

The high temperature emf data obtained in this study and the calorimetric data of Predel and Stein suggest that the maximum heat of mixing is shifted towards the Ga rich side rather than centered at $x_{\text{Ga}} = 0.5$.

Conclusions

The thermodynamic properties of liquid gallium–indium alloys have been studied by high-temperature galvanic cell techniques using calcia-stabilized Zirconia as the solid-oxide electrolytes. The experimental method employed produced data which are quite reproducible in the temperature range from 800 to 950 °C. The derived values of the heat of mixing were found to be sensitive to the absolute errors in measurement, however. The activities of gallium in the alloys show a positive derivation from ideality. The enthalpy of mixing derived from the data of this work is consistent with values obtained by calorimetric methods.

Literature Cited

- (1) Bros, J.-P., *C.R. Acad. Sci., Ser. C*, **263**, 977 (1966).
- (2) Bros, J.-P., Castanet, R., Laffitte, M., *C.R. Acad. Sci., Ser. C*, **264**, 1804 (1967).
- (3) Chatterji, D., Smith, J. V., *J. Electrochem. Soc.*, **120**, 770 (1973).

- (4) Coughlin, J. P., Bull. 542, U.S. Bureau of Mines, U.S. Government Printing Office, Washington, D.C., 1954.
- (5) Danilin, V. N., Yatsenko, S. P., *Akad. Nauk SSSR*, **2**, 145 (1970).
- (6) Denny, J. P., Hamilton, J. H., Lewis, J. R., *J. Met.*, **39** (1952).
- (7) Etsell, T. H., Flengas, S. N., *J. Electrochem. Soc.*, **119**, 1 (1972).
- (8) Hardaway, III, J. B., Patterson, J. W., Wilder, D. R., Schieltz, J. D., *J. Am. Ceram. Soc.*, **54**, 94 (1971).
- (9) Hoshino, H., Nakamura, Y., Shimoji, M., Niwa, K., *Ber. Bunsenges.*, **69**(2), 114 (1956).
- (10) Kiukkola, K., Wagner, C., *J. Electrochem. Soc.*, **104**, 379 (1957).
- (11) Klinedinst, K. A., Rao, M. V., Stevenson, D. A., *J. Electrochem. Soc.*, **119**, 1261 (1972).
- (12) Klinedinst, K. A., Stevenson, D. A., *J. Chem. Thermodyn.*, **4**, 565 (1972).
- (13) Klinedinst, K. A., Stevenson, D. A., *J. Chem. Thermodyn.*, **5**, 21 (1973).
- (14) Levine, S. R., Kolodney, M., *J. Electrochem. Soc.*, **116**, 1420 (1969).
- (15) Macur, G. J., Edwards, R. K., Wahlbeck, P. G., *J. Phys. Chem.*, **72**, 1047 (1968).
- (16) Patterson, J. W., Bogren, C. C., Rapp, R. A., *J. Electrochem. Soc.*, **114**, 752 (1967).
- (17) Patterson, J. W., *J. Electrochem. Soc.*, **118**, 1033 (1971).
- (18) Predel, B., Stein, D. W., *J. Less-Common Met.*, **16**, 49 (1969).
- (19) Ramanarayanan, T. A., Worrell, W. L., unpublished work, 1974.
- (20) Schmalzried, H., *Z. Elektrochem.*, **66**, 572 (1962).
- (21) Schottky, W. F., Bever, B., *Acta Metall.*, **7**, 322 (1958).
- (22) Seybolt, A. U., *J. Electrochem. Soc.*, **111**, 697 (1964).
- (23) Svirbely, W. J., Sells, S. M., *J. Phys. Chem.*, **58**, 33 (1954).
- (24) Terpilowsky, J., *Arch. Hutn.*, **4**, 355 (1959).
- (25) Treyakov, J. D., Muan, M., *J. Electrochem. Soc.*, **116**, 331 (1969).

Received for review September 2, 1975. Accepted March 25, 1976.

A Review of the Osmotic Coefficients of Aqueous H₂SO₄ at 25 °C

Joseph A. Rard, Anton Habenschuss, and Frank H. Spedding*

Ames Laboratory-ERDA and Department of Chemistry, Iowa State University, Ames, Iowa 50011

Among the most widely used isopiestic standards for aqueous solutions are NaCl, KCl, CaCl₂, and H₂SO₄. The osmotic coefficient data for NaCl and KCl have recently been reviewed and appear to be known with a high degree of accuracy. The purpose of this paper is to reexamine and update the osmotic coefficient data for H₂SO₄ at 25 °C. A semiempirical equation is given which represents the osmotic coefficients of this electrolyte to within the experimental error of the data from 0.1 to 27.7 m.

This laboratory has been concerned with the measurement of the activity coefficients of aqueous rare earth chloride, perchlorate, and nitrate solutions at 25 °C by the isopiestic method. In the course of these measurements KCl, CaCl₂, and H₂SO₄ solutions have been used as isopiestic standards. We found it necessary to reexamine the standard osmotic coefficients to ensure that they were reliable enough for our calculations.

