$ were made by Pickering (1891,1892). His results are summarized in tables 23 and 24. These measurements did not appear to be of the highest quality in that the temperatures were reported to only 3 significant figures and a very large scatter was observed for the calculated osmotic coefficients. His third set of experimental data seemed to be best, in that this set agreed with the present evaluation more closely than the first two sets, but this was still of poor precision.

The freezing point method was used by Hausrath (1902) for 8 molalities in the dilute range from 1×10^{-4} to 0.02 $mol{\cdot}kg^{-1}$. These results are shown in table 25.

The five measurements of Bedford (1910) for the range 0.001 to 0.008 $mol{\cdot}kg^{-1}$ appear in table 26 but were not included in the least squares fit, because of extreme deviations.

Randall and Scott (1927) have determined freezing points of 33 solutions from 0.001 to 0.1 $mol{\cdot}kg^{-1}$. Their results are presented in table 27.

Freezing point depressions were measured by Kunzler and Giauque (1952), but all molalities were above 30 $mol{\cdot}kg^{-1}$ and thus were omitted from this evaluation.

4. Electromotive Force Measurements

4.1. Electrochemical Cells

Electromotive force (emf) measurements have been confined mainly to 5 electrochemical cells. The first cell, A, is

$$\text{Pt};\ H_2,\ H_2SO_4(m),\ PbSO_4,\ PbO_2;\ \text{Pt}. \qquad (A)$$

The cell reaction can be written as

$$H_2 + H_2SO_4 + PbO_2 \rightleftarrows 2H_2O + PbSO_4.$$

Its emf is given by the Nernst equation

$$E = E^0 - \frac{RT}{2F}\ln\frac{4(m\gamma)^3}{a^2_w}. \qquad (7)$$

The next two cells, B and C, are

$$\text{Pt};\ H_2,\ H_2SO_4(m),\ Hg_2SO_4,\ Hg;\ \text{Pt} \qquad (B)$$

and

$$\text{Pt};\ H_2,\ H_2SO_4(m),\ Ag_2SO_4;\ Ag \qquad (C)$$

with the similar reactions.

$$(B)\ H_2 + Hg_2SO_4 \rightleftarrows 2Hg + H_2SO_4$$

and

$$(C)\ H_2 + Ag_2SO_4 \rightleftarrows 2Ag + H_2SO_4,$$

have the same emf expression

$$E = E^0 - \frac{RT}{2F}\ln 4(m\gamma)^3. \qquad (8)$$

A fourth cell, D,

$$\text{Pt};\ PbSO_4,\ PbO_2,\ H_2SO_4(m_r),\ H_2SO_4(m),\ Hg_2SO_4;\ Hg, \qquad (D)$$

for which the reaction can be written as

$$2Hg + 2H_2SO_4 + PbO_2 \rightleftarrows Hg_2SO_4 + PbSO_4 + 2H_2O$$

and its emf is given by

$$E - E^0 - \frac{RT}{F}\ln\frac{4(m\gamma)^3}{a_w} \qquad (9)$$

Cell E uses a lead amalgam electrode

$$\text{Pb-Hg (2 phase)},\ PbSO_4,\ H_2SO_4(m),\ H_2,$$

and has the reaction $Pb + H_2SO_4 \rightleftarrows PbSO_4 + H_2$.

The emf of this cell is given by eq (8) also.

4.2. Electromotive Force Measurements

Utilizing cell B, Randall and Cushman (1918) measured the free energy of dilution for 7 mole fractions corresponding to 0.005 to 8.2 mol·kg^{-1}. The results were given only to the nearest 0.1 mV but are in good agreement with all emf measurements. These data appear in table 28. The data of Lewis and Lacey (1914), Bronsted (1910) and Edgar (1918) were quoted by Randall and Cushman but were not used in this evaluation because each represented 2 data points and in one case data was given only to the nearest mV. Harned and Sturgis (1925) report emfs for only 2 compositions as did Randall and Langford (1927) and both of these were also omitted from this evaluation.

Vosburgh and Craig (1929) calculated and measured the potentials of cell D. The emfs of solutions from 0.05 to 3.5 mol·kg^{-1} were measured and the resulting activity coefficients are shown in table 29.

The emf of cell B was measured with varying additions of acetic acid by MacDougall and Blumer (1933). These authors also report measurements for 6 solutions where no acetic acid was added. These molalities vary from 0.05 to 2.2 mol·kg^{-1} and the data are presented in table 30.

Similarly, Trimble, and Ebert (1933) report measurements of cell B with ethylene glycol additions. Table 31 lists the data for 6 compositions from 0.005 to 1 mol·kg^{-1}, for which there was no ethylene glycol added.

Activity coefficients of H_2SO_4 have been determined as a function of temperature for 5 dilute solutions (0.001 to 0.02 mol·kg^{-1}) by Shrawder and Cowperthwaite (1934) and these results are tabulated in table 32. They employed cell E with a lead amalgam electrode.

In 1935, Hamer determined the emf of cell A for compositions of 0.005 to 7 mol·kg^{-1} and in a companion publication, Harned and Hamer (1935) reported emfs of cell B over a concentration range of 0.05 to 17.5 mol·kg^{-1}. These data are presented in tables 33 and 34, respectively. Both sets of measurements were carried out over a temperature range of 0–60°C.

About 25 years later, the behavior of both cell A and B over the temperature range 5–55°C was painstakingly reinvestigated by Beck, Singh, and Wynne-Jones (1959) (cell A), Beck, Dobson and Wynne-Jones (1960) (cell B), and again in 1965 by Covington, Dobson, and Wynne-Jones (cells A, B, and C). The data for cell A (1959) is listed in table 35 for 12 molalities from 0.1 to 8.3 mol·kg^{-1}. The emfs for two of these molalities were measured in an air thermostat, the remainder in a water thermostat. Data for the nine molalities from 0.1 to 8 mol·kg^{-1} for cell B (1960) are presented in table 36.

Tables 37 and 38 reflect the dilute region data for the cells A and B, respectively. Covington et al. (1965) report data for the composition range of 0.007 to 0.1 mol·kg^{-1} and 5 data sets for cell A (table 37), 13 data sets for cell B (table 38) and 7 data points for cell C, which are shown in table 39. Four of the points in table 38 were measured using a glass electrode in place of the H_2 electrode in cell B. Good agreement between the hydrogen and glass electrodes was observed.

The remarkable consistency among nearly all of the emf measurements over a 50 year period as well as the interrelations of calorimetric data and derived thermochemical quantities from these data and the emf data will be discussed in the section 5.

Ferguson and France (1921) determined transference numbers for only two H_2SO_4 solutions and these data were not included in the present evaluation.

4.3. Other Activity Coefficient Calculations

Duisman and Giauque (1968) used a variety of data sources to derive thermodynamic quantities for the lead storage cell and a set of emf values from third law considerations. The third law method was also used by Gardner, Mitchell and Cobble (1969) to calculate a set of activity coefficients as a function of temperature.

Wirth (1971) presents a summary of emf measurements of H_2SO_4 solutions and uses the dissociation of the bisulfate ion to calculate activity coefficients.

Recently, Lilley and Briggs (1975), employed earlier emf data (Shrawder and Cowperthwaite, 1934) to calculate activity coefficients in the dilute region of 0.001 to 0.02 mol·kg^{-1}.

Pitzer (1976) and Pitzer, Roy and Silvester (1977) have taken into account the dissociation of the HSO_4^- ion to describe some of the thermodynamic properties of sulfuric acid solutions. These treatments are, for the most part, consistent with the present results.

None of the results of these indirect methods were included in the present evaluation, but all played a role in the critical evaluation process.

5. Correlation of Results

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 resulting from the Gibbs-Duhem equation and the definitions of activity and the osmotic coefficient (Staples and Nuttall, 1977). The Gibbs-Duhem equation provides a relationship between activity coefficients, which are a measure of solute activity, and osmotic coefficients, which are a measure of solvent activity.

When the Debye-Huckel limiting law was included as the initial term, a negative distance of closest approach, "α" (size parameter), was obtained and it was not possible to fit the sulfuric acid data to an equation of the form of either a Hamer-Wu or a Friedman type, discussed by Staples and Nuttall (1977).

This does not indicate a failure of the Debye-Huckel model but rather that the lack of data in the extremely dilute region makes the fit by certain correlating equations mathematically impossible. Certain choices could have been made to fix the "α" value in the Debye expression. For example, the denominator in the limiting law could have been chosen as $(1 + I^{1/2})$ or $(1 + 1.51I^{1/2})$, but it was felt that such a restriction would distort the curve slightly, so that the data that were available might not be fit well over the entire concentration range for which measurements were made. Attempts to fix the limiting slope did result in a larger standard deviation of the correlating equations.

