

Thermodynamic Properties of 0–6 mol kg⁻¹ Aqueous Sulfuric Acid from 273.15 to 328.15 K

Simon L. Clegg

School of Environmental Sciences, University of East Anglia, Norwich, UK NR4 7TJ

Joseph A. Rard

Earth Sciences Division, Physical Sciences Department, Lawrence Livermore National Laboratory, University of California, Livermore, CA 94550, USA

Kenneth S. Pitzer

Department of Chemistry, University of California, Berkeley, CA 94720, USA

Generalised equations are presented for an extended form of the Pitzer molality-based thermodynamic model, involving an ionic strength-dependent third virial coefficient. Compatibility with the established formulation is retained. Osmotic coefficients, emf measurements, degrees of dissociation of the HSO₄⁻ ion, differential enthalpies of dilution and heat capacities for aqueous H₂SO₄ from 273.15 to 328.15 K, 0–6.1 mol kg⁻¹ and at 1 atm pressure have been critically evaluated. Treating this solution as the mixture H⁺–HSO₄⁻–SO₄²⁻–H₂O, and using hydrogen sulfate dissociation constants from the literature, the model parameters were fitted to the data yielding a self-consistent representation of activities, speciation and thermal properties together with the standard potentials of four electrochemical cells and standard-state heat capacities of the SO₄²⁻ ion as functions of temperature. The model equations represent the experimental data accurately (without the use of mixture parameters $\theta_{\text{HSO}_4, \text{SO}_4}$ and $\psi_{\text{HSO}_4, \text{SO}_4, \text{H}}$), and should yield values of the osmotic coefficient that are suitable for use as an isopiestic standard over this temperature and molality range. The new model will also enable improved prediction of the properties of mixed acidic sulfate systems.

1. Introduction

Aqueous sulfuric acid is a major industrial chemical, and its thermodynamic properties have been studied extensively over many years.¹ Recent evaluations include those by Staples² and Rard *et al.*³ (osmotic and activity coefficients at 298.15 K), Bolsaitis and Elliott⁴ (partial pressures) and Zeleznik⁵ (properties of aqueous and solid phases, excluding vapour pressures). Sulfuric acid is also an important component of atmospheric aerosols,⁶ notably in the stratosphere,⁷ and of brines. A knowledge of the sulfate–hydrogensulfate equilibrium is required to calculate solubilities and partial pressures of volatile acids such as HCl and HNO₃ in acidified sulfate mixtures, and for relating hydrogen-ion activities in seawater and estuarine waters to pH measurements.⁸

For practical applications, a treatment of aqueous H₂SO₄ thermodynamics that readily generalises to solution mixtures is required. The Pitzer ion-interaction model⁹ has previously been applied to represent evaluated osmotic coefficients, emf and enthalpy data for that system.^{10–12} However, to achieve the accuracy that is often required, and to incorporate more recent experimental work on the osmotic coefficient, heat capacity and hydrogensulfate dissociation constant, a more detailed and comprehensive treatment is worthwhile.

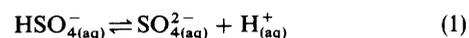
Here we utilise an extended form of the Pitzer ion-interaction model to represent osmotic coefficients, vapour pressure, emf, enthalpy of dilution, heat capacity and degree of dissociation data from 0 to 6.1 mol kg⁻¹, $T = 273.15$ to 328.15 K. The equations and parameters presented provide an accurate and self-consistent description of these thermodynamic properties, and will form the basis of an improved model for solution mixtures at moderate temperature and molality.

2. The Model

The Pitzer ion-interaction model is based upon an expression for the excess Gibbs energy of the solution in terms of an extended Debye–Hückel function and a virial expansion in

terms of the molalities of the dissolved species, which may be ionic or neutral solutes.⁹ The model treats strong electrolytes as fully dissociated in solution. In addition to earlier work on the thermodynamics of aqueous H₂SO₄,¹⁰ the model has been used successfully in numerous geochemical applications.¹³

Raman spectral studies have shown that the first dissociation of sulfuric acid (H₂SO₄ ⇌ H⁺ + HSO₄⁻) is essentially complete at <40 mol kg⁻¹ (14 mol dm⁻³) and 298.15 K (see also Section 3.5).¹⁴ However, this is not the case for the second dissociation reaction involving the hydrogensulfate ion, whose dissociation must be considered explicitly:



$$K_{\text{HSO}_4} = a(\text{H}^+)a(\text{SO}_4^{2-})/a(\text{HSO}_4^-) \\ = m(\text{H}^+)\gamma_{\text{H}}m(\text{SO}_4^{2-})\gamma_{\text{SO}_4}/[m(\text{HSO}_4^-)\gamma_{\text{HSO}_4}] \quad (2)$$

where $K_{\text{HSO}_4}/\text{mol kg}^{-1}$ is the thermodynamic dissociation constant of HSO₄⁻ in solution, m and a denote molality and activity, respectively, and γ_i is the activity coefficient of species i .

The basic model equations for osmotic (ϕ) and ionic activity coefficients contain the cation–anion (ca) interaction parameters $\beta_{\text{ca}}^{(0)}$, $\beta_{\text{ca}}^{(1)}$, $\beta_{\text{ca}}^{(2)}$ and C_{ca} , which are functions of temperature and pressure. A series of additional parameters may be included to describe interactions between ions and any neutral species present, but these are not required here.

Three terms relate to the H⁺, SO₄²⁻ pairwise interaction; in the first order in molality this effect is given by the sum $1/K_{\text{HSO}_4} + \beta_{\text{H}, \text{SO}_4}^{(0)} + \beta_{\text{H}, \text{SO}_4}^{(1)}$. In second or higher order, the effect of each term is different; hence there is no objection to the inclusion of all three.¹⁰ The limiting effective K_{HSO_4} at infinite dilution is the reciprocal of this sum. Since $\beta_{\text{H}, \text{SO}_4}^{(0)}$ and $\beta_{\text{H}, \text{SO}_4}^{(1)}$ are small in comparison to $1/K_{\text{HSO}_4}$, their effect is to modify the limiting K_{HSO_4} only slightly from 0.0105 to 0.010424 mol kg⁻¹. The $\beta^{(2)}$ terms used for 2 : 2 and higher charged electrolytes are inappropriate for this system and

would only add to the redundancies. They are therefore omitted.

In practical applications, several workers have employed empirical extensions of the model to represent better experimental results at high ionic strength. For example, Archer,¹⁵ for the system NaCl–H₂O, assumed an ionic strength dependence of the third virial coefficient, leading to an additional parameter, $C_{ca}^{(1)}$. Test calculations showed that this type of extension leads to a valuable improvement in quality of fit when applied to aqueous H₂SO₄, and it has been adopted here. (The original C_{ca} remains from the earlier formulation, but is now designated $C_{ca}^{(0)}$.) It is important that the extended equations for aqueous H₂SO₄ are also applicable to solution mixtures containing other components; indeed the extensions may also prove useful for other solutes. In Appendix I are given generalised equations of the extended model for excess Gibbs energy and osmotic and activity coefficients, for a solution containing an indefinite number of ionic solutes. Equations for the system H₂SO₄–H₂O are given below:

$$\begin{aligned} \ln(\gamma_H) = & \mathcal{F} + m(\text{HSO}_4)(2B_{H, \text{HSO}_4} + ZC_{H, \text{HSO}_4}^T) \\ & + m(\text{SO}_4)(2B_{H, \text{SO}_4} + ZC_{H, \text{SO}_4}^T) \\ & + m(\text{H})m(\text{HSO}_4)C_{H, \text{HSO}_4}^T + m(\text{H})m(\text{SO}_4)C_{H, \text{SO}_4}^T \\ & \{ + 2m(\text{Pb})\Phi_{H, \text{Pb}} \} + m(\text{HSO}_4)m(\text{SO}_4)\psi_{\text{HSO}_4, \text{SO}_4, \text{H}} \quad (3) \end{aligned}$$

$$\begin{aligned} \ln(\gamma_{\text{HSO}_4}) = & \mathcal{F} + m(\text{H})(2B_{H, \text{HSO}_4} + ZC_{H, \text{HSO}_4}^T) \\ & + m(\text{H})m(\text{HSO}_4)C_{H, \text{HSO}_4}^T + m(\text{H})m(\text{SO}_4)C_{H, \text{SO}_4}^T \\ & + m(\text{SO}_4)(2\Phi_{\text{HSO}_4, \text{SO}_4} + m(\text{H})\psi_{\text{HSO}_4, \text{SO}_4, \text{H}}) \quad (4) \end{aligned}$$

$$\begin{aligned} \ln(\gamma_{\text{SO}_4}) = & 4\mathcal{F} + m(\text{H})(2B_{H, \text{SO}_4} + ZC_{H, \text{SO}_4}^T) \\ & + 2m(\text{H})m(\text{HSO}_4)C_{H, \text{HSO}_4}^T + 2m(\text{H})m(\text{SO}_4)C_{H, \text{SO}_4}^T \\ & + m(\text{HSO}_4)(2\Phi_{\text{HSO}_4, \text{SO}_4} + m(\text{H})\psi_{\text{HSO}_4, \text{SO}_4, \text{H}}) \quad (5) \end{aligned}$$