Hamer and Wu (12) have published an extensive tabulation of osmotic coefficient data for uni-univalent electrolyte solutions at 25 °C. These authors neglected to correct vapor pressure measurements for the nonideal behavior of the solvent vapor although this correction is as large as the standard deviation of their semiempirical equations for NaCl and KCl. One advantage of their data treatment is that they made the osmotic coefficient data consistent for NaCl and KCl, by use of experimental isopiestic ratios. Gibbard et al. (9) have recently reported new vapor pressure measurements for NaCl solutions and have determined least-squares equations that accurately represent both their data and other osmotic coefficient data as a function of temperature and concentration. Gibbard et al. corrected these data, when

necessary, to the presently accepted temperature scale, accepted values of the physical constants, and for the nonideal behavior of water vapor. These two reviews are in substantial agreement and the osmotic coefficients of NaCl and KCl solutions appear to be known fairly accurately.

H₂SO₄ has not received as much attention as NaCl and KCl so we decided to examine the available osmotic coefficients for this electrolyte. New data have appeared since Robinson and Stokes' review (21), and older data need to be updated with respect to temperature scales and corrected to the same values of the vapor pressure of pure water and for the nonideal behavior of water vapor. In addition, it was felt desirable to have an empirical equation to represent these osmotic coefficient data. The use of such equations would help to eliminate differences that occur when different workers use graphical interpolations of the same tabulated standard data. Such equations are available for NaCl and KCl (9, 12). No reliable equation is available which describes the H₂SO₄ data over wide concentration ranges. A future paper will deal with the osmotic coefficients of CaCl₂ solutions.

Discussion

H₂SO₄ has been used as an isopiestic standard for measurements on a number of other electrolytes. In principle each of these measurements could be used to generate H₂SO₄ osmotic coefficients, provided that accurate osmotic coefficient data are available for these other electrolytes from different measurements. It turns out, however, that NaCl and KCl are about the only salts for which accurate osmotic coefficients are available from more direct methods and for which the necessary H₂SO₄ isopiestic data exist. Because of the scarcity of accurate H₂SO₄ data at high concentrations, some of the available

H₂SO₄-NaOH isopiestic data were also used in the following analysis.

Since Hamer and Wu (12) have made their osmotic coefficient data for NaCl and KCl consistent, we chose to use their results as standards to calculate the osmotic coefficients of H₂SO₄ solutions in equilibrium with them. To utilize the full accuracy of their isopiestic data, Hamer and Wu's osmotic coefficients were corrected for the nonideal behavior of the solvent vapor. If the vapor pressure above the solution is low, as it is for aqueous solutions at 25 °C, then the nonideal behavior of water vapor can be represented by use of the second virial coefficient. Then,

$$\phi = \left(\frac{1000}{\nu m M_1} \right) \ln (p_0/p) + \frac{1000B(p_0 - p)}{\nu m M_1 R T} = \phi_0 + \delta \phi \quad (1)$$

where ϕ is the osmotic coefficient of the solution, ϕ_0 is the osmotic coefficient of the solution if the solvent vapor were ideal, $\delta\phi$ is the correction for the nonideal behavior of the vapor, M_1 is the molecular weight of water, ν is the number of particles formed by the dissociation of one molecule of solute, R is the universal gas constant, T is the temperature in K, B is the second virial coefficient of water vapor (pressure form of the virial equation), p_0 is the vapor pressure of pure water at the temperature of interest, and p is the vapor pressure of water above the solution of molality m . The IUPAC molecular weights for H₂SO₄ (98.074 g/mol) and H₂O (18.0154 g/mol) were used in the following calculations. The vapor pressure above a solution depends on the concentration of each component of that solution. Conversion of the osmotic coefficients to a constant pressure, p_0 , can be neglected since this correction is several orders of magnitude smaller than $\delta\phi$ for aqueous solutions at 25 °C. B was calculated from eq 3 of McCullough et al. (18) and is equal to $-1994 \text{ cm}^3/\text{mol}$ at 25 °C (this value was obtained using a modest extrapolation of experimental data and is within a few percent of values reported in other reviews). The value of R used is $8.3143 \text{ J}/(\text{K mol})$. Inserting numerical values gives

$$\phi_0 = (55.508/\nu m) \ln (p_0/p) \quad (2)$$

and

$$\delta\phi = -3.564 \times 10^{-3}(p_0 - p)/\nu m \quad (3)$$

where p and p_0 are in millimeters of mercury.

Values of p_0 were taken from Wexler and Greenspan (28). Since Hamer and Wu's NaCl and KCl data were corrected to the International Practical Temperature Scale of 1968 (IPTS-68), $p_0 = 23.767$ was used in calculations for these salts. The data for H₂SO₄ are based on IPTS-48 or nearly equivalent earlier temperature scales, so $p_0 = 23.754$ was used for calculations involving this solute. Correction of these osmotic coefficient data to IPTS-68 will be discussed later. Six-tenths of $\delta\phi$ was added to ϕ_0 for NaCl and KCl when they were used as isopiestic standards. This was done since only the direct vapor pressure measurements for NaCl and KCl require this correction; isopiestic, emf, and freezing point depression measurements do not. Six-tenths is the approximate fraction of the data points for NaCl and KCl that need to be corrected (because the data for NaCl and KCl were made consistent using isopiestic data, it is difficult to give a better estimate of this fraction). If 0.4 or 0.8 had been used for this fraction the resulting osmotic coefficients of H₂SO₄ would be changed by only ± 0.0002 – 0.0003 , depending on concentration. As shall be seen below, this is less than a tenth of the standard deviation for the best fit so no significant error will result from this approximation.