Accordingly, only an equation describing ϕ or ln γ vs molality, terms of a polynomial expressed in powers in the square root of molality, is presented. The dependence of both $1 - \phi$ and γ on the half power of concentration is well recognized (e.g., Pitzer and Brewer, 1961, p. 334 and others). The empirical equation

$$\ln\gamma = \sum_{j=1}^{9} B_j m^{j/2} \tag{10}$$

has been chosen to correlate the experimental data. Reasons for the choice of an equation which does not include the Debye-Huckel limiting law are discussed later.

The osmotic coefficient and excess Gibbs energy can be expressed in terms of the same parameters (Staples and Nuttall, 1977) by

$$\phi = 1 + \sum_{j=1}^{9}\left(\frac{j}{j+2}\right)B_j m^{j/2} \tag{11}$$

and

$$\Delta G^{ex} = \nu mRT\sum_{j=1}^{9}\left(\frac{2}{j+2}\right)B_j m^{j/2} \tag{12}$$

Values for the parameters of these equations are determined by a least squares fit of experimental data using eq (10) for experiments such as galvanic cell measurements that measure solute activity and yield values of γ, and eq (11) for experiments such as vapor pressure measurements that measure solvent activity and yield values of ϕ. All the original data were used in a single fitting program to determine the best values for the parameters.

The equations which accurately describe the data over the range of molalities from about 0.001 to 28 mol·kg^{-1} are eqs (10) and (11) and the parameters and their standard deviations for these equations are presented in table 40.

A set of parameters for eqs (10) and (11) was calculated by a non-linear least-squares method minimizing $\Sigma w_i [f_{\mathrm{Obs}} - f_{(\mathrm{calc})}]^2$ where the function, $f_{\mathrm{obs}} = \ln\gamma$, or $f_{\mathrm{obs}} = \phi$, and f_{calc} was obtained from eq (10) or (11), respectively. The weight assigned is w_i. The summation extends over all experimental points.

Initially, parameters were obtained from only osmotic coefficient data and then, eq (10) was used to calculate γ_r and, where necessary, a_w, reference values (eq [11]) to be used in the emf calculations. Then values of m, lnγ, from emf measurements, were combined with m, ϕ data obtained from vapor pressure, freezing point and isopiestic methods, and new parameters were determined. Using these parameters a new set of γ_r, and a_w were calculated and the fitting procedure repeated. The parameters remained essentially unchanged after two iterations. This procedure has been described (Staples and Nuttall, 1977) and all computer programs have been documented (Staples and Nuttall, 1976).

Initially all the experimental data were weighted equally and included in the fitting procedure. The data were divided into sets according to source and the root-mean-square deviation of the points of each set from the curve obtained in the intial fit was taken as an estimate of the standard deviation of the set. Using weights inversely proportional to these estimates of standard deviations additional fits of the data were made. The results of these calculations together with a subjective evaluation of experimental procedures were used to arrive at final weights for the experimental points.

Data were weighted zero when deviations in γ (ϕ or lnγ) were beyond a reasonable value, generally 0.015 (more than twice the standard deviation of the fit) or about 1 percent of the calculated value of ϕ of lnγ. Sometimes it was necessary to weight individual points zero and such points are indicated by an asterisk in the data tables (1–39). Generally, individual points that were weighted zero occurred either at the most dilute or most concentrated end of the experimenter's range.

Many of the more dilute or more concentrated data in the emf measurements received zero weight due to electrode solubility. This was done to avoid introducing errors while correcting for solubility, since these solutions more resemble mixed electrolyte systems when the electrode solubility affects the emf.

In all, about 645 individual data points were considered worth processing. Of these data, 515 were based on osmotic coefficients derived from activities of the solvent and 380 of these osmotic coefficients received non-zero weights. Of the remaining 130 activity coefficients, 95 received non-zero weights. Thus, a total of 510 data points comprised the final least-squares calculations. Table 41 lists the weighting factor used for each set of experimental data.

The vapor pressure results of Collins (1933), Grollman and Frazer (1925), Hornung and Giauque (1955), and Shankman and Gordon (1939) were all weighted equally at the highest weight of one.

The data of Hepburn (1928) received a weight of 0.1 and Jones (1951) a weight of 0.2. The remaining vapor pressure measurements of Abel (1946), McHaffie (1927) and von Meyeren (1932) were assigned zero weight due to the very large deviations from the majority of results and the extremely high concentrations encountered.

Many of the isopiestic measurements were weighted high. These include Robinson (1939), Scheffer, Janis, and Ferguson (1939), Stokes (1945a,b), Robinson (1945), Rard and Spedding (1977), and Rard and Miller (1977,1978). Only the data of Scatchard, Hamer, and Wood (1938) received a lower weight of 0.5.

Table 18. Freezing Point Measurements. Jones et al (1907)

m/(mol/kg)	θ/K	L /(J/mol)	J /(J/mol)	Φ (0°C)	Φ (25°C)
0.1005*	0.397	-4.315	0.050	0.7074	0.6737
0.2021	0.770	-6.879	0.151	0.6818	0.6520
0.3038	1.156	-9.092	0.290	0.6804	0.6515
0.4066	1.570	-10.644	0.465	0.6899	0.6619
0.6151	2.440	-12.978	0.914	0.7030	0.6798
0.8279*	3.300	-17.639	1.492	0.7085	0.6781
1.0395*	4.189	-25.399	2.179	0.7132	0.6781
1.5892*	7.443	-45.511	4.450	0.8171	0.7729
2.1652*	11.296	-100.009	7.538	0.8853	0.8232
2.7680*	16.275	-91.462	11.503	0.9713	0.9122
3.0596*	21.000	361.987	13.682	1.2098	1.2513

Table 19. Freezing Point Measurements. Jones (1902)

0.1005*	0.397	-4.315	0.050	0.7074	0.6737
0.2021*	0.817	-6.879	0.151	0.7284	0.6936
0.3038	1.173	-9.092	0.290	0.6904	0.6616
0.4066	1.593	-10.644	0.465	0.7000	0.6720
0.5102	2.032	-11.751	0.673	0.7109	0.6836
1.0395*	4.190	-25.399	2.179	0.7134	0.6783
1.5892*	7.443	-45.511	4.450	0.8171	0.7729
2.1652*	11.296	-100.009	7.538	0.8853	0.8232
2.7680*	16.275	-91.462	11.503	0.9713	0.9122

Table 20. Freezing Point Measurements. Jones (1893)

0.001348*	0.0070	-0.053	0.000	0.9700	0.9431
0.003591	0.0184	-0.192	0.000	0.9182	0.8809
0.005825	0.0293	-0.348	0.001	0.9013	0.8596
0.008053	0.0388	-0.508	0.001	0.8633	0.8191
0.010270	0.0487	-0.667	0.001	0.8497	0.8040
0.013480	0.0623	-0.892	0.002	0.8281	0.7815
0.035500*	0.1575	-2.156	0.010	0.7948	0.7508
0.056790	0.2330	-3.019	0.021	0.7345	0.6954
0.077360	0.3087	-3.675	0.033	0.7147	0.6784
0.097250	0.3838	-4.229	0.048	0.7067	0.6727
0.177000	0.4543	-4.745	0.064	0.6952	0.6628

Table 21. Freezing Point Measurements. Loomis (1893)

0.0100*	0.04493	-0.648	0.001	0.8051	0.7596
0.0200*	0.08619	-1.316	0.004	0.7721	0.7253
0.0500*	0.20652	-2.771	0.017	0.7399	0.6990
0.1005*	0.39679	-4.315	0.050	0.7070	0.6733
0.2021*	0.76996	-6.879	0.151	0.6818	0.6519
0.2021*	0.76996	-6.879	0.151	0.6818	0.6519
0.1005*	0.39700	-4.315	0.050	0.7074	0.6737
0.3038*	1.15600	-9.092	0.290	0.6804	0.6515

Table 22. Freezing Point Measurements. Roth and Knothe (1960)

m/(mol/kg)	θ/K	L /(J/mol)	J /(J/mol)	Φ (0° C)	Φ (25° C)
0.03142	0.136	-1.956	0.003	0.7755	0.7321
0.06489*	0.265	-3.292	0.003	0.7315	0.6964
0.10770*	0.425	-4.504	-0.004	0.7068	0.6785

Table 23. Freezing Point Measurements. Pickering (1891)