$$\begin{aligned} \phi - 1 = & (2/\sum_i m_i)[-A_\phi I^{3/2}/(1 + 1.2\sqrt{I}) \\ & + m(\text{H})m(\text{HSO}_4)(B_{H, \text{HSO}_4}^\phi + Z[C_{H, \text{HSO}_4}^{(0)} \\ & + C_{H, \text{HSO}_4}^{(1)} \exp(-\omega_{H, \text{HSO}_4}\sqrt{I})]) \\ & + m(\text{H})m(\text{SO}_4)\{ B_{H, \text{SO}_4}^\phi + Z[C_{H, \text{SO}_4}^{(0)} \\ & + C_{H, \text{SO}_4}^{(1)} \exp(-\omega_{H, \text{SO}_4}\sqrt{I})] \} \\ & \{ + m(\text{H})m(\text{Pb})\Phi_{H, \text{Pb}}^\phi + m(\text{HSO}_4)m(\text{SO}_4)(\Phi_{\text{HSO}_4, \text{SO}_4}^\phi \\ & + m(\text{H})\psi_{\text{HSO}_4, \text{SO}_4, \text{H}}) \} \quad (6) \end{aligned}$$

and

$$\begin{aligned} \mathcal{F} = & -A_\phi[\sqrt{I}/(1 + 1.2\sqrt{I}) + (2/1.2)\ln(1 + 1.2\sqrt{I})] \\ & + m(\text{H})m(\text{HSO}_4)[\beta_{H, \text{HSO}_4}^{(1)}g'(\alpha_{H, \text{HSO}_4}\sqrt{I}) \\ & + 2ZC_{H, \text{HSO}_4}^{(1)}h'(\omega_{H, \text{HSO}_4}\sqrt{I})/I] \\ & + m(\text{H})m(\text{SO}_4)[\beta_{H, \text{SO}_4}^{(1)}g'(\alpha_{H, \text{SO}_4}\sqrt{I}) \\ & + 2ZC_{H, \text{SO}_4}^{(1)}h'(\omega_{H, \text{SO}_4}\sqrt{I})/I] \\ & \{ + m(\text{H})m(\text{Pb})\Phi_{H, \text{Pb}}^\phi + m(\text{HSO}_4)m(\text{SO}_4)\Phi_{\text{HSO}_4, \text{SO}_4}^\phi \} \quad (7) \end{aligned}$$

Superscript T denotes 'total'. For clarity, ion charges are omitted from the species molalities in the above equations. In some electrochemical cells (Section 3.2), PbSO₄ or Hg₂SO₄ are present at low molalities. To the first order, their influence is accounted for *via* an increase in the ionic strength of the solution (both salts); and in the case of PbSO₄ only, by the unsymmetrical mixing functions $\Phi_{H, \text{Pb}}$, $\Phi_{H, \text{Pb}}^\phi$ and $\Phi'_{H, \text{Pb}}$ given in the terms in braces in eqn. (3), (6) and (7). In the above equations I is the ionic strength (in mol kg⁻¹), and A_ϕ is the Debye–Hückel constant, as recently calculated by

Archer and Wang.¹⁶ Here we represent their A_ϕ using a Chebychev polynomial, see Appendix II.

Archer¹⁷ has discussed the effect of differences between his Debye–Hückel constants and those from earlier evaluations, which are greatest at extremes of temperature and pressure, on representations of solution properties using the Pitzer model. Of relevance to the present study, we note maximum differences of 1% in Debye–Hückel slopes for apparent molal enthalpy (A_H/RT) and 2.5% for apparent molal heat capacity (A_C/R) from values tabulated by Pitzer,⁹ which are based on the equation of Bradley and Pitzer¹⁸ for the relative permittivity of water.

The functions B_{ca} , B_{ca}^ϕ , C_{ca}^T , Φ_{ca} , Φ_{ca}^ϕ and Φ'_{ca} contain model parameters and (in some cases) unsymmetrical mixing terms, and are defined in Appendix I, as are the molality-dependent functions Z , $g'(x)$ and $h(x)$. The coefficient α_{ca} (which appears in B_{ca} and B_{ca}^ϕ) is normally set constant for broad ranges of electrolytes, typically to 1.4 mol^{-1/2} kg^{1/2} for 2 : 2 metal sulfates¹⁹ and 2.0 mol^{-1/2} kg^{1/2} for most other valence types. However, values for individual cation–anion combinations can also be assigned, which is the approach we take here. An analogous coefficient ω_{ca} also appears in functions $h(x)$ and $h'(x)$.

Model equations for apparent molal enthalpy ($L^\phi/J \text{ mol}^{-1}$) and heat capacity ($C_p^\phi/J \text{ mol}^{-1} \text{ K}^{-1}$) may be obtained by partial differentiation of the excess Gibbs energy expression with respect to temperature, with pressure and molality held constant:

$$L^\phi = -T^2\{\partial[G^{\text{ex}}/(n_w T)]/\partial T\}/m(\text{H}_2\text{SO}_4) \quad (8)$$

$$C_p^\phi = C_p^\phi + \partial L^\phi/\partial T \quad (9a)$$

$$= C_p^\phi - T\{2\partial[G^{\text{ex}}/(n_w T)]/\partial T + T\partial^2[G^{\text{ex}}/(n_w T)]/\partial T^2\}/m(\text{H}_2\text{SO}_4) \quad (9b)$$

where G^{ex} is the excess Gibbs energy of the mixture, n_w the number of kg of solvent (water) and $m(\text{H}_2\text{SO}_4)$ the stoichiometric molality of sulfuric acid. The excess Gibbs energy per kg of solvent can be expressed in terms of the activity and osmotic coefficients, yielding for pure aqueous H₂SO₄:

$$G^{\text{ex}}/(n_w RT) = 3m(\text{H}_2\text{SO}_4)[\ln(\gamma_\pm) + 1 - \phi_{\text{st}}] \quad (10)$$

for ideality defined on the molality basis, where R is the gas constant (8.3144 J mol⁻¹ K⁻¹). The stoichiometric mean activity coefficient γ_\pm and osmotic coefficient ϕ_{st} of H₂SO₄ are related to the quantities in eqn. (3), (5) and (6) by:

$$\phi_{\text{st}} = \phi[m(\text{H}^+) + m(\text{HSO}_4^-) + m(\text{SO}_4^{2-})]/[3m(\text{H}_2\text{SO}_4)] \quad (11)$$

$$\gamma_\pm^3 = \gamma_H^2\gamma_{\text{SO}_4}[m(\text{H}^+)^2m(\text{SO}_4^{2-})/\{4[m(\text{H}_2\text{SO}_4)]^3\}] \quad (12)$$

For pure aqueous solutions of strong electrolytes the equations for L^ϕ and C_p^ϕ are straightforward, and have been presented many times before for the model without the additional parameter $C_{ca}^{(1)}$.^{9,20,21} Archer gives equations which include $C_{ca}^{(1)}$ for thermal properties of pure aqueous solutions of 1 : 1 electrolytes.¹⁵ Similar equations for aqueous H₂SO₄ would be extremely complicated, as the dissociation of HSO₄⁻ varies with temperature, and so introduces extra differentials. We therefore differentiate eqn. (10) numerically to obtain the required quantities in the expressions for L^ϕ and C_p^ϕ , using centred finite difference formulae incorporating either four (for $\partial/\partial T$) or five (for $\partial^2/\partial T^2$) terms. The step size was set to $5.0 \times 10^{-3}T$, where T is the temperature of the measurement.

3. The Data

Sulfuric acid and its aqueous solutions have been the subject of thermodynamic investigation for at least a century, resulting in a very large body of experimental measurements.

Much early work is summarised in compilations of Bichowsky and Rossini,²² and Timmermans.²³ Sources of data have been compiled by Staples and Wobbeking¹ and Staples *et al.*²⁴ Previous evaluations of the thermodynamic properties of aqueous H₂SO₄ include those of Giauque *et al.*²⁵ (0–100% acid and for solid hydrates; $T \leq 300$ K), Pitzer *et al.*¹⁰ (0–6 mol kg⁻¹; temperatures at, or close to, 298.15 K), Staples² (0–28 mol kg⁻¹; 298.15 K), Rard *et al.*³ (0.1–27.7 mol kg⁻¹; 298.15 K) with later improvements,^{26,27} and Zeleznik⁵ (0–100% acid and for solid hydrates; $T \leq 350$ K). Vapour–liquid equilibrium in the H₂SO₄–H₂O system, with an emphasis on high temperatures, has been evaluated by Gmitro and Vermeulen²⁸ and more recently by Bolsaitis and Elliott.⁴

The aim of the present study is to provide an accurate and self-consistent description of aqueous solution activities and thermal properties of aqueous H₂SO₄ from 273 to 328 K and molalities up to 6 mol kg⁻¹, within a framework (the Pitzer model) that allows ready extension to more complex mixtures. We have attempted to be comprehensive in our consideration of the available data, though we cannot claim complete coverage. Measurements included in the present study cover the period 1899 to the present, during which there have been several revisions both to atomic masses and temperature scales. Changes in atomic masses only affect molality in the fifth significant figure, and these molalities are often quoted to only three or four figures. For consistency we

have generally used molar masses of H₂O and H₂SO₄ given by the authors of the various studies, otherwise we have used the following values from the 64th edition of the CRC Handbook,²⁹ based upon the 1969 IUPAC recommendations:³⁰ $M(\text{H}_2\text{O}) = 18.0152 \text{ g mol}^{-1}$ and $M(\text{H}_2\text{SO}_4) = 98.073 \text{ g mol}^{-1}$.

Conversions of temperature scales to the current ITS-90 are tabulated by Goldberg and Weir.³¹ In general, the δT applicable to the experimental temperatures, for example -0.014 K at 25°C for IPTS-48 and -0.006 K for IPTS-68,³¹ are of the same order as the accuracy of temperature control which is typically 0.01–0.02 K. Also, the changes in most thermodynamic properties (ϕ , emf *etc.*) with temperature are low enough that the change Δ , due to any temperature correction, is small relative to the precision of measurement and the fit of the model. Therefore, where experimental temperatures have been quoted in $^\circ\text{C}$ they have been converted to absolute values simply by adding 273.15 K. Note that absolute temperatures given by Covington *et al.*³² and Beck *et al.*^{33,34} are based upon an ice point of $273.16 \text{ K} = 0^\circ\text{C}$.³⁵ In this instance we have subtracted 0.01 K from the temperatures given by those authors.