The isopiestic data of Robinson (19, 20), Scatchard et al. (22), and Sheffer et al. (24) were recalculated using Hamer and Wu's (12) osmotic coefficient equations for NaCl and KCl, corrected for the nonideal behavior of the solvent vapor. Stokes (26) has

measured the isopiestic ratios for NaOH and H₂SO₄ corresponding to H₂SO₄ molalities of 1.67–21.65. These data can be combined with direct vapor pressure measurements for NaOH (17) and bithermal equilibrium vapor pressures (27) to yield another set of osmotic coefficients. Unfortunately, the two sets of NaOH vapor pressure measurements show large differences at high concentrations. Both sets of NaOH solution vapor pressure data were corrected for nonideal vapor behavior and fitted to a polynomial equation. The osmotic coefficients for H₂SO₄, calculated from these data, were used only in the concentration region where the two sets of NaOH vapor pressure data are in good agreement (4.37–7.95 m for H₂SO₄). Thus, Stokes' 8 lowest and 18 highest isopiestic concentrations could not be used. All of these data that were used are listed in Table I.

H₂SO₄ has also been studied by direct vapor pressure measurements (11, 15, 23). Values of $\delta\phi$ were calculated for H₂SO₄ from eq 3, using the experimental vapor pressure data for its solutions, and these values were fitted to an equation of the form

$$\delta\phi = \sum_i D_i m^i \quad (4)$$

These coefficients, and the standard deviation of the fit, are given in Table II. For H₂SO₄ the full $\delta\phi$ correction was made for each point determined by direct vapor pressure measurements. Equation 4 should be used only for the concentration range given in Table II since it does not exhibit correct limiting behavior at lower concentrations.

To see if it was necessary to correct the H₂SO₄ data from IPTS-48 to IPTS-68, the correction to the osmotic coefficient

$$\delta\phi^* = \frac{1000\bar{L}_1\delta T}{\nu m M_1 R T^2} \quad (5)$$

was calculated for several values of ϕ . In this equation \bar{L}_1 is the relative partial molal enthalpy of the solvent and δT is the difference between the IPTS-68 and the IPTS-48 temperature scales. Since $\delta T = 0.0085^\circ$ at 25 °C,

$$\delta\phi^* = (2.671 \times 10^{-6}/\nu m)\bar{L}_1 \quad (6)$$

Using Giauque et al. (8) enthalpy data for H₂SO₄, $\delta\phi^* = -5 \times 10^{-6}$ at 1.0 m and -7×10^{-5} at 28.5 m . This is at least an order of magnitude smaller than the previous correction and can be neglected. Thus, p/p_0 changes more slowly with temperature than either p or p_0 . Conversion of isopiestic and vapor pressure data to the atomic weights of IUPAC-69 amounts to changes of about 0.01% and can be neglected.

The vapor pressures above aqueous solutions of sulfuric acid have been reported by Grollman and Frazer (11), Shankman and Gordon (23), and Hornung and Giauque (15). These vapor pressure data were recalculated to conform to Wexler and Greenspan's data for pure water (28) and for the nonideal behavior of the solvent vapor. While these corrections are not large, they do put all of the vapor pressure data on a more self-consistent basis. The data at low concentrations were not used if the vapor pressure of the solution differed by less than 1 mm of mercury from that of the pure solvent, since the errors in the osmotic coefficients from these measurements could be 1% or larger. Thus, Grollman and Frazer's seven lowest concentrations were not used. The corrected vapor pressure data used here are reported in Table I. The measurements of Jones (16), although in reasonable agreement with the above measurements over most of the concentration range, were not included in Table I since they were reported to only two–three significant figures. Collins (3) measured the vapor pressures of H₂SO₄ solutions as a function of temperature and his values around 25 °C are reported to only three significant figures. In addition, in most cases a slight extrapolation of his data to 25 °C was involved. Consequently his data were not accurate enough to include in this analysis. As discussed by Glueckauf and Kitt (10), early vapor