0.0026925*	0.016	-0.167	0.000	1.0649	1.0220
0.0052945*	0.026	-0.378	0.000	0.8800	0.8305
0.0078672*	0.038	-0.565	0.001	0.8655	0.8157
0.0103288*	0.052	-0.725	0.001	0.9021	0.8534
0.0143046*	0.062	-0.966	0.001	0.7766	0.7296
0.0157158*	0.067	-1.052	0.002	0.7639	0.7173
0.0733023*	0.297	-3.554	0.003	0.7257	0.6923
0.0841741*	0.334	-3.871	0.001	0.7107	0.6792
0.1054873*	0.417	-4.447	-0.003	0.7080	0.6795
0.1250917	0.484	-4.952	-0.010	0.6930	0.6666
0.1436174	0.558	-5.422	-0.017	0.6959	0.6711
0.1653676	0.633	-5.970	-0.029	0.6856	0.6625
0.1853065	0.705	-6.467	-0.042	0.6814	0.6596
0.0026925	0.014	-0.167	0.000	0.9818	0.8889
0.0052945*	0.028	-0.378	0.000	0.9477	0.8982
0.0078672*	0.035	-0.565	0.001	0.7972	0.7474
0.0103288	0.049	-0.725	0.001	0.9501	0.8013
0.0143046	0.067	-0.966	0.001	0.8392	0.7922
0.0157158	0.072	-1.052	0.002	0.8209	0.7743
0.0210062	0.093	-1.384	0.002	0.7932	0.7473
0.0265172	0.116	-1.697	0.003	0.7837	0.7329
0.0313263	0.137	-1.951	0.003	0.7835	0.7401
0.0364430	0.155	-2.200	0.003	0.7619	0.7198
0.0415748	0.177	-2.430	0.004	0.7627	0.7220
0.0527401	0.217	-2.874	0.004	0.7370	0.6992
0.0630419	0.254	-3.232	0.003	0.7217	0.6862
0.0733023	0.294	-3.554	0.003	0.7184	0.6850
0.0841741	0.332	-3.871	0.001	0.7065	0.6749
0.1054873	0.412	-4.447	0.003	0.6995	0.6710
0.1250917	0.480	-4.952	-0.010	0.6873	0.6609
0.1436174	0.550	-5.422	-0.017	0.6859	0.6612
0.1653676	0.627	-5.970	-0.029	0.6791	0.6560
0.1853065	0.699	-6.467	-0.042	0.6756	0.6538
0.2076572	0.798	-7.013	-0.060	0.6797	0.6591
0.2610071	0.891	-8.235	-0.113	0.6046	0.5868
0.2943597	1.100	-8.914	-0.155	0.6595	0.6534
0.3162074	1.190	-9.316	-0.186	0.6748	0.6593
0.3689276	1.370	-10.151	-0.272	0.6656	0.6532
0.4211840*	1.530	-10.816	-0.374	0.6726	0.6629

Table 24. Freezing Point Measurements. Pickering (1892)

m/(mol/kg)	θ/K	L /(J/mol)	J /(J/mol)	Φ (0°C)	Φ (25°C)
0.0005098*	0.0041	-0.013	0.000	1.4411	1.4236
0.0010197*	0.0042	-0.040	0.000	0.7881	0.7108
0.0015194*	0.0089	-0.074	0.000	1.0497	1.0158
0.0020192*	0.0118	-0.112	0.000	1.0472	1.0087
0.0025854*	0.0123	-0.154	0.000	0.8680	0.8259
0.0030393*	0.0170	-0.196	0.000	1.0023	0.9578
0.0040902*	0.0220	-0.282	0.000	0.9638	0.9161
0.0051414*	0.0271	-0.367	0.000	0.9445	0.8952
0.0071014*	0.0381	-0.512	0.001	0.9614	0.9114
0.0081531*	0.0400	-0.584	0.001	0.8791	0.8294
0.0091540*	0.0469	-0.650	0.001	0.9180	0.8688
0.0101658*	0.0479	-0.714	0.001	0.8443	0.7955
0.0122499*	0.0611	-0.842	0.001	0.8937	0.8459
0.0143046*	0.0676	-0.966	0.001	0.8467	0.7998
0.0162477*	0.0745	-1.084	0.002	0.8216	0.7751
0.0182938*	0.0830	-1.211	0.002	0.8129	0.7668
0.0204738*	0.0921	-1.350	0.002	0.8060	0.7601
0.0246830*	0.1095	-1.594	0.002	0.7948	0.7493
0.0286085*	0.1268	-1.810	0.003	0.7941	0.7500
0.0329885*	0.1451	-2.034	0.003	0.7880	0.7450
0.0364480*	0.1578	-2.200	0.003	0.7756	0.7336
0.0409684*	0.1747	-2.403	0.004	0.7639	1.7231
0.0461717*	0.1955	-2.621	0.004	0.7585	0.7190
0.0510714*	0.2147	-2.811	0.004	0.7531	0.7148
0.1234517*	0.4848	-4.910	-0.009	0.7034	0.6768
0.1441731*	0.5612	-5.436	-0.018	0.6972	0.6725
0.1653886*	0.6408	-5.970	-0.029	0.6939	0.6708
0.1864376*	0.7186	-6.495	-0.043	0.6903	0.6686

Table 25. Freezing Point Measurements. Hausrath (1902)

0.0001150*	0.000564	-0.001	0.000	0.8789	0.8732
0.0003315*	0.001580	-0.006	0.000	0.8541	0.8412
0.0006458*	0.003179	-0.019	0.000	0.8821	0.8616
0.0013390	0.007026	-0.061	0.000	0.9403	0.9086
0.0022430	0.011550	-0.130	0.000	0.9228	0.8826
0.0041750	0.021020	-0.289	0.000	0.9022	0.8542
0.0094200	0.045070	-0.667	0.001	0.8573	0.8081
0.0164600	0.075690	-1.097	0.002	0.8239	0.7775

Table 26. Freezing Point Measurements. Bedford (1902)

m/(mol/kg)	θ/K	L /(J/mol)	J /(J/mol)	Φ (0°C)	Φ (25°C)
0.001*	0.00537	-0.039	0.000	0.9623	0.9853
0.002*	0.01024	-0.111	0.000	0.9175	0.8792
0.004*	0.01928	-0.275	0.000	0.8637	0.8161
0.006*	0.02832	-0.432	0.000	0.8458	0.7959
0.008*	0.03704	-0.574	0.001	0.8296	0.7799

Table 27. Freezing Point Measurements. Randall and Scott (1927)

0.0041400	0.020888	-0.230	0.000	0.9041	0.8656
0.0060200	0.029714	-0.362	0.000	0.8845	0.8427
0.0009760	0.005232	-0.034	0.000	0.9606	0.9364
0.0031240	0.015978	-0.161	0.000	0.9165	0.8398
0.0051260	0.025620	-0.299	0.000	0.8955	0.8552
0.0063320	0.031211	-0.385	0.000	0.8833	0.8411
0.0076490	0.036970	-0.479	0.001	0.8662	0.8226
0.0007826	0.004208	-0.025	0.000	0.9636	0.9413
0.0011087	0.005936	-0.041	0.000	0.9595	0.9340
0.0023097	0.011934	-0.109	0.000	0.9259	0.8932
0.0045200	0.022578	-0.256	0.000	0.8951	0.8558
0.0074880	0.036349	-0.468	0.001	0.8698	0.8264
0.0111160	0.052222	-0.727	0.001	0.8418	0.7963
0.0166120	0.076345	-1.101	0.002	0.8234	0.7773
0.0220140	0.098742	-1.439	0.002	0.8036	0.7581
0.0357780	0.154080	-2.169	0.003	0.7715	0.7293
0.0541600*	0.224830	-2.925	0.004	0.7436	0.7061
0.1055900*	0.420960	-4.449	-0.003	0.7141	0.6855
0.1282000*	0.507490	-5.031	-0.011	0.7090	0.6829
0.1051600*	0.419270	-4.438	-0.003	0.7141	0.6855
0.0009783*	0.005308	-0.034	0.000	0.9723	0.9480
0.0013135	0.006993	-0.051	0.000	0.9541	0.9270
0.0017968	0.009374	-0.078	0.000	0.9349	0.9048
0.0028863	0.014831	-0.145	0.000	0.9208	0.8859
0.0068080*	0.027652	-0.419	0.001	0.7278	0.6851
0.0122910*	0.048756	-0.809	0.001	0.7108	0.6650
0.0009289	0.004990	-0.032	0.000	0.9627	0.9389
0.0011841	0.006293	-0.045	0.000	0.9524	0.9263
0.0019566	0.010187	-0.088	0.000	0.9330	0.9020
0.0312230	0.135880	-1.946	0.003	0.7797	0.7362
0.0390920	0.166860	-2.321	0.003	0.7647	0.7233
0.0694940*	0.282590	-3.438	0.003	0.7284	0.6942
0.1012600	0.403680	-4.335	-0.002	0.7140	0.6850