The data are discussed below. Tables 1–5 list, for each data type, the concentration and temperature ranges of measurement, the numbers of experimental points, which measurements were rejected as being in error and the relative weight assigned to each dataset.

Table 1 Availability of isopiestic (iso) and direct vapour pressure (vp) data for aqueous H₂SO₄

molality/mol kg ⁻¹	T/K	no. of observations ^a	method	standard	w_r	rejected ^a	N	ref.
1.673–21.65	298	33 (13)	iso	NaOH	1.0	11	1	37
2.083–4.354	298	12	iso	NaCl	1.0	0	2	38
0.019–4.349	298	18	iso	NaCl	0.25	3	3	39
0.091–2.830	298	23	iso	KCl	0.25/0.75 ^b	1	4	40
0.091–4.374	298	28	iso	NaCl	0.25/0.75 ^b	2	5	40
0.195–3.136	298	53	iso	KCl	0.25	0	6	41
1.918–22.63	298	20 (10)	vp	—	1.0	1	7	48
0.073–2.871	298	13	vp	—	1.0	9	8	50
13.88–27.74	298	3 (0)	vp	—	—	—	9	115
7.326–12.58	298	9 (0)	vp	—	—	—	10	51
0.346–4.361	298	44	iso	NaCl	1.0	0	11	26
4.349–19.33	298–409	146 (24) ^c	vp	—	0.1	2	12	47
1.133–40.78	298 ^d	12 (3)	vp	—	—	3	13	49
2.091–4.355	298	16	iso	NaCl	1.0	0	14	43
0.141–0.170	298	4	iso	KCl	1.0	0	15	42
0.442–0.487	298	3	iso	KCl	1.0	0	16	— ^e
0.189–4.175	323	44	iso	NaCl	1.0	5	17	116
1.450–4.096	273	8	iso	NaCl	0.25	2	18	55
1.033	273	1	iso	urea	0.25	0	19	55
1.14–9.56	273–373	99 (61)	vp	—	—	61	20	117
5.217–23.79 ^f	203–250	9	vp	—	—	—	21	52
4.026–4.420	298	4	iso	NaCl	1.0	0	22	— ^h

N is the dataset number, referred to in the figures. Note also the work of Giauque *et al.*²⁵ who have evaluated solvent and solute activities (and other properties) of aqueous H₂SO₄ over the entire mole fraction range. Glueckauf and Kitt,¹¹⁸ using a bithermal isopiestic technique, have obtained osmotic coefficients to 76 mol kg⁻¹. Their values were not included in our calculations because they reported that it was necessary to normalise their measurements to lower molality results from other studies. Osmotic coefficients relative to the NaCl isopiestic standard were calculated using eqn. (7) and (36) of Archer.¹⁵ Note the following errors in Archer's eqn. (36): lines three and four should read:

$$+ b_{i,6} 100 [T^\circ / (T - 200 \text{ K})]^2 + b_{i,7} 200 (T^\circ / T)^2 + b_{i,8} [T / (500 T^\circ)]^3$$

Also, the coefficient $b_{3,12}$ should have the value 0.066 220 250 84. ^a The second number in parentheses gives the number of data points within the fitted molality range 0–6.10 mol kg⁻¹; the figure in the 'rejected' column refers only to those points within the fitted range. Molalities of the rejected data for each reference: 1.673–4.376, 5.002, 5.144;³⁷ 0.0187, 0.0456, 3.815;³⁹ 0.0909, 0.0908, 4.374;⁴⁰ 2.239;⁴⁸ 0.073–1.282, 2.468;⁵⁰ 3.399, 5.490;⁴⁷ 0.3037, 0.2576, 0.1894, 2.1157, 3.1911;¹¹⁶ 1.450, 2.186 mol kg⁻¹.⁵⁵ ^b Molalities below 1.0 mol kg⁻¹ are given the lower weight of 0.25. ^c Molality and temperature ranges are those of the experimental determinations. Only five values (two of which were rejected) were used here, taken from the interpolated 298.15 K isotherm in Collins' Table 3.⁴⁷ ^d Data for some other temperatures given graphically. ^e J. A. Rard, work in progress. ^f Vapour pressures also measured along the freezing curve of sulfuric acid tetrahydrate and hexahydrate (argued by Zhang *et al.*⁵² to have composition H₂SO₄ · 6.5H₂O). ^g Representative data presented only in graphical form, and also as fitting equations. ^h J. A. Rard and D. G. Archer, unpublished data.

Table 2 Availability of emf data for cells I–IV

cell	molality/mol kg ⁻¹	T/K	no. of observations ^a	int. ^b	w _r	rejected ^a	N	ref.
I	0.1000–8.272	278–328	77 (69)	yes	1.0	0	1	33
I	0.0073–0.096	298	5	no	1.0	0	2	32
I	0.01945–0.997 ^c	298	19	yes	—	19	3	59
II	0.0050–0.050	298	2	yes	—	2	4	119
II	0.1003–7.972	278–328	54 (47)	no	1.0	7	5	34
II	0.0073–0.096	298	13	no	1.0 ^d	0	6	32
II	0.0506–2.386	298	7	yes	1.0	0	7	66
II	0.0506–8.207	298	5 (4)	yes	1.0	0	8	120
II	0.0010–0.010	298	5	no	—	5	9	121
II	0.0050–1.041	298	6	yes	1.0 ^d	2	10	67
II	0.1000–4.000	298	7	yes	1.0	2	11	122
III	0.0536–3.499	298	10	yes	1.0	2	12	123
IV	0.0010–0.020	273–323	25	yes	1.0	12	13	63

^a See first sentence of footnote^a in Table 1. Molalities of the rejected data for each reference: 1.872, 5.767 (278 K); 0.1003, 1.872 (318 K); 0.1003, 1.872, 5.767 (328 K);³⁴ 0.02506, 0.2529;⁶⁷ 2.0, 4.0;¹²² 0.5154, 1.036;¹²³ 0.001 and 0.002 (all temperatures); 0.005, 0.02 (273 K).⁶³ ^b Emfs reported in international volts. ^c Measured values (Table 1 of ref. 59) using Hamer's preferred methods (4, 5 and 6) of electrode preparation. ^d For molalities < 0.04 mol kg⁻¹, relative weights are reduced to 0.5 as the model-calculated emf is sensitive to the amount of Hg₂SO₄ assumed to be present (see text).

Table 3 Availability of enthalpy data (enthalpies of dilution) for aqueous H₂SO₄

molality ^a /mol kg ⁻¹	T/K	no. of observations ^b	w _r	rejected ^b	N	ref.
(> 100 wt.%)–0.506 ^c	298	72 (10)	1.0	4	1	70
6.423–0.001	298	25 (24)	2.23	0	2	71
3.679–0.003	298	45	0.86	7	3	72
0.050–0.003 ^d	298	11	0.045	6	4	73
30.860–6.07 ^e	253	10 (1)	—	—	5	70
0.005–6.0 ^f	303–598	—	—	—	6	75

^a Range given for initial molality, *m*₁. ^b See first sentence of footnote^a of Table 1. Molalities (*m*₁) of the rejected data for each reference: 1.508, 1.040, 0.726, 0.506;⁷⁰ 0.0251 (two points), 0.0125, 0.00627, 0.00313 (two points);⁷³ 0.00305, 0.00504, 0.00508, 0.0174 (three points), 0.0846.⁷² ^c See also corrections given by Giauque *et al.*²⁵ Differential enthalpies of dilution were calculated as Δ_{dil}H = L*(*m*₂) – L*(*m*₁) = ΔA_L(H₂O) (Table 3 of Kunzler and Giauque⁷⁰). ^d Reported mol dm⁻³ concentrations were converted to molality using densities compiled by Söhnel and Novotný.¹²⁴ ^e The single data point within the fitted range was not used. ^f Experiments carried out at 7–40 MPa, and therefore not relevant to the present study.

Table 4 Availability of heat capacities for aqueous H₂SO₄

molality/mol kg ⁻¹	T/K	no. of observations ^a	w _r	rejected ^a	N	ref.
(> 100 wt.%)–1.149 ^b	298	75 (13)	1.0	2	1	70
0.563–0.052	298	9	1.0	0	2	81
2.230–0.044 ^c	298	13	1.0	4	3	76
1.013–0.103	298	8	0.50	2	4	80
1.013–0.103	328	8	0.50	2	5	80
1.013–0.103	313	8	0.50	2	6	80
(100 wt.%)–0.035	293	37 (20)	0.25	1	7	77
1.013–0.103	283	8	0.50	0	8	80
30.869–4.508	253	11 (2) ^d	—	—	—	70
9.2468	214–300	11	—	—	—	125
8.5385	230–319	14	—	—	—	125
6.9377	213–296	11	—	—	—	125
55.509	284–305	4	—	—	—	126
27.754	239–306	12	—	—	—	126
18.503	182–298 ^e	12	—	—	—	127
18.503	244–296 ^e	8	—	—	—	128
13.881	251–305	9	—	—	—	128

Socolik⁷⁸ tabulates the specific heats (to three figures) of Savarizky (unreferenced) at 295.65, 313.15, 333.15 and 353.15 K from 6.06 to 100 wt.% H₂SO₄. ^a See first sentence of footnote^a of Table 1. Molalities of the rejected data for each reference: 1.586, 1.231;⁷⁰ 0.0444, 0.0713, 0.1748, 0.5515;⁷⁶ 0.1035, 0.1781 (*T* ≥ 298.15 K);⁸⁰ 0.0347.⁷⁷ ^b See also corrections given by Giauque *et al.*²⁵ ^c These heat capacities are on a (g H₂O)⁻¹ basis.⁷⁶ This is not stated in the paper, and caused Zeleznik⁵ to reject their results as erroneous. ^d These two data points not used. ^e Includes supercooled solutions.