Table I. Experimental Osmotic Coefficients for H₂SO₄

<i>m</i>	ϕ	<i>m</i>	ϕ	<i>m</i>	ϕ
Stokes-Isopiestic vs. NaOH (26)					
4.376	1.2004	5.144	1.3196	7.937	1.6828
4.881	1.2815	6.056	1.4517		
5.002	1.2980	6.865	1.5568		
Robinson-Isopiestic vs. NaCl (20)					
2.0831	0.8556	3.5567	1.0759	4.0465	1.1540
3.0051	0.9910	3.5738	1.0778	4.3242	1.2006
3.1495	1.0132	3.9005	1.1327	4.3481	1.2019
3.4061	1.0523	3.9455	1.1373	4.3537	1.2052
Sheffer, Janis, and Ferguson-Isopiestic vs. NaCl (24)					
0.0188 ^a	0.8222	0.5197	0.6709	1.544	0.7827
0.0455 ^a	0.7044	0.6401	0.6807	2.183	0.8707
0.0958	0.6753	0.7335	0.6893	2.830	0.9618
0.1881	0.6646	0.8820	0.7035	3.156	1.0112
0.2867	0.6607	1.046	0.7217	3.815	1.1115
0.3842	0.6637	1.268	0.7474	4.349	1.2058
Scatchard, Hamer, and Wood ^b -Isopiestic vs. KCl (22)					
0.0909	0.6851	0.2792	0.6679	0.8892	0.7017
0.0908	0.6814	0.2846	0.6674	1.3651	0.7624
0.0908	0.6837	0.3662	0.6702	1.7065	0.8042
0.0940	0.6806	0.3742	0.6708	1.9351	0.8362
0.1858	0.6691	0.4609	0.6751	1.9998	0.8437
0.1889	0.6665	0.4705	0.6756	2.6023	0.9303
0.1901	0.6681	0.6222	0.6824	2.8298	0.9655
0.1965	0.6670	0.8867	0.7018		
Scatchard, Hamer, and Wood ^b -Isopiestic vs. NaCl (22)					
0.0909 ^a	0.6676	0.3662	0.6701	1.9351	0.8373
0.0908	0.6794	0.3742	0.6691	1.9998	0.8445
0.0908	0.6853	0.4609	0.6736	2.6023	0.9304
0.0940	0.6793	0.4705	0.6746	2.8298	0.9651
0.1858	0.6663	0.6222	0.6813	3.1663	1.0166
0.1889	0.6653	0.8867	0.7025	3.3892	1.0497
0.1901	0.6668	0.8892	0.7015	3.9291	1.1360
0.1965	0.6656	1.0109	0.7209	4.3145	1.1976
0.2792	0.6657	1.3651	0.7626	4.3741	1.1990
0.2846	0.6662	1.7065	0.8042		
Robinson-Isopiestic vs. KCl (19)					
0.1946	0.6680	1.316	0.7583	2.518	0.9138
0.2213	0.6665	1.368	0.7632	2.544	0.9198
0.3495	0.6685	1.456	0.7730	2.629	0.9356
0.3614	0.6712	1.575	0.7909	2.639	0.9367
0.4832	0.6751	1.627	0.7934	2.641	0.9363
0.5833	0.6816	1.776	0.8167	2.663	0.9450
0.6376	0.6816	1.873	0.8284	2.696	0.9506
0.7101	0.6904	1.873	0.8291	2.711	0.9510
0.7492	0.6945	1.951	0.8392	2.757	0.9554
0.7908	0.6991	2.108	0.8602	2.777	0.9562
0.8666	0.7056	2.127	0.8592	2.800	0.9627
0.9068	0.7096	2.203	0.8692	2.866	0.9719
0.9788	0.7198	2.283	0.8852	2.867	0.9759
1.015	0.7241	2.302	0.8871	3.024	0.9994
1.024	0.7248	2.308	0.8902	3.032	1.0015
1.051	0.7276	2.412	0.9036	3.120	1.0173
1.151	0.7377	2.412	0.9039	3.136	1.0196
1.185	0.7451	2.476	0.9105		
Shankman and Gordon-Direct Vapor Pressure (23)					
1.918	0.8305	4.947	1.2994	10.135	1.8955
2.239	0.8739	5.454	1.3677	11.235	1.9850
3.659	1.0967	5.833	1.4243	12.72	2.0718
3.776	1.1140	6.671	1.5367	15.12	2.1909
4.218	1.1868	7.540	1.6458	20.65	2.3562
4.279	1.1930	8.383	1.7402	22.63	2.3883
4.339	1.2031	9.400	1.8346		

Table I. Continued

<i>m</i>	ϕ	<i>m</i>	ϕ	<i>m</i>	ϕ
Grollman and Frazer-Direct Vapor Pressure (11)					
1.282	0.7426	1.772	0.8150	2.468	0.9026
1.671	0.8030	2.009	0.8453	2.871	0.9742
Hornung and Giauque-Direct Vapor Pressure (15)					
13.88	2.1360	18.51	2.3098	27.74	2.4340
Harned and Owen-emf (14)					
0.500	0.6684	1.000	0.7168	1.500	0.7751

^a This point was not used in the least-squares fit. ^b These values from 0.09 to 2.83 *m* were given weights of 0.75 in the least-squares fit.

Table II. Parameters for Equation 4

D_0	8.8×10^{-4}
D_1	2.241×10^{-4}
D_2	-1.624×10^{-5}
D_3	3.013×10^{-7}
σ	4.9×10^{-5}
Concn range	0.3–27.7 <i>m</i>

pressure measurements are of inadequate accuracy by modern standards and were not included in this analysis.

Glueckauf and Kitt (10), using a bithermal isopiestic technique, have studied sulfuric acid from 20 to 76 *m*. Since these data are not independent of the other sulfuric acid data at lower concentrations, and because of the very low vapor pressures involved, these data are not included in this analysis. In addition, most of Glueckauf and Kitts's data are outside the concentration region normally used for isopiestic measurements. Also, Giauque et al. partial molal free energies of water (β) for concentrations above 27.7 *m*, based on freezing point depression measurements, could be used to obtain water activities at high concentrations. However, it was necessary to tie their data to the H₂SO₄ water activity at 27.7 *m* in order to get water activities at higher concentrations so these values are not included here.