Table 28. Emf Measurements
Randall and Cushman (1918) Cell B

m/mol·kg^{-1}	E/V	γ/γ_r	γ
0.005001 *	-0.061521	2.02572	0.6592
0.049997	0.000000	1.00000	0.3254
0.050569	0.000100	0.99125	0.3226
0.504900	0.058520	0.45208	0.1471
1.031280	0.079427	0.38075	0.1239
3.536800	0.135846	0.46677	0.1519
3.206420	0.203969	1.21160	0.3943

m_r = 0.049997 γ_r = 0.3254

Table 29. Emf Measurements
Vosburgh and Craig (1929) CELL D

m/ mol·kg^{-1}	E/ V	γ/γ_r	γ	a_w
0.053550	0.030910	0.83822	0.2101	0.997997
0.100000	0.000000	1.00001	0.2506	0.996437
0.103500	-0.002101	1.02024	0.2557	0.996319
0.257900	-0.048316	1.35346	0.3392	0.990966
0.510400	-0.084429	1.73445	0.4347	0.981496
1.036000	-0.126243	2.49181	0.6244	0.960006
1.065000	-0.128644	2.57752	0.6459	0.958754
1.964000	-0.174959	4.50692	1.1294	0.915167
2.206000	-0.185763	5.25833	1.3177	0.901623
3.499000	-0.237580	11.90747	2.9840	0.816725

m_r = 0.100000 γ_r = 0.2506

Table 30. Emf Measurements
MacDougall and Blumer (1933) Cell B

m/mol·kg^{-1}	E/V	γ/γ_r	γ
0.050400	0.000000	1.00000	0.3238
0.136900	0.025409	0.71181	0.2305
0.274100	0.042915	0.55993	0.1813
0.547200	0.061521	0.45454	0.1472
1.093000	0.083228	0.39969	0.1294
1.642000	0.098933	0.39991	0.1295
2.184000 *	0.112638	0.42906	0.1399

m_r = 0.050400 γ_r = 0.3238

Table 31. Emf Measurements
Trimble and Ebert (1933) Cell B

m/mol·kg^{-1}	E/V	γ/γ_r	γ
0.005000 *	-0.061621	2.02107	0.6562
0.025000 *	-0.019206	1.21503	0.3945
0.050000	0.000000	1.00000	0.3247
0.250000	0.039413	0.55614	0.1806
0.500000	0.059420	0.46732	0.1517
1.000000	0.080227	0.40093	0.1302

m_r = 0.050000 γ_r = 0.3247

Table 32. Emf Measurements
Shrawder and Cowperthwaite (1934) Cell E

m/ mol·kg^{-1}	E/ V	γ/γ_r	γ	a_w
0.001000 *	0.090511	1.91105	0.8483	0.999950
0.002000 *	0.067443	1.73853	0.7717	0.999902
0.005000 *	0.038933	1.45709	0.6468	0.999768
0.010000	0.018936	1.22389	0.5433	0.999560
0.020000	0.000000	1.00000	0.4439	0.999175

m_r = 0.020000 γ_r = 0.4439

Table 33. Emf Measurements
Hamer (1935) Cell A

m/ mol·kg^{-1}	E/ V	γ/γ_r	γ	a_w
0.000500 *	0.157391	3.37585	0.8460	0.999974
0.000700 *	0.145499	3.28296	0.8227	0.999964
0.001000 *	0.133107	3.16964	0.7943	0.999950
0.002000 *	0.109810	2.90071	0.7269	0.999902
0.003000 *	0.096728	2.71536	0.6805	0.999857
0.005000 *	0.081016	2.44911	0.6137	0.999768
0.007000 *	0.071086	2.26341	0.5672	0.999683
0.010000 *	0.060503	2.08439	0.5225	0.999560
0.020000 *	0.040860	1.73504	0.4348	0.999175
0.030000 *	0.029926	1.53577	0.3849	0.998812
0.050000 *	0.016572	1.30248	0.3264	0.998117
0.070000	0.008135	1.15751	0.2901	0.997442
0.100000	-0.000685	1.01795	0.2551	0.996437
0.200000	-0.018217	0.80033	0.2006	0.993019
0.500000	-0.042119	0.59078	0.1481	0.981899
1.000000	-0.062745	0.49743	0.1247	0.961551
1.500000	-0.078242	0.48800	0.1223	0.938906
2.000000	-0.089186	0.47728	0.1196	0.913203
3.000000	-0.111514	0.54215	0.1359	0.851736
4.000000	-0.132239	0.65628	0.1645	0.779527
5.000000	-0.152038	0.81844	0.2051	0.702020
6.000000	-0.170249	1.01165	0.2535	0.624260
7.000000	-0.187879	1.25879	0.3155	0.549743

m_r = 0.100000 γ_r = 0.2506

Table 34. Emf Measurements
Harned and Hamer (1935) Cell B

m/mol·kg^{-1}	E/V	γ/γ_r	γ
0.050000	-0.017206	1.27978	0.3208
0.100000	0.000000	1.00000	0.2507
0.200000	0.017446	0.73627	0.1971
0.500000	0.041064	0.58048	0.1455
1.000000	0.061161	0.48891	0.1226
1.500000	0.075035	0.46720	0.1171
2.000000	0.086289	0.46923	0.1176
3.000000	0.106766	0.53217	0.1334
4.000000	0.125172	0.64348	0.1613
5.000000	0.142208	0.80095	0.2008
6.000000	0.157673	0.99702	0.2500
7.000000	0.171633	1.22971	0.3083
8.000000	0.184312	1.49267	0.3742
9.000000	0.195676	1.78136	0.4467
10.000000 *	0.205720	2.08112	0.5217
11.000000 *	0.215323	2.42731	0.6085
12.000000 *	0.224175	2.79965	0.7019
13.000000 *	0.232469	3.20475	0.8034
14.000000 *	0.240341	3.65030	0.9151
15.000000 *	0.247724	4.12630	1.0345
16.000000 *	0.254866	4.65609	1.1673
17.000000 *	0.261709	5.23359	1.3121
17.500000 *	0.265100	5.55170	1.3918

m_r = 0.100000 γ_r = 0.2507

Table 35. Emf Measurements
Beck, Singh, and Wynne-Jones (1959) Cell A

m/ mol·kg^{-1}	E/ V	γ/γ_r	γ	a_w
0.100000	0.000000	1.00001	0.2506	0.996437
0.108500	-0.002191	0.97539	0.2444	0.996152
0.199600	-0.017756	0.79241	0.1986	0.993033
0.291700	-0.027579	0.69809	0.1749	0.989743
0.471700	-0.040314	0.59801	0.1499	0.982991
0.471700	-0.040424	0.59972	0.1503	0.982991
1.129000	-0.066803	0.48766	0.1222	0.955960
1.129000	-0.066383	0.48867	0.1225	0.955960
2.217000	-0.094402	0.48856	0.1224	0.900988
2.217000	-0.094372	0.48818	0.1223	0.900988
3.900000	-0.129384	0.62908	0.1575	0.787091
3.900000	-0.129154	0.62533	0.1567	0.787091
4.973000	-0.149871	0.77943	0.1953	0.704135
6.095000	-0.170118	0.98479	0.2468	0.617000
7.199000	-0.189224	1.24549	0.3121	0.535498
8.272000	-0.205970	1.51846	0.3805	0.462692

m_r = 0.100000 γ_r = 0.2506

Table 36. Emf Measurements
Beck, Dobson and Wynne-Jones (1969) Cell B

$m/\text{mol}\cdot\text{kg}^{-1}$	E/V	γ/γ_r	γ
0.100300	0.000000	1.00000	0.2505
0.174500	0.013880	0.82399	0.2064
0.387700	0.034540	0.63393	0.1588
0.553000	0.044060	0.56898	0.1425
0.977600	0.060980	0.49927	0.1251
1.872000	0.084290	0.47739	0.1196
3.911000	0.123440	0.63108	0.1581
5.767000	0.153000	0.92160	0.2309
7.972000	0.182840	1.44609	0.3622

m_r = 0.100300 γ_r = 0.2505

Table 37. Emf Measurements
Covington, Dobson, and Wynne-Jones (1965) Cell A

$m/\text{mol}\cdot\text{kg}^{-1}$	E/V	γ/γ_r	γ	a_w
0.007233	0.010010	1.09253	0.5356	0.999671
0.010316	0.000000	1.00000	0.5360	0.999548
0.057097	-0.045030	0.58059	0.3112	0.997876
0.095426	-0.057820	0.48370	0.2593	0.996590
0.095677	-0.057600	0.47968	0.2571	0.996582