Table 5 Availability of degree of dissociation data ($\text{HSO}_4^- \rightleftharpoons \text{SO}_4^{2-} + \text{H}^+$) for aqueous H_2SO_4

molality/mol kg ⁻¹	method ^a	T/K	no. of observations ^b	w _r	rejected ^b	N	ref.
0.01–0.304	1	300	10	—	10	1	129
0.02–4.00 ^c	2	298	10	—	10	2	130
0.00025–0.050	3	298	7	1.0	0	3	131
0.00090–2.634	4	298	13	1.0	0	4	86
0.264–42.62	2	298 ^d	18 (9)	1.0	3	5	84
0.050–40.15 ^e	2	273–323	38 (16)	1.0/0.3	2	6	14
0.052–29.26	5	298 ^d	12 (6)	1.0	2	7	85

References above are restricted to studies of the variation of α as a function of concentration, and do not include those whose sole aim is to determine the infinite-dilution value of K_{HSO_4} . Kerker¹³² recalculated α from literature data (including those of Sherrill and Noyes¹³¹) but many values are grossly discordant with other work, and have not been included here. ^a Methods: 1, spectrophotometry; 2, Raman spectroscopy; 3, conductance; 4, molar volume; 5, NMR. ^b See first sentence of footnote ^a of Table 1. Molalities of the rejected data for each reference: 0.52, 1.03;⁸⁵ 2.915, 1.377, 0.264;⁸⁴ 0.502, 0.504.¹⁴ ^c Concentrations in mol dm⁻³. ^d Temperature not specified. Presumably at a 'room temperature' close to 298 K. ^e Measurements at 273.15 and 323.15 K were given relative weights of 0.30. Data were also reported in this study for the first dissociation step at very high molalities ($\text{H}_2\text{SO}_4 \rightleftharpoons \text{H}^+ + \text{HSO}_4^-$).

3.1 Vapour Pressure and Isopiestic Measurements

Available osmotic coefficients and vapour pressures relevant to the present study are summarised in Table 1. Early (and less reliable) data not included here, some of it from the 19th century, have been considered by Abel³⁶ and are also listed in bibliographies such as that of Staples and Wobbeking.¹ Many of the osmotic coefficient data^{37–41} were used in the published evaluation of Rard *et al.*,³ with newer data^{26,42,43} (also included in Table 1) leading to minor revisions.²⁶ Rard and Platford²⁷ have critically assessed the osmotic coefficients of H_2SO_4 at 298.15 K to 27 mol kg⁻¹, comparing the evaluation of Robinson and Stokes⁴⁴ with the later work of Rard *et al.*^{3,26} and of Staples.² A number of serious objections were raised to the latter study, concerning the use of freezing-point depression data (see Section 3.6), the overall goodness of fit, and circularity regarding the use of CaCl_2 as isopiestic standard. Because of this (osmotic coefficients of aqueous CaCl_2 being largely determined from isopiestic equilibrium with H_2SO_4 solutions) such data are not included here.

Aqueous NaCl was the standard for most of the isopiestic data listed in Table 1. In the work of Rard *et al.*³ and Rard²⁶ the osmotic coefficients of NaCl were calculated using the equation of Hamer and Wu.⁴⁵ Since their work, Clarke and Glew⁴⁶ and Archer¹⁵ have published substantial critical reviews of the thermodynamics of aqueous NaCl that refine its osmotic coefficient. At 298.15 K their studies agree with each other to within 0.0006 in ϕ , but comparisons with the equation of Hamer and Wu show systematic differences of up to 0.003. All isopiestic data for which aqueous NaCl was the standard have therefore been adjusted to Archer's values of ϕ_{NaCl} (see also footnotes to Table 1), which we consider to be the most reliable. For measurements relative to aqueous KCl the best-fit equation of Hamer and Wu⁴⁵ for ϕ_{KCl} , used by Rard *et al.*,³ was also adopted here. Note, however, that we have not attempted to correct for the non-ideal behaviour of water vapour, which was not considered by Hamer and Wu.⁴⁵ We estimate this correction to be negligible at low molalities, and no more than 0.1% at high molality. The osmotic coefficients of H_2SO_4 for which aqueous NaOH was the standard are based upon the evaluation of Rard *et al.*³ of ϕ_{NaOH} and were taken directly from their Table 1.

Water vapour pressures determined by Collins,⁴⁷ and Shankman and Gordon,⁴⁸ Jones⁴⁹ and Grollman and Frazer⁵⁰ have been used to calculate osmotic coefficients. Careful attention was given to the use of values of the vapour pressures of pure water compatible with the actual temperature scales used in the original measurements. For the

last three studies, corrections were made for the non-ideality of the vapour phase by use of the second virial coefficient of water vapour as tabulated by Rard and Platford.²⁷ The resulting osmotic coefficients differ by ≤ 0.0002 (Shankman and Gordon⁴⁸) and < 0.0005 (Grollman and Frazer⁵⁰) from those given previously by Rard *et al.*³ Such corrections were not made for the results of Collins⁴⁷ because they are imprecise around 298.15 K. We note that the dew-point determinations of Hepburn,⁵¹ for higher molalities than used here, are of quite low precision and deviate by up to 0.04 in ϕ from the evaluation of Giauque *et al.*²⁵ and are probably unreliable. The recent vapour pressure measurements made by Zhang *et al.*⁵² at temperatures below 250 K are outside the scope of the present study. However, brief comparisons indicate that some of the data are inconsistent with H_2O chemical potentials tabulated by Zeleznik⁵ and also with water activities calculated by us.⁵³ For further discussion of both vapour pressure and isopiestic data, see Rard *et al.*³ and Rard.²⁶

Relative weights (w_r) for the different data sets are given in Table 1, and are reduced for the determinations of Robinson⁴¹ (for KCl as isopiestic standard) which are more scattered than his later measurements relative to NaCl,³⁸ and for the results of Scatchard *et al.*⁴⁰ because they did not use replicate samples. For these authors the weights were further decreased for $m(\text{H}_2\text{SO}_4) < 1.0$ mol kg⁻¹, where data are more scattered, and where agreement with the more recent work of Rard²⁶ is poor, possibly owing to insufficient time being allowed to achieve isopiestic equilibrium in the earlier study. The data of Scheffer *et al.*³⁹ deviate systematically from the evaluated osmotic coefficients of Rard *et al.*³ and all other isopiestic data at low molalities and were weighted 0.25. Olynyk and Gordon⁵⁴ have noted that later experiments by the same group agreed more closely with the work of Scatchard *et al.*,⁴⁰ but the results of that redetermination do not appear to have been published. The data of Platford⁵⁵ at 273.15 K appear to be reliable but are quite scattered, and have also been given a reduced weight.

All direct vapour pressure and isopiestic data given non-zero weights are shown in Fig. 1–3.

3.2 EMF Measurements

Sources of emf data are listed in Table 2 for the following electrochemical cells:



$$E = E^\circ + (RT/2F)\ln[m(\text{H}^+)^2\gamma_{\text{H}}^2 m(\text{SO}_4^{2-})\gamma_{\text{SO}_4}/a_w^2] \quad (13)$$

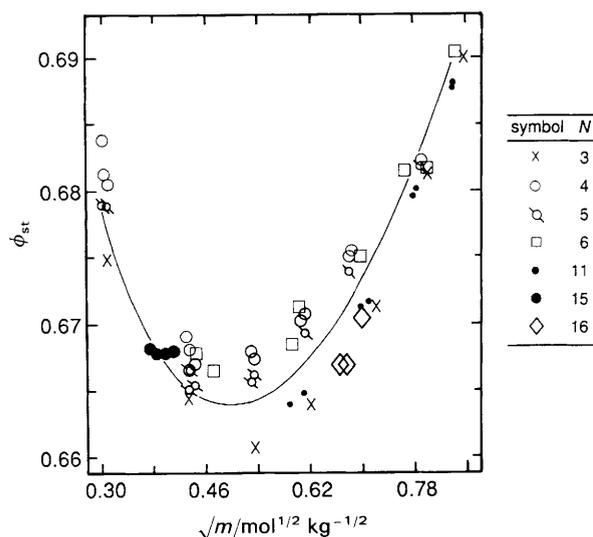
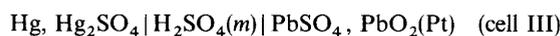


Fig. 1 Stoichiometric osmotic coefficient (ϕ_{st}) of aqueous H_2SO_4 at 298.15 K and low molality, plotted against $[m(\text{H}_2\text{SO}_4)]^{1/2}$. See also Fig. 2 for measurements at higher molalities. (—) Fitted model (Section 5). Key: symbols are related to the dataset numbers (N) in Table 1.



$$E = E^\circ - (RT/2F)\ln[m(\text{H}^+)^2\gamma_{\text{H}}^2 m(\text{SO}_4^{2-})\gamma_{\text{SO}_4}] \quad (14)$$



$$E = E^\circ + (RT/F)\ln[m(\text{H}^+)^2\gamma_{\text{H}}^2 m(\text{SO}_4^{2-})\gamma_{\text{SO}_4}/a_w] \quad (15)$$



$$E = E^\circ + (RT/2F)\ln[m(\text{H}^+)^2\gamma_{\text{H}}^2 m(\text{SO}_4^{2-})\gamma_{\text{SO}_4}] \quad (16)$$

where E and E° are, respectively, the measured and standard emfs (in V) of the cell and F ($96\,484.6 \text{ C mol}^{-1}$) is Faraday's constant. Note that we do not consider here emf measurements involving electrolyte mixtures $\text{HCl-H}_2\text{SO}_4\text{-H}_2\text{O}$ ^{56,57} or $\text{NaHSO}_4\text{-Na}_2\text{SO}_4$,⁵⁸ although the model could be used to account for the ion interactions that occur.¹⁰ Similarly, emf measurements for cells involving the $\text{Ag}_2\text{SO}_4/\text{Ag}$ electrode are not analysed because Ag_2SO_4 is too soluble in aqueous H_2SO_4 to yield meaningful results for pure aqueous H_2SO_4 solutions.