Sulfuric acid has also been studied by emf measurements (13, 25). These emf data are in good agreement with Sheffer et al. isopiestic measurements (24) from 0.5 to 1.5 *m* but are in disagreement with all of the other data at high concentrations, so emf data were not used above 1.5 *m*. Harned and Hamer (13) obtained water activities above 0.1 *m* by use of emf data from two different cells which were coupled to yield the water activities of the H₂SO₄ solutions. Below 0.1 *m* they obtained water activities from activity coefficients that were calculated assuming that the Debye-Huckel equation was obeyed for dilute solutions. Stokes (25) calculated water activities from these same data assuming that the water activity equals the mole fraction of the solvent at 0.0005 *m*. Osmotic coefficients calculated from the water activities reported by these two sources differ by 0.085 at 0.05 *m*, by 0.033 at 0.1 *m*, and by 0.003 or less above 0.5 *m*. Consequently, the results from these emf data must be considered uncertain below 0.5 *m*. The water activity data based on these measurements, as reported by Harned and Owen (14), were used to calculate values of ϕ at 0.5, 1.0, and 1.5 *m* and these points are included in Table I. A reinvestigation of sulfuric acid solutions using a mercury sulfate cell (7) indicates that Harned and Hamer's measurements are reliable only in this concentration range.

Attempts were made by us to fit Harned and Hamer's dilute solution mean molal activity coefficients (13) to the Debye-Huckel equation and also to this equation with a linear term in the molality added. In each case a very poor fit resulted and negative ion-size parameters were obtained. The Debye-Huckel theory can account for positive deviations from the limiting law, but the large amount of ionic association present in dilute H₂SO₄ solutions gives rise to sizable negative deviations. While it is

Table III. Parameters for Equation 7

<i>i</i>	r_i	A_i
1	0.750	$-5.545\ 523\ 727 \times 10$
2	0.875	$2.087\ 446\ 992 \times 10^2$
3	1.000	$-2.887\ 967\ 991 \times 10^2$
4	1.125	$1.777\ 105\ 198 \times 10^2$
5	1.250	$-4.112\ 741\ 365 \times 10$
6	3.125	$2.039\ 232\ 617 \times 10^{-3}$
7	3.375	$-6.467\ 613\ 632 \times 10^{-4}$

possible to correct these data for the presence of ionic association, the second dissociation constant of H₂SO₄ appears to be known only to about $\pm 9\%$ (5). This factor, coupled with uncertainties in the Debye-Huckel ion size parameter for H₂SO₄ (4), restricts the precision to which this data can yield activity coefficients and, hence, water activities. As a consequence, data that require extrapolation to infinite dilution such as emf and diffusion coefficient measurements will not yield entirely reliable osmotic coefficients until very accurate data are obtained for very dilute solutions. Harned and Hamer (13) give references for much of the dilute solution data.

In recent years there has been a renewal of interest in the determination of sulfuric acid thermodynamic properties using mercury sulfate and lead sulfate cells (1, 2, 4, 6, 7). Use of the mercury sulfate cell gives results that, after extrapolation to yield E^0 , yield the mean molal activity coefficient, γ_{\pm} , of sulfuric acid. The lead sulfate cell results in values of γ_{\pm}^3/a_1^2 and either a_1 or γ_{\pm} must be obtained from some other source. Because of uncertainties in the extrapolation of these data using the Debye-Huckel equation to obtain the E^0 's, and because of the uncertainty in the second dissociation constant of sulfuric acid, the resulting activity coefficients are not as reliable as desired, although they are known much more accurately than from previous measurements. Third law thermodynamic analyses of data for these cells (6, 7) have helped to resolve some of the remaining discrepancies between results for these two electrode systems. Because of the above considerations, these emf data were not used by us but the resulting "third law" activity coefficients (7) will be compared to our results later in this paper.

All of the osmotic coefficients in Table I (174 points) were fitted to an equation of the form

$$\phi = 1 - (A/3)m^{1/2} + \sum_i A_i m^{r_i} \quad (7)$$

where $A = (0.5108)(2)(\sqrt{3})(2.302\ 585) = 4.0743$. This equation is equivalent to the Debye-Huckel limiting law with a power series added. No ion-size parameter term was included since, as mentioned above, the Debye-Huckel equation is not obeyed by the dilute solutions. The A_i 's were determined by a least-squares fit. These coefficients and the powers, r_i , for the best fit are listed in Table III. The standard deviation of this fit is 0.0033. The errors in the A_i 's (standard deviations) increase as the powers increase, being 1.6–1.9% for the first five terms and