m_r = 0.010316 γ_r = 0.5360

Table 38. Emf Measurements
Covington, Dobson, and Wynne-Jones (1965) Cell B

$m/\text{mol}\cdot\text{kg}^{-1}$	E/V	γ/γ_r	γ
0.007283	-0.009370	1.11073	0.5954
0.010316	0.000000	1.00000	0.5360
0.017138	0.013680	0.85845	0.4601
0.021505	0.019930	0.80458	0.4313
0.040055	0.036250	0.65973	0.3536
0.057097	0.045200	0.58380	0.3129
0.084016	0.054910	0.51044	0.2736
0.095426	0.057980	0.48667	0.2609
0.095677	0.058130	0.48729	0.2612
0.008791	-0.004170	1.05319	0.5645
0.023612	0.022410	0.78149	0.4189
0.026077	0.024940	0.75563	0.4050
0.059169	0.045730	0.57116	0.3061

m_r = 0.010316 γ_r = 0.5360

Table 39. Emf Measurements
Covington, Dobson, & Wynne-Jones (1965) Cell C

$m/\text{mol}\cdot\text{kg}^{-1}$	E/V	γ/γ_r	γ
0.007283 *	-0.007780	1.15751	0.6204
0.010316 *	0.000000	1.00000	0.5360
0.021505 *	0.013150	0.67478	0.3617
0.057097 *	0.033820	0.43453	0.2329
0.084016 *	0.052300	0.47701	0.2557
0.095426 *	0.046190	0.35840	0.1921
0.095677 *	0.047460	0.36944	0.1980

m_r = 0.010316 γ_r = 0.5360

Table 40. Parameters and their Standard Deviation, σ, for the Correlating Equations (10, 11, 12)

Parameters		σ
$B_1 = -7.277095$	$(\text{kg}\cdot\text{mol}^{-1})^{1/2}$	0.022
$B_2 = 12.823710$	$(\text{kg}\cdot\text{mol}^{-1})$	0.11
$B_3 = -14.283353$	$(\text{kg}\cdot\text{mol}^{-1})^2$	0.22
$B_4 = 10.001749$	$(\text{kg}\cdot\text{mol}^{-1})^3$	0.22
$B_5 = -4.343328$	$(\text{kg}\cdot\text{mol}^{-1})^4$	0.13
$B_6 = 1.175436$	$(\text{kg}\cdot\text{mol}^{-1})^5$	0.042
$B_7 = -0.1933648$	$(\text{kg}\cdot\text{mol}^{-1})^6$	0.0084
$B_8 = 1.770399\cdot10^{-2}$	$(\text{kg}\cdot\text{mol}^{-1})^7$	0.0009
$B_9 = -6.917679\cdot10^{-4}$	$(\text{kg}\cdot\text{mol}^{-1})^8$	0.00004

Table 41. Weighting Factors Used for Experimental Data

Type of Measurement	References	Weight[a]
Vapor Pressure		
	Grollman & Frazer (1925)	0.9
	Hepburn (1928)	0.5
	McHaffie (1927)	0.0
	von Meyeren (1932)	0.0
	Collins (1933)	1.0
	Shankman & Gordon (1939)	1.0
	Abel (1946)	0.0
	Jones (1951)	0.5
	Hornung & Giaugue (1955)	1.0
Isopiestic		
	Scatchard, Hamer & Wood (1938) vs. NaCl	0.5
	Scatchard, Hamer & Wood (1938) vs. KCl	0.5
	Scheffer, Janis & Ferguson (1939) vs. NaCl	0.9
	Robinson (1939) vs KCl	1.0
	Stokes (1945b) vs NaOH	1.0
	Stokes (1945a) vs $CaCl_2$	1.0
	Robinson (1945) vs NaCl	1.0
	Rard & Spedding (1977) vs $CaCl_2$	1.0
	Rard & Miller (1977)	1.0
	Rard & Miller (1978)	0.5
Freezing Point		
	Pickering (1891) set 1	0.05
	Pickering (1891) set 2	0.0
	Pickering (1892)	0.0
	Jones, et al. (1907, 1902)	1.0
	Jones, et al. (1893)	1.0
	Loomis (1893, 1894 a,b)	0.0
	Hausrath (1902)	1.0
	Bedford (1910)	0.0
	Randall & Scott (1927)	1.0
	Roth & Knothe (quoted in 1960)	0(except 1 pt.)
Emf		
	Randall & Cushman (1918), cell B	1.0
	Vosburgh & Craig (1929), cell D	1.0
	Trimble & Ebert (1933), cell B	1.0
	MacDougall & Blumer (1933), cell B	1.0
	Shrawder & Cowperwaithe (1934), cell E	1.0
	Hamer (1935), cell A	1.0
	Harned & Hamer (1935), cell B	1.0
	Beck, Singh & Wynne-Jones (1959), cell A	1.0
	Beck, Dobson & Wynne-Jones (1960), cell B	1.0
	Covington, Dobson & Wynne-Jones (1965), cell A	1.0
	ibid., cell B	1.0
	ibid., cell C	0.0

[a] Values of weights apply to all data of each set except for those data followed by an asterisk (*) in tables I-39, which were assigned zero weight as discussed in section 5.

A number of the data taken at lower molalities around 0.1–0.2 mol·kg^{-1} in the isopiestic measurements were given a zero or a low weight. The apparent imprecision of these data may be due to the short times allowed for equilibration. Rard, Habenschuss, and Spedding (1976) state that the time of 2 weeks was not sufficient for the lower concentrations (0.02–0.05 mol·kg^{-1}) of Sheffer, Janis, and Ferguson (1939). If this is the case, then clearly the 3 days allowed by Scatchard, Hamer, and Wood (1938) were insufficient to insure that their lower concentrations came to equilibrium. The large scatter in their replicate data at 0.1 mol·kg^{-1} supports this as well as recent unpublished results of Rard and Miller (1978) (see table 17). Accordingly, the present author has weighted the 4 most dilute points zero, in each of these 3 experiments. Rard, Habenschuss, and Spedding (1976), in their osmotic coefficient evaluation, weighted these data 0.75 at molalities as high as 2.8 mol·kg^{-1}.

As shown in figure 1, the deviations of the osmotic coefficients of Scatchard et al. (1938) and others are quite linear and increase with dilution below about 0.4 mol·kg^{-1}. This would indicate that either the fitting function has a strong systematic bias in this region or that there is a systematic error in the experimental determinations. Since there are only a few vapor pressure measurements and a large number of emf measurements in this region, with the vapor pressure confirming the emf results, it seems suspicious that the isopiestic results, which follow the fitting equation in all other concentration ranges, would deviate only near 0.1 mol·kg^{-1}. This is the region where the isopiestic method reaches its limit of experimental reliability. It is also interesting to note that the data of Scheffer et al. (1939) have a slightly lower deviation than Scatchard et al. and that Scheffer allowed 2 weeks equilibration in this low concentration range and Rard and Miller (1978) allowing an 8 week equilibration, had slightly lower values.

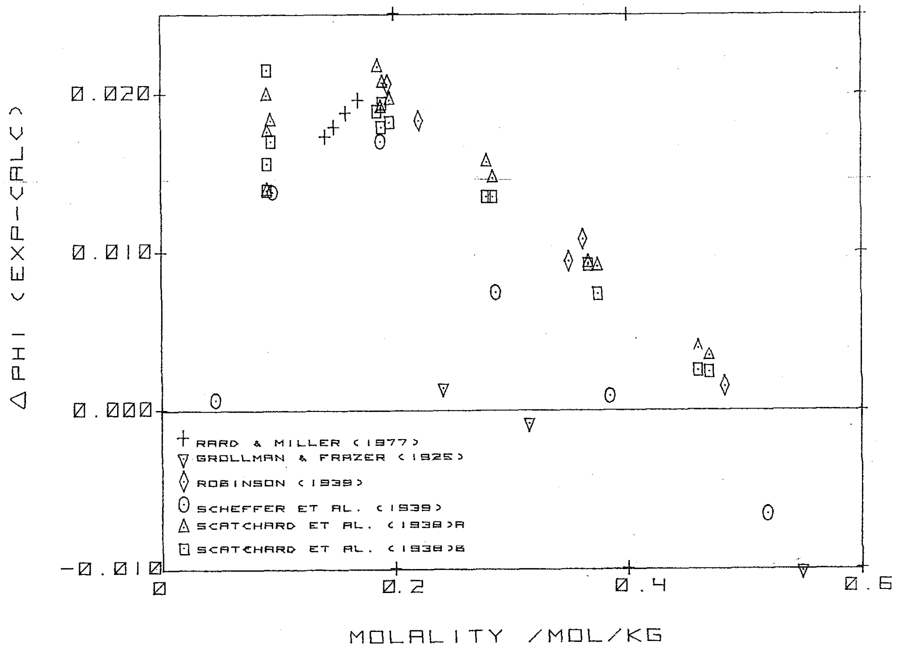

FIGURE 1. Deviations of the osmotic coefficient (near 0.1 molal) from those calcualated from equation (11) (experimental — calculated).