Early work of Hamer⁵⁹ and Harned and Hamer⁶⁰ has been reported by several authors to be inconsistent with modern data.³²⁻³⁴ Further comparisons by one of us (J. A. R.) suggested that a partial cause of the discrepancies, for at

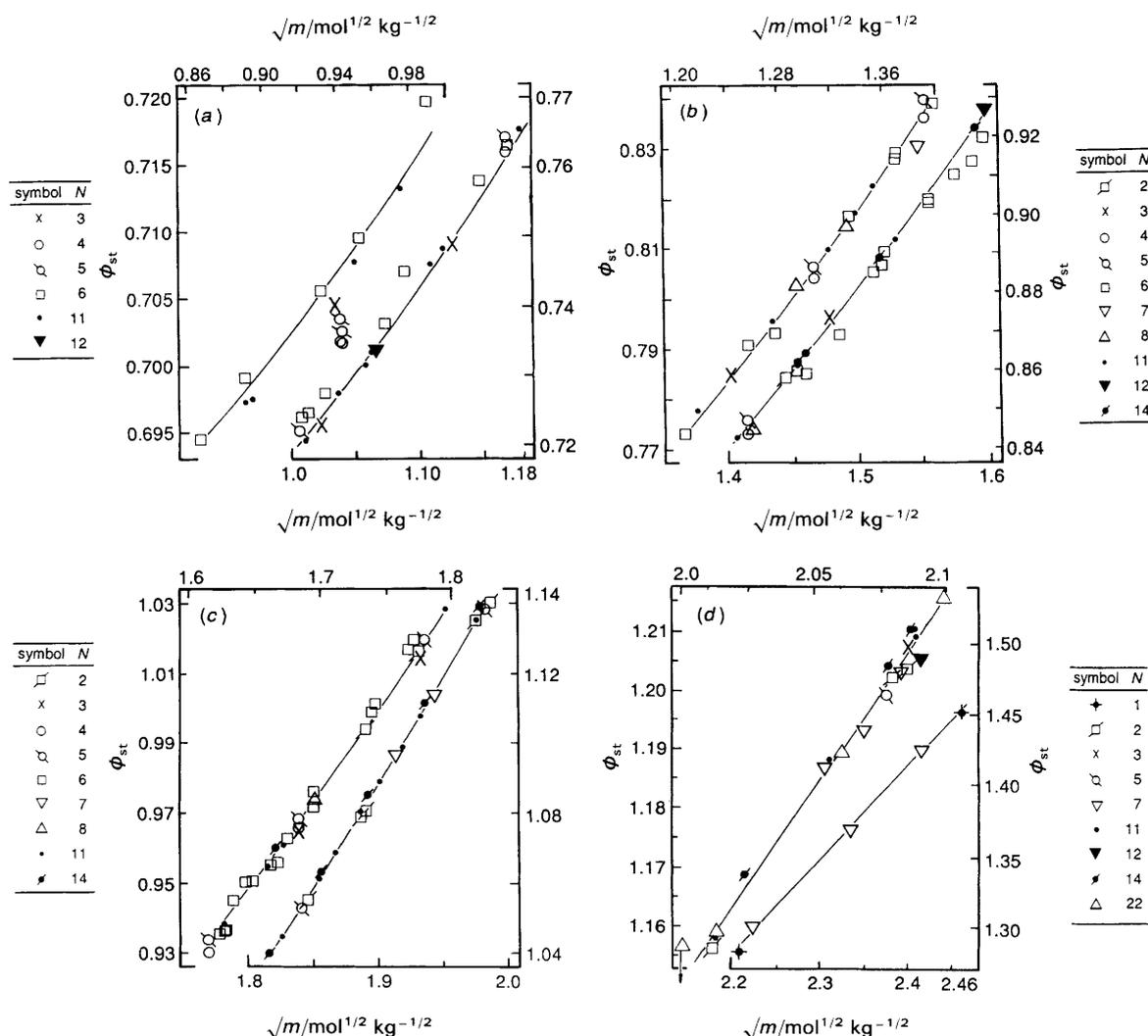


Fig. 2 Stoichiometric osmotic coefficient (ϕ_{st}) of aqueous H_2SO_4 at 298.15 K to 6 mol kg^{-1} , plotted against $[m(\text{H}_2\text{SO}_4)]^{1/2}$. For each of the four graphs, the plot (and ϕ_{st} axis) on the left are associated with the upper molality axis. See also Fig. 1 for low molalities. (—) Fitted model (Section 5). Key: symbols are related to the dataset numbers (N) in Table 1.

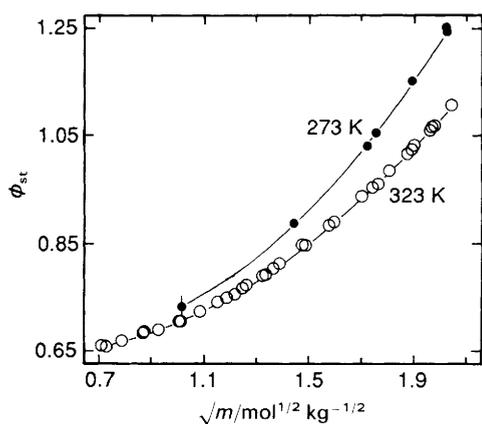


Fig. 3 Stoichiometric osmotic coefficient (ϕ_{st}) of aqueous H_2SO_4 at 273.15 and 323.15 K, plotted against $[m(\text{H}_2\text{SO}_4)]^{1/2}$. (—) Fitted model at each temperature (Section 5). N : (○) 17, (●) 18, (◐) 19.

least some of the measurements, might be systematic cyclic deviations introduced by their use of graphical smoothing and fitting equations to represent the experimental emfs, first as functions of molality and then as functions of temperature. Hamer⁵⁹ reported the actual experimental data for only four molalities at 298.15 K for a comparison of a variety of types of electrode preparations. Those emfs for cell I exhibited both a large average deviation (>1 mV) from the data of other workers, and a spread of *ca.* 1 mV (but 8–9 mV discrepancies for their preparation 7). The results of Hamer⁵⁹ and Harned and Hamer⁶⁰ are therefore not included in our analysis.

The published emf data span the period 1914–1965. The change from international to absolute volts [$1.0\text{ V (int.)} = 1.00033\text{ V (abs.)}$] occurred in 1948 and we have assumed that the results of all studies published after this year are in absolute volts, with the exception of the work of Beck *et al.*³³ as pointed out by Covington.⁶¹

For measurements at low molalities of H_2SO_4 , dissolved PbSO_4 and Hg_2SO_4 can contribute significantly to the total molality of the solution. The presence of the soluble sulfates in the cells is accounted for within the model by an increase in total ionic strength I (assuming both salts to be fully dissociated) and sulfate molality $m(\text{SO}_4^{2-})$. The solubility of PbSO_4 in aqueous H_2SO_4 above 0.005–0.009 mol kg^{-1} acid has been measured by Craig and Vinal at 273.15 and 298.15 K,⁶² and estimated for 0.001–0.02 mol kg^{-1} H_2SO_4 (273.15–323.15 K) by Shrawder and Cowperthwaite⁶³ by the interpolation and extrapolation of the measurements of earlier workers. There is reasonable agreement between the two sets of values.

Equilibrium concentrations of PbSO_4 , calculated from the tabulation of Shrawder and Cowperthwaite, are assumed to be present in the solutions in cells I, III and IV. For $m(\text{H}_2\text{SO}_4) > 0.02$ mol kg^{-1} the dissolved PbSO_4 concentration is low enough ($<2.2 \times 10^{-5}$ mol dm^{-3}) to be neglected. Pitzer *et al.*¹⁰ note that the PbSO_4/Pb electrode may be reliable only for $m(\text{H}_2\text{SO}_4) \geq 0.005$ mol kg^{-1} , therefore measurements for cell IV below this concentration have been rejected.