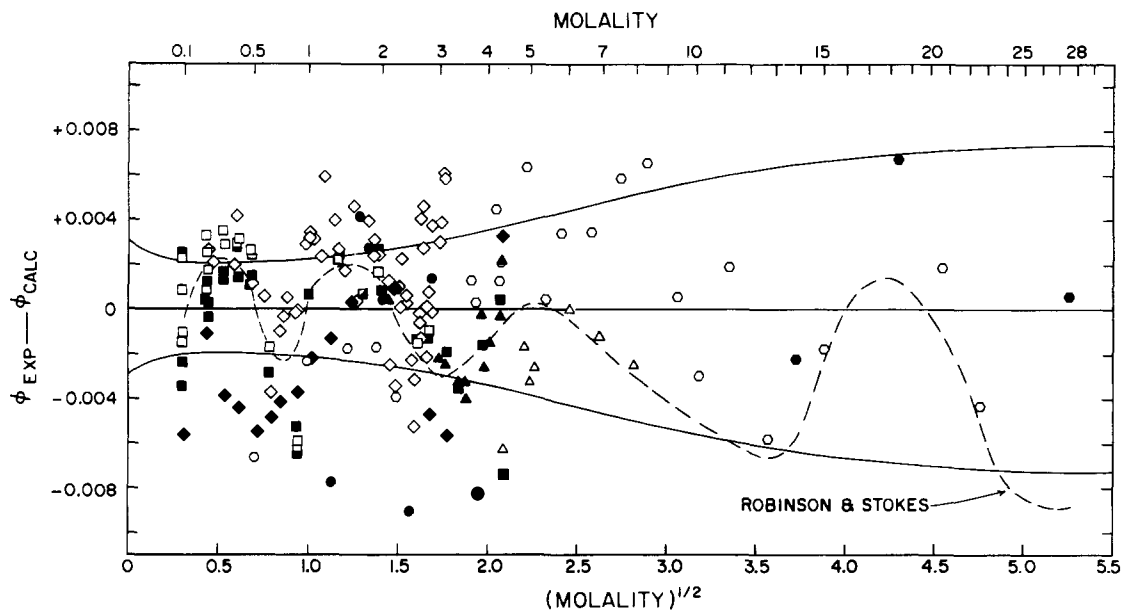


Figure 1. Differences between experimental and calculated osmotic coefficients for aqueous H_2SO_4 at 25°C : ϕ , Δ , Stokes (26); \blacktriangle , Robinson (20); \diamond , Robinson (19); \blacklozenge , Sheffer et al. (24); \square , Scatchard et al. vs. KCl (22); \blacksquare , Scatchard et al. vs. NaCl (22); \circ , Shankman and Gordon (23); \bullet , Grollman and Frazer (11); \odot , Hornung and Giauque (15); \circ , Harned and Owen (14).

3.2–3.4% for the two highest powers. Three of the points in Table I were given a weight of zero in the least-squares fit. The two most dilute points of Sheffer et al. (24) were given weights of zero since 2 weeks is clearly insufficient time to attain isopiestic equilibrium at these very low concentrations, and the third point was dropped because of its large deviation from the other data. Each set of Scatchard et al. isopiestic data (22) from 0.09 to 2.83 m was assigned weights of 0.75 (this has the effect of weighting each of these H_2SO_4 concentrations 1.5). This was done since they equilibrated their H_2SO_4 solutions against both NaCl and KCl solutions in this concentration range. All other points were given unit weights.

In the course of trying to represent the osmotic coefficients of sulfuric acid by eq 7, a considerable number of different polynomials were tried ranging from three to eight terms with different sets of powers in molality. In these fits, the r_i 's were not required to form a consecutive sequence. It was found that a minimum of seven polynomial coefficients was necessary to represent the experimental data. Series in m , $m^{1/2}$, and $m^{1/3}$ were found to be inadequate. However, a consecutive series in $m^{1/4}$, starting with $m^{3/4}$, worked fairly well while a number of nonconsecutive series in $m^{1/8}$ worked even better. The best $m^{1/8}$ fit was chosen to represent the H_2SO_4 data. In Figure 1 the differences between the experimental and calculated osmotic coefficients of sulfuric acid are shown as a function of the square root of the molality for the best fit.

Robinson and Stokes' osmotic coefficients listed for sulfuric acid (21) were corrected for the nonideal behavior of the solvent vapor (proportional to the amount of vapor pressure data used by them) and are compared to eq 7 in Figure 1. It should be noted that eq 7 and Robinson and Stokes' standards are in fair agreement. Most of the differences arise from the more limited set of data used to determine Robinson and Stokes' standard values. It can be seen that Shankman and Gordon's data fall slightly above the NaCl– H_2SO_4 isopiestic data while Stokes' NaOH– H_2SO_4 isopiestic data fall somewhat below the NaCl– H_2SO_4 data. Robinson and Stokes used Stokes' isopiestic data (27) up to 11.5 m and Shankman and Gordon's data (23) above this concentration. The average of these two sets of high concentration data is probably closer to the true values than either individual set so both sets of data were included in our data treatment. Although eq 7 represents the data up to 27.7 m , it

should be used with some caution above 19 m due to the scarcity of experimental data at these high concentrations.

The scatter of the data about eq 7 (Figure 1) indicates that the osmotic coefficients are known to about $\pm 0.3\%$ above 5 m and about $\pm 0.5\%$ below this concentration. Because of the scarcity of data at high concentrations, additional vapor pressure measurements would be desirable in the 3.5–28 m region. Also, additional dilute solution measurements are necessary for more reliable activity coefficients to be calculated from the presently available experimental data.