The freezing point data of Hausrath (1902) and of Randall and Scott (1927), were weighted 1 for compositions below 0.05 mol·kg^{-1}. The data of Bedford (1910) and effectively, Roth and Knothe (quoted, 1960) received zero weights. Pickering (1892) also was weighted zero and his other measurements were low weight (1891), one set $w = 0.05$ and the other set, $w = 0.1$. All other freezing point data, Loomis (1893, 1894 a,b), Jones et al. (1907, 1902, 1893) were weighted 0.1 to 0.5 (see table 41).

The sharp upturn in the deviations of the osmotic coefficients calculated from freezing point measurements is expected because of the wide scatter and apparently low reliability of many of the freezing point measurements and the increasing uncertainty in the temperature correction (uncertainty in thermal data between 0–25°C) as the concentration increases from dilute solutions to less ideal solutions.

However, the most convincing evidence that the deviations of the isopiestic and freezing point osmotic coefficients are more likely to result from the experimental error of about 0.1 mol·kg^{-1} is the consistency and reliability of the emf measurements. There are 12 sources of electrochemical cell measurements, made over about a 50 year period and all are very consistent among themselves as well as being consistent with most of the osmotic coefficient data. This agrees with Pitzer's (1976) and Pitzer, Roy, and Silvester's (1977) confidence in such emf results. In addition, the third law calculations of Gardner, Mitchell, and Cobble (1969), the discussion of Wirth (1971) and results of Pitzer (1976) and Pitzer, Roy, and Silvester (1977) are quite consistent with the emf measurements and hence with this evaluation. All emf measurements were assigned unit weight except those of cell C, which were weighted zero, due to the high solubility of Ag_2SO_4.

The evaluation of the osmotic coefficients by Rard, Habenschuss, and Spedding (1976) which was independent of emf data resulted in $\gamma = 0.247$ at 0.1 mol·kg^{-1} compared to the present value of 0.251. This also agrees well with what may be considered highly accurate emf measurements, by Covington et al, (1965) where $\gamma_{0.1} = 0.245$ and with the calculations of Pitzer et al. (1977), where $\gamma_{0.1} = 0.244$. A comparison of evaluations for values of ϕ and γ are shown in figures 2 and 3, respectively.

Some remarks are in order concerning the relationship of this correlation to those presented recently by Rard et al. (1977) and Pitzer et al. (1977) all of which include high quality data not available to the earlier reviewers (Robinson and Stokes, 1965; Harned and Owens, 1958).

Any correlating equation (fit) which uses a limited data base may possibly produce an incomplete picture. It was observed that a correlation using only ϕ data (all emf and freezing point measurments excluded) resulted in values nearly identical to those both Rard and Pitzer obtained at 0.1 mol·kg^{-1} and higher. Agreement among Rard and Pitzer (also Robinson and Stokes and Harned and Owen at concentrations above 0.1 m) is to be expected because of the nearly identical and limited data base that each used.

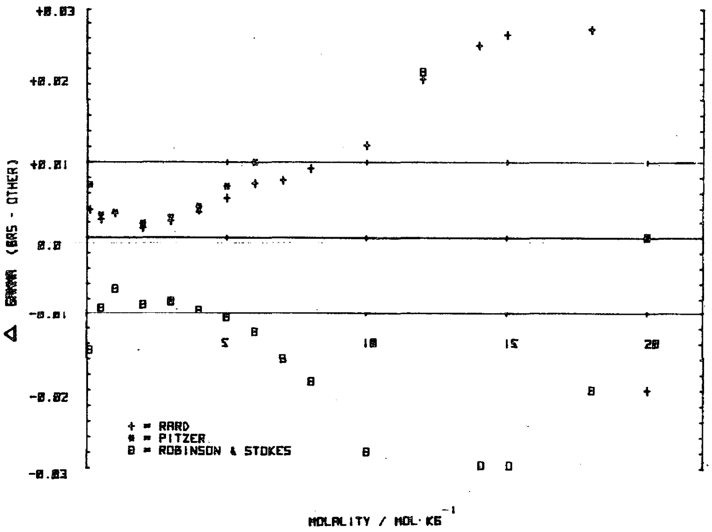

FIGURE 2. Comparison of evalations for the activity coefficient.

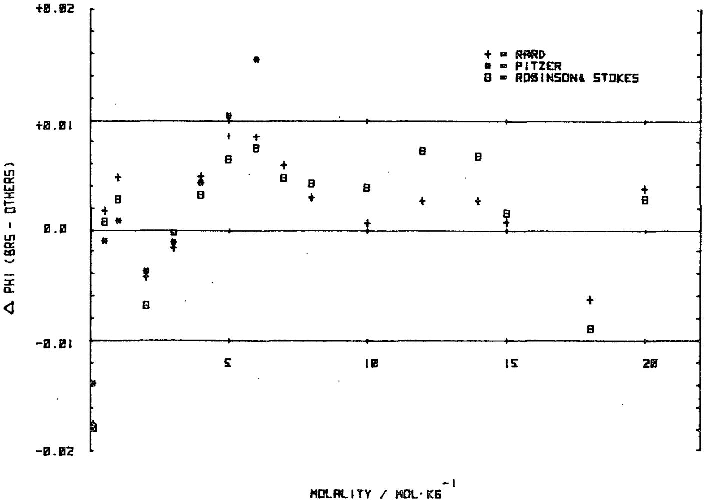

FIGURE 3. Comparison of evaluations for the osmotic coefficient.

This present correlation includes 175 freezing point measurements, none of which were considered by previous evaluators. Also included are 130 emf data points derived from 12 different authors' results (5 different electrochemical cells). Other evaluators have either excluded emf measurements entirely (Rard); used partly incorrect (Hamer's) results available to them (Robinson and Stokes; Harned and Owen), or used only 1 or 2 sets of data consisting of no more than 35 points (Pitzer). As mentioned, 380 ϕ values and 95 γ values were given non-zero weight in this correlation from a data base of about 650 points.

In addition, recent isopiestic measurements by Rard were included in this correlation (60 points in 1976–77 and recent unpublished data (1978) for 17 points). The ϕ values obtained from these measurements for the lower concentrations, around 0.15 $\mathrm{mol\cdot kg^{-1}}$ are slightly lower than earlier results, probably because of the much longer equilibration times of 8 weeks (compared with 2 days for Hamer's measurements). It should be noted that Rard's new values for ϕ are still not as low as the value calculated here for 0.1 $\mathrm{mol\cdot kg^{-1}}$ (they are only about 0.008 different) and there is good reason for this. A difference in a_w of 1 part in 10,000 (0.01%) at 0.1 $\mathrm{mol\cdot kg^{-1}}$ results in a difference in ϕ of 0.105, almost exactly the difference between our calculated value of 0.662 compared to 0.680 calculated by Rard or Pitzer. A fit of data only at 0.5 $\mathrm{mol\cdot kg^{-1}}$ or less substantiates a ϕ value of 0.66. A value of 0.680 is obtained if the emf and freezing point data are ignored. Rard (1977) states that ϕ is uncertain to about 0.5% at the lower concentrations of his evaluation (0.1 $\mathrm{mol\cdot kg^{-1}}$). At 0.01 $\mathrm{mol\cdot kg^{-1}}$, a difference of 0.01% in a_w results in a difference of 0.185 in ϕ, nearly 23%.

Above 0.1 $\mathrm{mol\cdot kg^{-1}}$ the present results of ϕ agree with Pitzer's to within 0.006 up to $m = 5$ (Pitzer only goes up to 6 $\mathrm{mol\cdot kg^{-1}}$). Agreement with Rard and Robinson and Stokes, above 0.1 $\mathrm{mol\cdot kg^{-1}}$, is similarly good, as high as $m = 15$ or 20 $\mathrm{mol\cdot kg^{-1}}$. This agreement is within any experimental uncertainty. Agreement in γ at 0.1 $\mathrm{mol\cdot kg^{-1}}$ is 0.008 with both Rard and Pitzer. Agreement in γ is acceptable up to 5 $\mathrm{mol\cdot kg^{-1}}$ (near Pitzer's limit).