Mercury(II) sulfate is more soluble than PbSO_4 . Solubilities of 7.5×10^{-4} to 1.1×10^{-3} mol kg^{-1} at 298.15 K in 0.002 to 2.0 mol kg^{-1} H_2SO_4 are listed by Brown and Land,⁶⁴ who combined their own measurements with interpolated values from the study of Craig *et al.*⁶⁵ (0.001 to 3.6–4.2 mol dm^{-3} H_2SO_4 , 273.15 and 301.15 K), which agree with the results of Brown and Land within experimental error.⁶⁴ Test calculations by us showed that the inclusion of dissolved Hg_2SO_4 at its equilibrium molality in cells II and III yielded an

improved model fit, and Hg_2SO_4 molalities estimated by interpolation from the data of Craig *et al.* were therefore adopted at all temperatures. As the effect of correction for solubility of Hg_2SO_4 on the emf was found to be significant only for $m(\text{H}_2\text{SO}_4) < 0.04$ mol kg^{-1} , the practical influence of its presence is restricted to 298.15 K. These corrections also proved quite sensitive to the concentration of Hg_2SO_4 specified. Therefore, in view of the very simple treatment of the effect of the dissolved salt, relative data weights for $m(\text{H}_2\text{SO}_4) < 0.04$ mol kg^{-1} (for cell II) were reduced by a factor of two. We also note that, for $m(\text{H}_2\text{SO}_4) > 0.06$ mol kg^{-1} , Hg^{I} may be present as the complex ion $\text{Hg}_2(\text{SO}_4)(\text{HSO}_4)^{-}$.⁶⁴

For cells of types I and II, at 298.15 K, there are two and six data sets, respectively, that were given non-zero weights. It is possible for systematic deviations in E° (bias potential) to occur for different electrode preparations of the same type, because of subtle differences in the physical and chemical state of solid electrode material. The data were therefore examined for this by calculating E° [from eqn. (13) and (14)] for individual measurements from the observed emf and using the model to obtain the activity term. For cell I an average ΔE° of -0.78 mV was found between the results of Covington *et al.*³² and Beck *et al.*³³ For cell II there was agreement to within one standard deviation (in the mean value of our derived E°) of the results of Beck *et al.*³⁴ except in the cases of MacDougall and Blumer⁶⁶ (*ca.* 0.4 mV) and Trimble and Ebert⁶⁷ (*ca.* 0.2 mV). To allow for these bias potentials, additional terms ΔE° were fitted, such that $E^\circ(\text{experimental}) = E^\circ(\text{true}) + \Delta E^\circ$, for the emf data of Covington *et al.*³² (cell I), and MacDougall and Blumer⁶⁶ and Trimble and Ebert⁶⁷ (cell II). The least-squares values of ΔE° were -0.78 , -0.32 and -0.22 mV, respectively. Consistency in the variation of E° with temperature for cells I, II and IV was also tested, by fitting E° at each temperature individually. For cell II at 318.15 K³⁴ and cell IV at 285.65 K⁶³ small deviations for E° were found from the general trends (*ca.* 0.1 mV), which were accommodated using ΔE° terms similar to that given above.

The question of whether dissolved Hg_2SO_4 gives rise to liquid-junction potentials within cell II has been examined by Dobson, who studied cells saturated with Hg_2SO_4 using both glass and hydrogen-gas electrodes.⁶⁸ There was no significant difference between the two sets of results, and it was concluded that there was no significant liquid-junction potential contribution to the emf in the molality range studied. Thus we made no corrections for this, although we note that the opposite view has been argued by Hamer.⁶⁹

With the exception of the low-molality data for cell II, all retained emf measurements have been given unit relative weight, and are shown in Fig. 4.

3.3 Apparent Molal Enthalpies

Sources of enthalpy data (differential enthalpies of dilution) are listed in Table 3. Experimental dilutions ($m_1 \rightarrow m_2$) (in mol kg^{-1}) are about 30% for the work of Kunzler and Giauque,⁷⁰ 15% or less for the determinations of Wu and Young⁷¹ and most of Groenier's work,⁷² but $>96\%$ for the results of Lange *et al.*⁷³ and 70–80% for the other three experiments of Groenier. The most precise data are those of Wu and Young,⁷¹ who have also derived L^ϕ from their own work and that of the other authors given above. They did this by first estimating L^ϕ at low molalities using the measured degrees of dissociation of Young and Blatz,⁷⁴ the enthalpy of dissociation of the hydrogensulfate ion and estimates of apparent molal enthalpies, $L^\phi(\text{H}, \text{H}, \text{SO}_4)$, (from L^ϕ of Li_2SO_4) and $L^\phi(\text{H}, \text{HSO}_4)$, and combining these generated

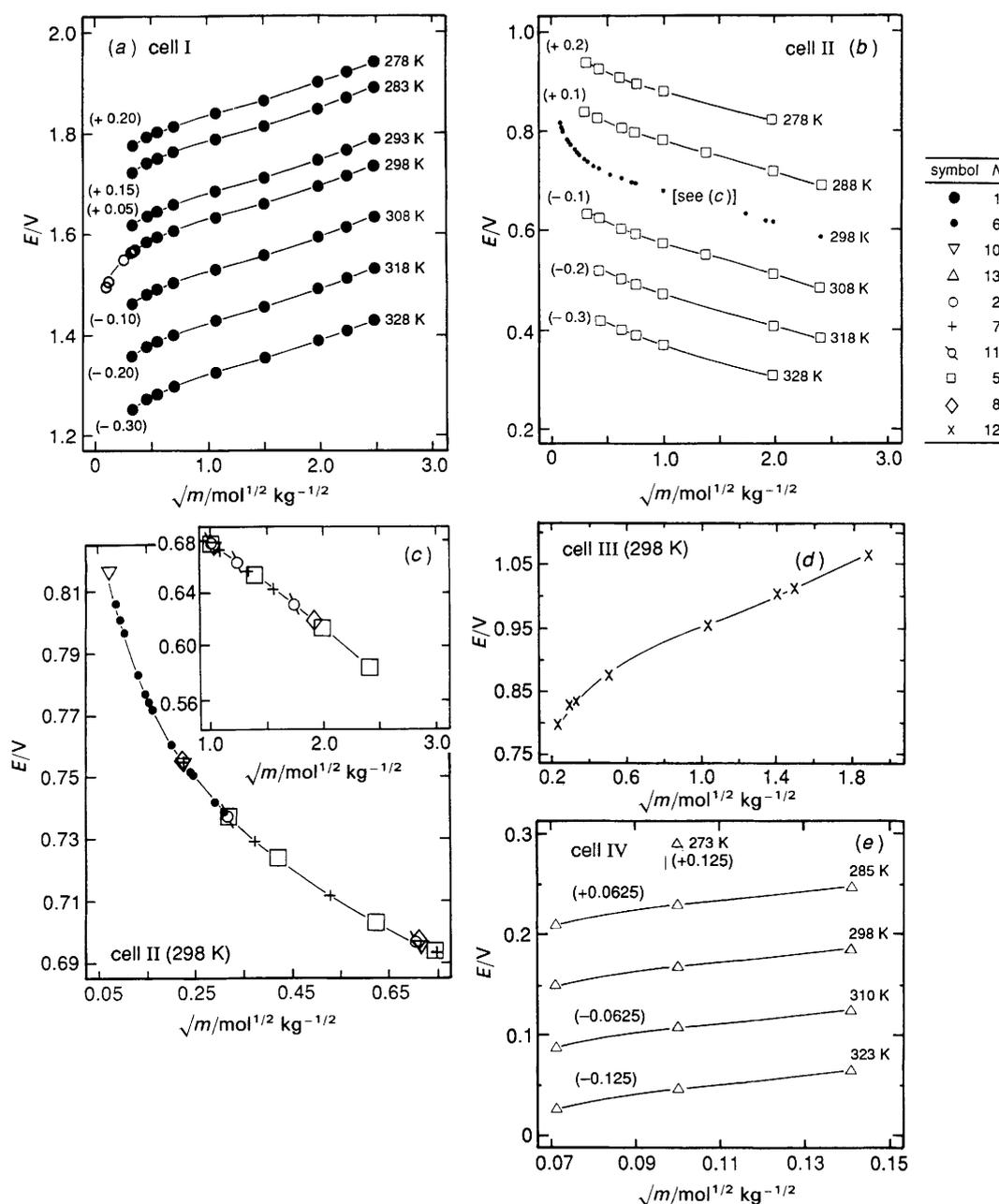


Fig. 4 Measured emf (E/V) of cells I-IV, plotted against $[m(\text{H}_2\text{SO}_4)]^{1/2}$. (a) Cell I; (b) cell II; (c) cell II, 298 K; (d) cell III, 298 K; (e) cell IV. For clarity, in parts (a), (b) and (e) the emfs are offset by fixed amounts (V), indicated by the numbers in parentheses. Fitted model (Section 5). Key: symbols are related to the dataset numbers (N) in Table 2.

values with integrated $\delta L^\circ/\delta\sqrt{m}$ obtained from the experimental $\Delta_{\text{dil}}H$ using a chord-area plot.

All dilution enthalpies were first assessed in a preliminary way by comparison with the L° of Wu and Young⁷¹ (their Table 5). The enthalpies of dilution obtained by Kunzler and Giauque⁷⁰ at the lowest H_2SO_4 molalities were found to deviate systematically from the results of other workers, probably because their calorimeter was optimised for concentrated solutions.²⁵ Those points were rejected as being in error, as were a few others with deviations of $>40 \text{ J mol}^{-1}$. The experiments of Lange *et al.*,⁷³ and three of the measurements of Groenier⁷² involve very large dilutions and the lowest values of m_2 . Groenier's three enthalpies of dilution show much larger deviations from values calculated from Table 5 of Wu and Young⁷¹ than the comparable data of Lange *et al.*, and were therefore rejected. In percentage terms, the results of Lange *et al.*⁷³ appear no less accurate than

other data, and when the size of the dilution is taken into account, generally agree well with Wu and Young's tabulation. However, test fits with our model showed systematic deviations of their values which were larger than the experimental errors. These deviations were related to differences between Wu and Young's method of analysis to obtain L° and values generated by our model below about 0.01 mol kg^{-1} . In view of the empirical nature of Wu and Young's estimates of L° in this region, the four measurements for which deviations from the model fit were $>100 \text{ J mol}^{-1}$ were rejected.

We note that Milioto and Simonson⁷⁵ at Oak Ridge National Laboratory have made many enthalpy of dilution measurements for aqueous H_2SO_4 from 0.005 to 6 mol kg^{-1} , from 303 to 598 K and at pressures of 7 to 40 MPa . Because our evaluation is restricted to a pressure of 1 atm , their results were not included in our fits.