In Table IV values of ϕ , a_1 , and γ_{\pm} are given at various concentrations. The mean molal activity coefficients were calculated from the equation

$$\ln \gamma_{\pm} = \int_1^{\phi} d\phi - \int_0^m (1 - \phi)/m dm \quad (8)$$

where the values of ϕ were obtained from eq 7. Integration of this expression gives

$$\ln \gamma_{\pm} = -Am^{1/2} + \sum_i A_i((r_i + 1)/r_i)m^{r_i} \quad (9)$$

where the A_i 's and r_i 's were taken from Table III. The absolute values of the mean molal activity coefficients are sensitive to the behavior of the equation for ϕ at very low concentrations whereas eq 7 is based only on data above 0.09 m . Ionic association in H_2SO_4 solutions causes the osmotic coefficients to fall below the limiting slope values at low concentrations. This is shown in Figure 2. The extended Debye–Hückel equation cannot, therefore, represent H_2SO_4 below 0.09 m as accurately as desired so values of ϕ calculated from eq 7 for concentrations below 0.09 m have some uncertainty. Consequently, there will be some uncertainty in the absolute values of γ_{\pm} when they are calculated from eq 9. Our values of γ_{\pm} are based almost entirely on vapor pressure and isopiestic measurements (only 3 data points out of 174 were based on emf measurements). From Table IV we see that $\gamma_{\pm} = 0.247$ at 0.1 m from these data. Recent emf results (4, 7) give $\gamma_{\pm} = 0.244$ – 0.246 at this concentration. Considering the uncertainties in extrapolation present in both of these data treatments, the agreement is excellent. If third law based emf values (7) are normalized to our value at 0.1 m , then the two sets of γ_{\pm} 's agree to within 0.002 up to 6 m .

Most tabulated values of γ_{\pm} from isopiestic and vapor pressure measurements have been normalized to values obtained

Table IV. Thermodynamic Properties of H₂SO₄ at 25 °C

<i>m</i>	ϕ	a_1	γ_{\pm}
0.1	0.6796	0.996 33	0.2468
0.2	0.6652	0.992 84	0.1937
0.3	0.6649	0.989 28	0.1690
0.4	0.6690	0.985 64	0.1542
0.5	0.6751	0.981 92	0.1442
0.6	0.6824	0.978 11	0.1370
0.7	0.6906	0.974 21	0.1316
0.8	0.6995	0.970 21	0.1274
0.9	0.7090	0.966 10	0.1243
1.0	0.7191	0.961 88	0.1218
1.2	0.7408	0.953 09	0.1185
1.4	0.7643	0.943 81	0.1167
1.6	0.7894	0.934 01	0.1162
1.8	0.8159	0.923 70	0.1166
2.0	0.8435	0.912 86	0.1177
2.2	0.8720	0.901 5	0.1195
2.4	0.9013	0.889 7	0.1218
2.6	0.9313	0.877 3	0.1247
2.8	0.9617	0.864 6	0.1280
3.0	0.9925	0.851 4	0.1318
3.2	1.0236	0.837 8	0.1360
3.4	1.0548	0.823 8	0.1407
3.6	1.0860	0.809 5	0.1457
3.8	1.1173	0.795 0	0.1512
4.0	1.1484	0.780 1	0.1570
4.5	1.2255	0.742 3	0.1734
5.0	1.3009	0.703 6	0.1922
5.5	1.3738	0.664 7	0.2135
6.0	1.4440	0.626 1	0.237
6.5	1.5111	0.588 1	0.264
7.0	1.5749	0.551 1	0.293
7.5	1.6353	0.515 4	0.324
8.0	1.6923	0.481 1	0.358
8.5	1.7460	0.448 4	0.395
9.0	1.7962	0.417 4	0.434
9.5	1.8433	0.388 1	0.475
10.0	1.8872	0.360 6	0.519
10.5	1.9281	0.334 8	0.565
11.0	1.9662	0.310 7	0.613
11.5	2.0016	0.288 2	0.664
12.0	2.0345	0.267 3	0.717
12.5	2.0650	0.247 8	0.771
13.0	2.0933	0.229 8	0.828
13.5	2.1196	0.213 0	0.886
14.0	2.1440	0.197 5	0.946
14.5	2.1667	0.183 1	1.008
15.0	2.1878	0.169 7	1.071
15.5	2.2076	0.157 3	1.136
16.0	2.2260	0.145 9	1.203
16.5	2.2433	0.135 3	1.271
17.0	2.2595	0.125 4	1.341
17.5	2.2748	0.116 3	1.413
18.0	2.2893	0.107 8	1.486
18.5	2.3029	0.100 0	1.561
19.0	2.3159	0.092 7	1.638
19.5	2.3282	0.086 0	1.716
20.0	2.3400	0.079 7	1.796
21.0	2.3618	0.068 5	1.960
22.0	2.3814	0.058 9	2.131
23.0	2.3987	0.050 7	2.306
24.0	2.4134	0.043 7	2.485
25.0	2.4249	0.037 8	2.664
26.0	2.4326	0.032 8	2.839
27.0	2.4353	0.028 6	3.005

from emf measurements. This review resulted in a set of mean molal activity coefficients independent of this normalization procedure, and allows an independent check of the thermodynamic consistency of sulfuric acid data at 25 °C.