Pitzer et al. (1977) using additional data and a more elaborate treatment (1977), report $\gamma = 0.514$ at $m = 0.01$ based on the bisulfate equilibrium. It is our opinion that the form of the equation to attain the Debye-Huckel limiting slope (perhaps at too high a concentration for this electrolyte) accounts for a slight distortion of each curve from the observed experimental values.

Several models, using a Debye-Huckel form of limiting law, may be used for these correlations. Both Pitzer and Rard's equations approach the Debye-Huckel limit (by choice); the equation used here does not. However, it does reproduce the experimental data from about .001 to 28 $\mathrm{mol\cdot kg^{-1}}$ to within the experimental uncertainty.

The use of an equation which does not follow the Debye-Huckel limiting law (our eqs 10,11) results in an "error" in the activity coefficient at low molalities. The "error" introduced by the use of our equation amounts to about -2% at $m = 0.0001$ $\mathrm{mol\cdot kg^{-1}}$, with good agreement at 0.002 $\mathrm{mol\cdot kg^{-1}}$ with Pitzer et al. (1977), while a deviation of about $+4\%$ at $m = 0.01$ $\mathrm{mol\cdot kg^{-1}}$ is observed. Concentrations higher than 0.1 $\mathrm{mol\cdot kg^{-1}}$ again bring good agreement with theory and experiment.

Negative deviations from the DHLL, due to association of ions have been observed. Sulfuric acid is one example of this deviation, due to the ionic equilbrium: $HSO_4^- \rightleftharpoons H^+ + SO_4^=$. A mean (stoichiometric) molal activity coefficient, $\gamma_\pm$, calculated on the basis of 100% dissociation is the measure of the departure of that solution from ideality (model). If one includes a K_2 (the bisulfate ionization constant) and $\gamma_{HSO_4^-}$ (a single ion) the $\gamma'_\pm$ is different from the above because new parameters have been added. The $\gamma'_\pm$ now becomes a measure of the departure of a solution of 3 kinds of ions from ideality. It has been shown that $\gamma_\pm = \alpha\gamma'_\pm$ (Robinson and Stokes, 1965), where α is the degree of dissociation. The final results of the correlations should be essentially the same.

The comparisons between the present evaluation and the experimental data is made in figure 4.

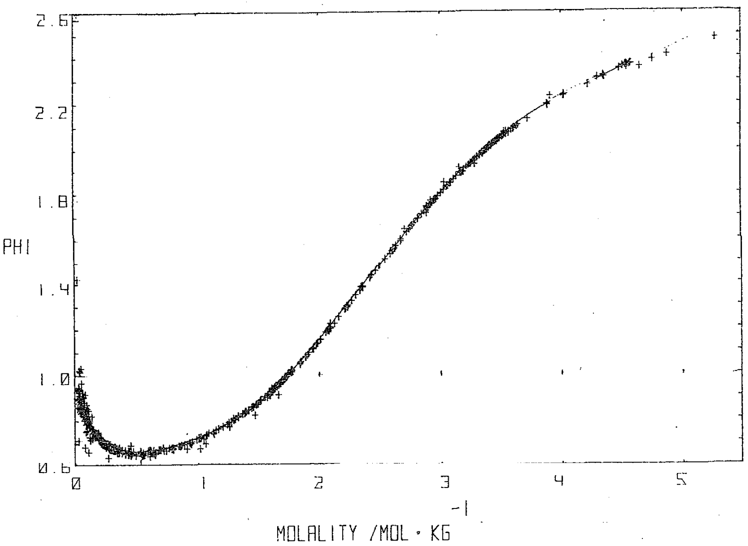

FIGURE 4. Osmotic coefficient vs $m^{1/2}$ (experimental and calculated).

Even though there are more than 100 data points below 0.1 mol·kg^{-1}, it was not possible to fit this dilute range with our correlating equation using the theoretical slope because the available data simply do not conform to the theoretical slope. The procedure adopted was to describe the data in the dilute solutions with the limiting slope as an adjustable parameter. When this is done the data are consistent over the entire range of molalities from 0.001 to 28 mol·kg^{-1}.

6. Recommended Values for the Mean Activity and Osmotic Coefficients of H_2SO_4 in Water at 298.15 K

Table 42 presents recommended values for ϕ, γ, ΔG^{ex}, and a_w at rounded molalities up to 30 mol·kg^{-1}. Parameters of the correlating eqs (10,11,12) from which table 42 was derived are given in table 40.

Figures 5 and 6 show a plot of the deviations of the observed values of the osmotic coefficient and mean activty coefficient respectively, from the values calculated for the observed concentrations. The base lines are derived from eqs (10), γ, and (11), ϕ.

The osmotic and mean activity coefficients as a function of molality, are illustrated in figures 4 and 7, respectively, and the excess Gibbs energy as a function of molality is shown in figure 8. Figure 9 shows the Debye-Huckel limiting law as a graph of ln γ (activity coefficient) vs $m^{1/2}$.

The tabulated values of mean activity and osmotic coefficients as well as the activities of water and excess Gibbs energy given in table 42, together with the equations (10,11,12) from which they were calculated, are recommended for use as reference data from about 0.001 up to a molality of 22 mol·kg^{-1} and, with caution, up to near 28 mol·kg^{-1}. Additional points are for rough extrapolation only.

The resulting values for ϕ and γ of the present evaluation generally agree well with those of Rard, Habenschuss, and Spedding (1976) and Pitzer, Roy, and Silvester (1977) but disagree to some extent, with previous tabulations (Robinson and Stokes, 1965 and Harned and Owen, 1958). It is generally accepted that previous tabulations which were based on Harned and Hamer's (1935) emf data, reflect errors in the emf measurements.

The four reference systems noted in section 1, NaCl, KCl, $CaCl_2$ and H_2SO_4, are entirely self-consistent and mutually consistent with the uni-univalent charge-type electrolytes, Hamer and Wu (1972).

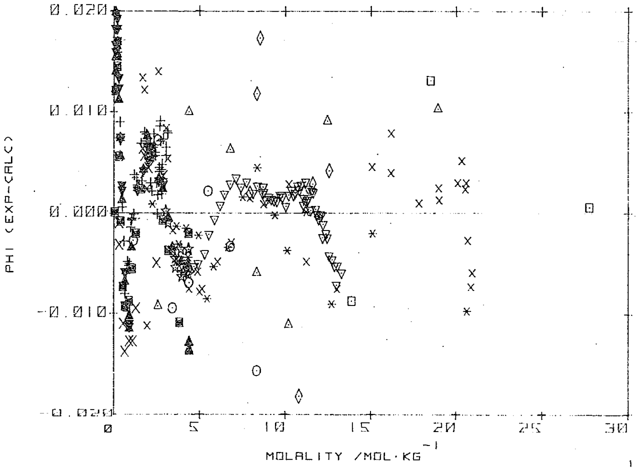

FIGURE 5. Deviations of the osmotic coefficients from those calculated from equation (11), (experimental − calculated).

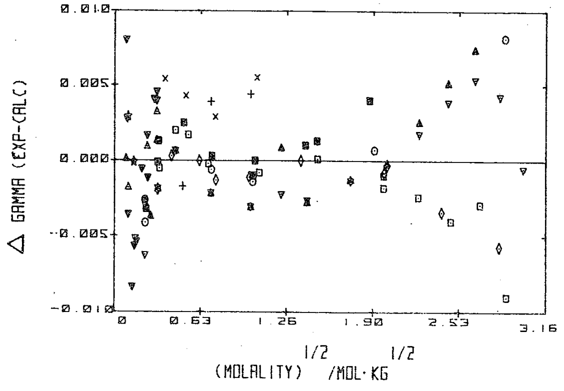

FIGURE 6. Deviations of the activity coefficients from those calculated from equation (10) (experimental − calculated).

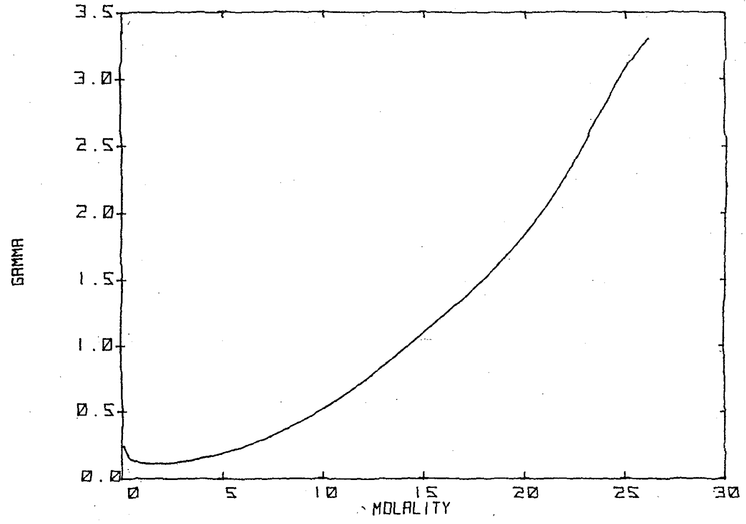

FIGURE 7. The activity coefficient as a function of molality.