Relative weights were assigned to each dataset as $1/\sigma^2$ (comparisons made with differential enthalpies of dilution calculated from Wu and Young's tabulated L^ϕ), normalised to unit values for the measurements of Kunzler and Giauque, see Table 3. All data given non-zero weights are plotted in Fig. 5 as $\partial L^\phi/\partial\sqrt{m}$, corrected for the difference between this quantity and the measured $-\Delta_{\text{dil}}H/(\sqrt{m_1} - \sqrt{m_2})$. This correction, significant to the scale of this plot only for the results of Lange *et al.*,⁷³ is also shown, as is the range of dilution ($\sqrt{m_1}$ to $\sqrt{m_2}$). Data were fitted as differential enthalpies of dilution, $\Delta_{\text{dil}}H = L^\phi(m_2) - L^\phi(m_1)$, calculated from eqn. (8) for initial (m_1) and final (m_2) molalities.

3.4 Apparent Molal Heat Capacities

Heat capacity measurements for $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$ are summarised in Table 4. For completeness we have included all the data of Giauque and co-workers^{25,70} even though many of their determinations are outside the molality range of the present study. Abel³⁶ considers that, of measurements made prior to about 1945, only the data of Randall and Taylor,⁷⁶ Biron⁷⁷ and to a lesser extent Savarizky (tabulated by Socolik⁷⁸) are reliable. Biron's work has been used by Craig and Vinal⁷⁹ in their study of aqueous H_2SO_4 related to the lead storage battery, and that of Savarizky by Giauque *et*

*al.*²⁵ to estimate temperature coefficients of partial molal properties. Here we have not used the work of Savarizky, since results were reported to only three significant figures, although Savarizky's values appear to be fairly consistent with other data at lower temperatures for molalities >1.0 mol kg^{-1} .

Apparent molal heat capacities, $C_p^\phi/\text{J mol}^{-1} \text{K}^{-1}$, are calculated from measured specific heats, $c_p/\text{J K}^{-1} (\text{g})^{-1}$, by the equation:

$$C_p^\phi = [1000/m(\text{H}_2\text{SO}_4)](c_p - c_p^\circ) + M(\text{H}_2\text{SO}_4)c_p \quad (17)$$

where $c_p^\circ/\text{J g}^{-1} \text{K}^{-1}$ is the specific heat of pure water at the experimental temperature and $M(\text{H}_2\text{SO}_4) = 98.073 \text{ g mol}^{-1}$ is the molar mass of H_2SO_4 . From eqn. (17) it is clear that at low molalities (below *ca.* 1 mol kg^{-1}), where c_p and c_p° are almost the same, the calculated C_p^ϕ are very sensitive to experimental error and to the choice of c_p° .

Heat capacities for $m(\text{H}_2\text{SO}_4) \leq 1.0$ mol kg^{-1} have been measured by Hovey and Hepler,⁸⁰ Larson *et al.*,⁸¹ Randall and Taylor,⁷⁶ and Biron.⁷⁷ The results of the first two studies used c_p° taken from Kell.⁸² The data of Biron⁷⁷ at 293.15 K are treated by Craig and Vinal⁷⁹ as assuming a defined c_p° of 1.0 cal $\text{g}^{-1} \text{K}^{-1}$. It is unclear if Biron's experimental c_p are relative to this value, which would then require a transformation of $c_p/\text{cal g}^{-1} \text{K}^{-1} \rightarrow c_p[c_p^\circ(293.15 \text{ K})/1.0]$. However, test

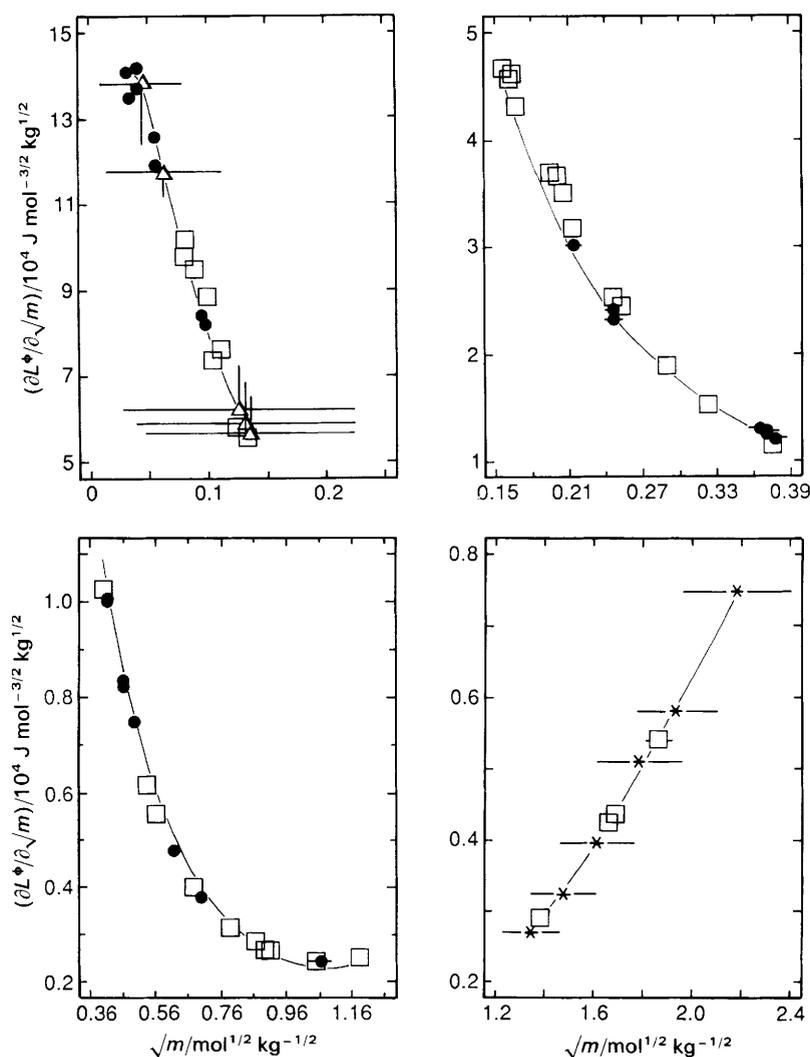


Fig. 5 Differential of the apparent molal enthalpy with respect to $[m(\text{H}_2\text{SO}_4)]^{1/2}$, calculated from enthalpies of dilution at 298.15 K, and plotted against the mean of the square roots of the initial and final molalities. Horizontal lines indicate the extent of the dilution $\sqrt{m_1} \rightarrow \sqrt{m_2}$. Vertical lines indicate the extent of the correction $-\Delta_{\text{dil}}H/[(\sqrt{m_1} + \sqrt{m_2})/2]$ to the true differential as plotted, which was estimated from the tabulated L^ϕ of Wu and Young.⁷¹ (—) Fitted model (Section 5). The dataset numbers (N) of Table 3 are: (*) 1, (●) 2, (□) 3, (△) 4.

calculations showed that this would have a negligible effect on the apparent molal heat capacity, so C_p^ϕ has simply been calculated from eqn. (17) assuming c_p° equal to $1.0 \text{ cal g}^{-1} \text{ K}^{-1}$. Randall and Taylor⁷⁶ used $c_p^\circ = 0.9979 \text{ cal g}^{-1} \text{ K}^{-1}$, equivalent to a molal heat capacity of water of $17.976 \text{ cal mol}^{-1} \text{ K}^{-1}$ (using the atomic masses current at the time). We have followed Giauque *et al.*²⁵ in adjusting Randall and Taylor's data (their Table 2) by the factor $(c_p^\circ/\text{cal mol}^{-1} \text{ K}^{-1})/17.976$ before calculating C_p^ϕ .

The measurements of Kunzler and Giauque⁷⁰ at 298.15 K, for which $m(\text{H}_2\text{SO}_4) > 1.2 \text{ mol kg}^{-1}$, were considered prior to the data at lower molalities, and apparent molal heat capacities were calculated using $c_p^\circ = 4.1796 \text{ J g}^{-1} \text{ K}^{-1}$, as listed in the CRC Handbook²⁹ and due to Osborne *et al.*,⁸³ rather than the value recommended by Kell.⁸² At 298.15 K, these c_p° differ by only $0.0003 \text{ J g}^{-1} \text{ K}^{-1}$, and the effect of this difference upon the calculated C_p^ϕ is negligible.

Unit relative weights were assigned to the data of Kunzler and Giauque,⁷⁰ Larson *et al.*⁸¹ and Randall and Taylor.⁷⁶ The apparent molal heat capacities of Hovey and Hepler⁸⁰ at their lowest molalities and 298.15 K deviate systematically from those of other workers. These data were therefore given relative weights of 0.50 at all temperatures, and the values for the two lowest molalities for $T \geq 298.15 \text{ K}$ were weighted zero. At the lower temperature of 283.15 K there was very good agreement with our model, even for the most dilute solutions, so all points were retained. The very early results of Biron⁷⁷ appear to be consistent with other data, though there are no other measurements at the same temperature for comparison. We have cautiously assigned them a relative weight of 0.25. All data given non-zero weights are plotted in Fig. 6.

The infinite-dilution value of the apparent molal heat capacity, which varies as a function of temperature, is considered further in Section 3.7.