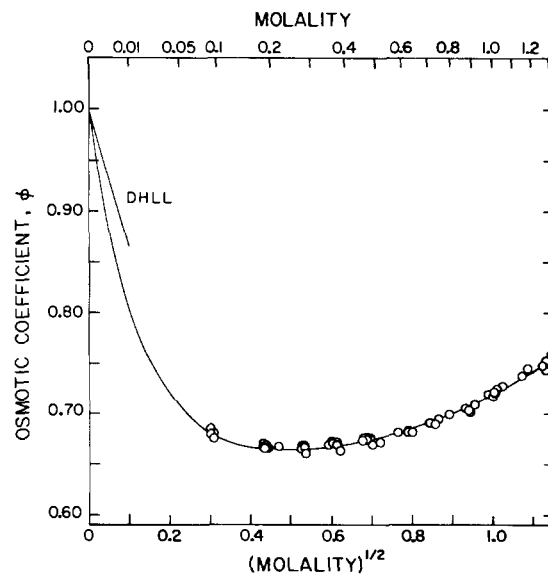


Figure 2. Dilute solution osmotic coefficients for aqueous H₂SO₄ at 25 °C. The Debye–Huckel limiting law is indicated by DHLL.

Summary

Osmotic coefficient data for aqueous solutions of H₂SO₄ at 25 °C have been reviewed and updated. The osmotic coefficients of H₂SO₄ seem to be known to about ±0.5% below 5 *m* and ±0.3% from 5 to 27.7 *m* but some additional data would be desirable, especially at high concentrations. Equation 7 reliably represents the presently available experimental osmotic coefficient data and new standard data can easily be incorporated within its framework. It has been shown that activity coefficients based on isopiestic and vapor pressure measurements are in good agreement with recent emf values.

Literature Cited

- Beck, W. H., Dobson, J. V., Wynne-Jones, W. F. K., *Trans. Faraday Soc.*, **56**, 1172 (1960).
- Beck, W. H., Singh, K. P., Wynne-Jones, W. F. K., *Trans. Faraday Soc.*, **55**, 331 (1959).
- Collins, M., *J. Phys. Chem.*, **37**, 1191 (1933).
- Covington, A. K., Dobson, J. V., Lord Wynne-Jones, *Trans. Faraday Soc.*, **61**, 2050 (1965).
- Covington, A. K., Dobson, J. V., Lord Wynne-Jones, *Trans. Faraday Soc.*, **61**, 2057 (1965).
- Duisman, J. A., Giaque, W. F., *J. Phys. Chem.*, **72**, 562 (1968).
- Gardner, W. I., Mitchell, R. E., Cobble, J. W., *J. Phys. Chem.*, **73**, 2021 (1969).
- Giaque, W. F., Hornung, E. W., Kunzler, J. E., Rubin, T. R., *J. Am. Chem. Soc.*, **82**, 62 (1960).
- Gibbard, Jr., H. F., Scatchard, G., Rousseau, R. A., Creek, J. L., *J. Chem. Eng. Data*, **19**, 281 (1974).
- Glueckauf, E., Kitt, G. P., *Trans. Faraday Soc.*, **52**, 1074 (1956).
- Grollman, A., Frazer, J. C. W., *J. Am. Chem. Soc.*, **47**, 712 (1925).
- Hamer, W. J., Wu, Y.-C., *J. Phys. Chem. Ref. Data*, **1**, 1047 (1972).
- Harned, H. S., Hamer, W. J., *J. Am. Chem. Soc.*, **57**, 27 (1935).
- Harned, H. S., Owen, B. B., "The Physical Chemistry of Electrolytic Solutions", Reinhold, New York, N.Y., 1958, p 574.
- Hornung, E. W., Giaque, W. F., *J. Am. Chem. Soc.*, **77**, 2744 (1955).
- Jones, E. R., *J. Appl. Chem.*, **1**, S144 (1951).
- Kangro, W., Groeneveld, A., *Z. Phys. Chem. (Frankfurt am Main)*, **32**, 110 (1962).
- McCullough, J. P., Pennington, R. E., Waddington, G., *J. Am. Chem. Soc.*, **74**, 4439 (1952).
- Robinson, R. A., *Trans. Faraday Soc.*, **35**, 1229 (1939).
- Robinson, R. A., *Trans. R. Soc., N.Z.*, **75** (2), 203 (1945).
- Robinson, R. A., Stokes, R. H., "Electrolyte Solutions", 2d ed, Butterworth, London, 1965.
- Scatchard, G., Hamer, W. J., Wood, S. E., *J. Am. Chem. Soc.*, **60**, 3061 (1938).
- Shankman, S., Gordon, A. R., *J. Am. Chem. Soc.*, **61**, 2370 (1939).
- Sheffer, H., Janis, A. A., Ferguson, J. B., *Can. J. Res., Sect. B*, **17**, 336 (1939).
- Stokes, R. H., *J. Am. Chem. Soc.*, **67**, 1686 (1945).
- Stokes, R. H., *J. Am. Chem. Soc.*, **67**, 1689 (1945).
- Stokes, R. H., *J. Am. Chem. Soc.*, **69**, 1291 (1947).
- Wexler, A., Greenspan, I., *J. Res. Nat. Bur. Stand., Sect. A*, **75**, 213 (1971).

Received for review May 12, 1975. Accepted March 18, 1976. This work was performed for the U.S. Energy Research and Development Administration under Contract No. W-7405-eng-82.