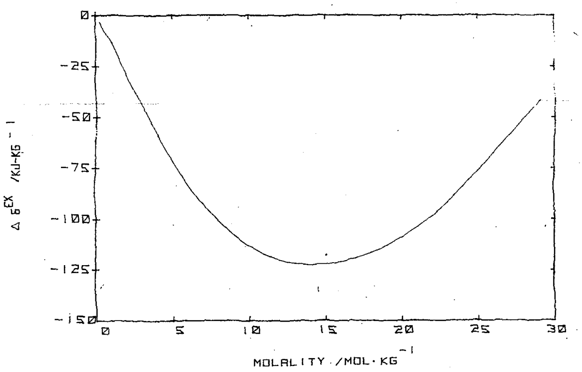

FIGURE 8. The excess Gibbs energy as a function of molality.

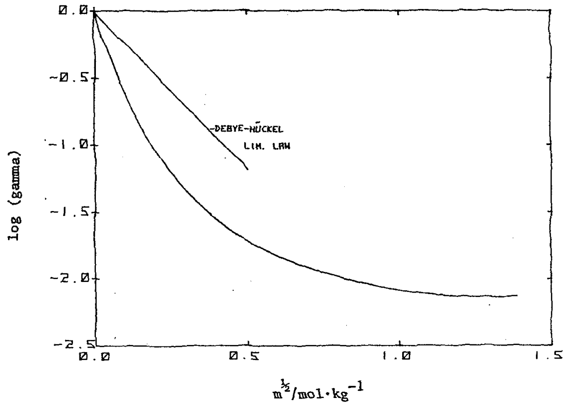

FIGURE 9. The natural logarithm of the activity coefficient as a function of the square-root of molality.

Table 42. H_2SO_4 Recommended values of γ and ϕ at 298.15 K

m (mol/kg)	γ	ϕ	a_w	ΔG^{ex} (J/kg)
0.001	0.8045	0.9295	0.999950	-1.1
0.002	0.7402	0.9037	0.999902	-3.0
0.003	0.6962	0.8851	0.999857	-5.5
0.004	0.6623	0.8703	0.999812	-8.4
0.005	0.6345	0.8578	0.999768	-11.6
0.006	0.6110	0.8469	0.999725	-15.2
0.007	0.5906	0.8373	0.999683	-18.9
0.008	0.5726	0.8287	0.999642	-23.0
0.009	0.5566	0.8209	0.999601	-27.2
0.010	0.5420	0.8137	0.999560	-31.7
0.010	0.5420	0.8137	0.999560	-31.7
0.020	0.4453	0.7635	0.999175	-85.1
0.030	0.3902	0.7332	0.998812	-150.5
0.040	0.3528	0.7124	0.998461	-224.4
0.050	0.3254	0.6973	0.998117	-304.9
0.060	0.3041	0.6859	0.997778	-391.0
0.070	0.2870	0.6771	0.997442	-481.8
0.080	0.2728	0.6702	0.997107	-576.5
0.090	0.2609	0.6647	0.996772	-674.8
0.100	0.2508	0.6605	0.996437	-776.2
0.1	0.2508	0.6605	0.99644	-776
0.2	0.1946	0.6481	0.99302	-1911
0.3	0.1700	0.6547	0.98944	-3183
0.4	0.1557	0.6651	0.98572	-4536
0.5	0.1463	0.6760	0.98190	-5943
0.6	0.1395	0.6864	0.97799	-7391
0.7	0.1343	0.6965	0.97399	-8871
0.8	0.1303	0.7062	0.96993	-10375
0.9	0.1272	0.7158	0.96578	-11900
1.0	0.1247	0.7255	0.96155	-13441
1.0	0.1247	0.7255	0.96155	-13441
1.5	0.1187	0.7776	0.93891	-21297
2.0	0.1195	0.8400	0.91320	-29224
2.5	0.1248	0.9118	0.88409	-37053
3.0	0.1337	0.9897	0.85174	-44670
3.5	0.1456	1.0707	0.81666	-51999
4.0	0.1603	1.1520	0.77954	-58988
4.5	0.1775	1.2319	0.74112	-65607
5.0	0.1973	1.3090	0.70207	-71839
5.5	0.2195	1.3827	0.66298	-77676
6.0	0.2441	1.4525	0.62436	-83117
6.5	0.2711	1.5185	0.58658	-88165
7.0	0.3004	1.5805	0.54994	-92828
7.5	0.3321	1.6389	0.51463	-97112
8.0	0.3662	1.6936	0.48081	-101028
8.5	0.4028	1.7451	0.44857	-104586
9.0	0.4417	1.7935	0.41795	-107794
9.5	0.4832	1.8390	0.38899	-110665
10.0	0.5270	1.8817	0.36169	-113207
10.5	0.5732	1.9218	0.33602	-115432
11.0	0.6218	1.9593	0.31197	-117349
11.5	0.6726	1.9945	0.28949	-118969
12.0	0.7255	2.0272	0.26854	-120302
12.5	0.7805	2.0576	0.24906	-121359
13.0	0.8372	2.0857	0.23098	-122149
13.5	0.8954	2.1115	0.21425	-122684
14.0	0.9550	2.1351	0.19878	-122974
14.5	1.0157	2.1565	0.18452	-123030
15.0	1.0772	2.1758	0.17138	-122862
15.5	1.1393	2.1930	0.15928	-122480
16.0	1.2018	2.2082	0.14815	-121895
16.5	1.2644	2.2216	0.13791	-121116
17.0	1.3271	2.2334	0.12848	-120153
17.5	1.3896	2.2435	0.11980	-119014
18.0	1.4520	2.2523	0.11179	-117709
18.5	1.5143	2.2599	0.10440	-116243
19.0	1.5766	2.2665	0.09755	-114625
19.5	1.6389	2.2723	0.09120	-112859
20.0	1.7015	2.2775	0.08529	-110952
20.5	1.7644	2.2822	0.07977	-108908
21.0	1.8280	2.2866	0.07463	-106731
21.5	1.8924	2.2909	0.06981	-104423
22.0	1.9576	2.2951	0.06529	-101988
22.5	2.0237	2.2991	0.06106	-99428
23.0	2.0906	2.3030	0.05711	-96747
23.5	2.1577	2.3066	0.05342	-93945
24.0	2.2246	2.3096	0.05000	-91029
24.5	2.2902	2.3116	0.04685	-88001
25.0	2.3529	2.3121	0.04398	-84869
25.5	2.4108	2.3105	0.04141	-81641
26.0	2.4612	2.3057	0.03916	-78329
26.5	2.5008	2.2969	0.03727	-74949
27.0	2.5257	2.2827	0.03576	-71520
27.5	2.5313	2.2616	0.03469	-68068

Table 43. Standard deviation of calculated values at selected molalities

m	ϕ	$\sigma(\phi)$	$\ln\gamma$	$\sigma(\ln\gamma)$	γ	$\sigma(\gamma)$
0.001	0.9295	0.0002	-0.2176	0.0005	0.8044	0.0004
0.010	.8136	.0003	-0.6126	.0012	.5419	.0006
0.100	.6605	.0005	-1.3835	.0013	.2507	.0003
1.000	.7253	.0008	-2.0821	.0013	.1247	.0002
2.000	.8397	.0008	-2.1253	.0014	.1194	.0002
3.000	.9897	.0008	-2.0128	.0013	.1336	.0002
4.000	1.1522	.0009	-1.8310	.0014	.1603	.0002
5.000	1.3095	.0009	-1.6227	.0014	.1974	.0003
10.000	1.8854	.0009	-0.6361	.0016	.5294	.0008
15.000	2.1971	.0018	0.1006	.0024	1.1059	.0027
20.000	2.3403	.0022	0.6104	.0031	1.8411	.0056
25.000	2.4586	.0073	1.0400	.0078	2.8292	.0221
30.000	2.3187	0.0413	1.1653	0.0424	3.2070	0.1361

Acknowledgments

The author wishes to acknowledge the continuing support of the Office of Standard Reference Data, as well as support provided by the Department of Energy under Contract No. EW-78-03-0509-A001. Thanks go to J. A. Rard and D. G. Miller for access to their unpublished data of iospiestic measurements (1977,1978).

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