3.5 Degree of Dissociation of the Hydrogensulfate Ion

Studies of the degree of dissociation, α , are listed in Table 5. Considering the variety of methods used, agreement between these different datasets is quite good. As noted by Chen and Irish,⁸⁴ the derivation of ionic concentrations from Raman peak intensities is somewhat ambiguous because some of the

peaks overlap. At 298.15 K, α decreases steeply from 100% at infinite dilution to about 20% at $0.4\text{--}0.5 \text{ mol kg}^{-1}$, thereafter rising to a broad peak of *ca.* 30% from 2 to 6 mol kg^{-1} and then decreasing slowly. Speciations determined from NMR and Raman spectral data are least reliable for dilute solutions because of a lack of sensitivity, and two of the values of Hood and Reilly⁸⁵ for $m(\text{H}_2\text{SO}_4) < 2 \text{ mol kg}^{-1}$ have been discarded. However, the results of Chen and Irish⁸⁴ agree fairly well with values derived from molal volumes by Lindstrom and Wirth⁸⁶ to below 1.0 mol kg^{-1} . Chen and Irish⁸⁴ discuss several other studies of α and note that values calculated from NMR shifts and partial molal volumes are dependent to some degree on the results of the earlier Raman spectral measurements of Young *et al.*,¹⁴ because of the assumptions made in interpreting the data (*e.g.* an assumed relation between the chemical shifts of aqueous H^+ and HSO_4^- in NMR studies). At temperatures other than 298.15 K there are only the data of Young *et al.*¹⁴ One point at 273.15 K ($0.504 \text{ mol kg}^{-1}$) was discarded, and the remaining measurements at 273.15 and 323.15 K assigned relative weights of 0.3. All data retained at 298.15 K were given relative weights of 1.0.

Speciations of sulfuric acid over a range of molality and temperature, derived from fits of the Pitzer model to available thermodynamic data, have been plotted by Holmes and Mesmer.⁸⁷ In the case of the 298.15 K parametrisation of Harvie *et al.*¹¹ the model-generated α is consistent with the data listed in Table 5 to about 3 mol kg^{-1} ,¹³ but at higher molalities predicts a degree of dissociation that is lower than the direct experimental values. Wirth⁸⁸ has represented data for H_2SO_4 up to 2.89 mol kg^{-1} at 298.15 K with a much simpler thermodynamic model than used here. However, in that study the values of α were taken from the determinations of Young *et al.*¹⁴ and Lindstrom and Wirth,⁸⁶ and were not predicted by Wirth's model.

Note that even where the model is fitted simultaneously to activity, osmotic coefficient and thermal data the speciation is not fully constrained, particularly its variation with temperature; thus it is worthwhile including the measurements referred to in Table 5, though a low weight has been assigned to the data as a whole (Section 3.8), reflecting the uncertainties in the measurements and their interpretation. All values of α given non-zero weights are plotted in Fig. 7.

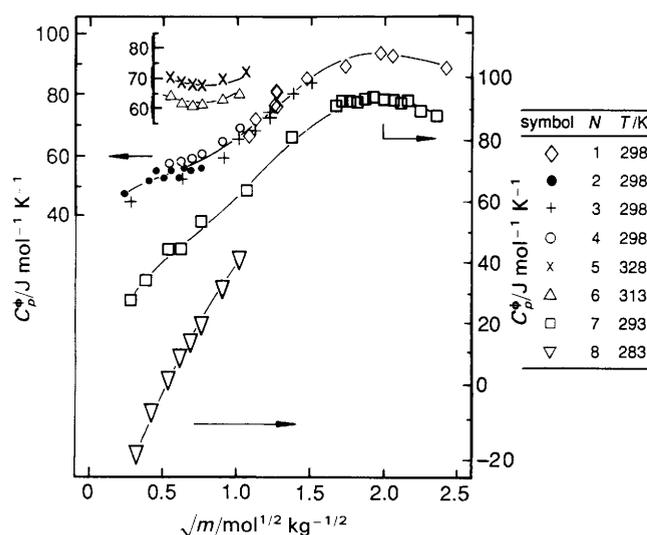


Fig. 6 Apparent molal heat capacity of H_2SO_4 at different temperatures (see key), plotted against $[m(\text{H}_2\text{SO}_4)]^{1/2}$. Note the use of three scales, with arrows indicating the datasets to which they apply. (—) Fitted model (Section 5). Key: symbols are related to the dataset numbers (N) in Table 4 and the temperature (T) of measurement.

3.6 Freezing-temperature Depression

Measurements of the freezing temperatures of solutions yield the osmotic coefficient of the solution at the freezing tem-

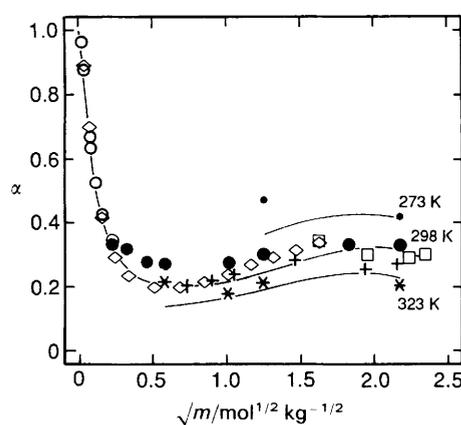


Fig. 7 Degree of dissociation (α) of the hydrogensulfate ion, at different temperatures, plotted against $[m(\text{H}_2\text{SO}_4)]^{1/2}$. (—) Fitted model (Section 5). The dataset numbers (N) of Table 5 are: (○) 3, (◇) 4, (+) 5, (●) 6, (□) 7, (all at 298.15 K); and (●) 6 (273.15 K), (*) 6 (323.15 K).

perature, *via* standard equations⁸⁹ involving the thermal properties of pure ice and water. The osmotic coefficients can be adjusted to some other reference temperature, usually 298.15 K, using partial molal enthalpies and heat capacities. Staples² (in his Tables 18–27) lists 155 freezing-temperature measurements from 10 studies,^{90–99} but rejected 80 of these data. Staples suggested that the deviation of the 75 freezing-temperature points retained in his fit from osmotic coefficients derived from emf measurements was due to experimental error in the freezing temperatures. Rard²⁶ and Rard and Platford²⁷ came to a similar conclusion, suggesting that the precipitating solid phase could well be dilute H₂SO₄ rather than pure ice.

A comparison of 298.15 K osmotic coefficients, calculated from the freezing temperatures and molalities tabulated by Staples,² with the present model (fitted to isopiestic and emf data) showed positive systematic deviations of the order of 0.02 in ϕ below 0.1 mol kg⁻¹, though there was reasonable agreement above this molality despite considerable scatter. A recalculation by using enthalpies of Wu and Young⁷¹ and heat capacities from sources listed in Table 4 yielded essentially the same results as obtained by Staples, and it was apparent that no conceivable error in the thermal data could account for the differences between the freezing points and other measurements. We therefore conclude that, below about 0.1 mol kg⁻¹, all the available freezing-point depression data are systematically in error. No freezing-temperature data have been included in the present evaluation.

3.7 Dissociation Constant (K_{HSO_4}) of the Hydrogensulfate Ion

The value of K_{HSO_4} [eqn. (2)] is such that it is difficult to determine using methods employed for weaker acids, for example emf measurements.¹⁰⁰ The double charge on the sulfate ion complicates the extrapolation of activity coefficients that is required, and renders this sensitive to model assumptions, especially from uncertainty in the value of the ion size parameter in the Debye–Hückel expression.^{58,101} Many determinations of K_{HSO_4} have been made, and are summarised in a number of reviews.^{102–104} By the early 1960s it was clear that, at 298.15 K, K_{HSO_4} lay between about 0.0102 and 0.0106 mol kg⁻¹.¹⁰² A previous application of the Pitzer model to aqueous H₂SO₄ involved a value of 0.0105 mol kg⁻¹.¹⁰

Evans and Monk¹⁰¹ have calculated K_{HSO_4} at 298.15 K from their own cell data and those of Nair and Nancollas,⁵⁶ Hamer¹⁰⁵ and Covington *et al.*⁵⁸ While the activity coefficient equations used by Evans and Monk¹⁰¹ are simpler than the Pitzer model expressions, these differences should have least effect on the calculated (stoichiometric) value of K_{HSO_4} at low molalities. The results of Evans and Monk also suggest that $K_{\text{HSO}_4} \approx 0.0104$ – 0.0105 for a comparable ion size term [in the Pitzer model it is 1.2, see eqn. (6) and (7)] and empirical constant Q of 0.3–0.6 mol⁻¹ dm³. A further re-analysis of emf data by Mussini *et al.*¹⁰⁶ yielded values of 0.01043 ± 0.00020 and 0.01039 ± 0.00018 mol kg⁻¹. Within the quoted uncertainties, these agree with earlier estimates obtained by other methods.¹⁰² In the present study we have therefore retained $K_{\text{HSO}_4} = 0.01050$ mol kg⁻¹ at 298.15 K.

Different estimates of the standard enthalpy change ($\Delta_r H^\circ$ /kJ mol⁻¹) for the dissociation reaction at 298.15 K are listed by Young and Irish¹⁰² and by Dickson *et al.*¹⁰⁴ and range from -20.5 to -23.8 kJ mol⁻¹. The previous application of the Pitzer model¹⁰ yielded -23.47 kJ mol⁻¹ which was assumed to remain constant with temperature as heat capacities were not included in that fit. A significantly smaller value of $\Delta_r H = -17.33 \pm 0.29$ kJ mol⁻¹ was reported by

Readnour and Cobble¹⁰⁷ based upon the enthalpy of solution of Na₂SO_{4(s)} in aqueous HCl.

Recently, Dickson *et al.*¹⁰⁴ have conducted new measurements of the dissociation constant of HSO₄⁻ in aqueous NaCl from 323 to 523 K. In their analysis, Dickson *et al.* included the K_{HSO_4} estimated by Pitzer *et al.*,¹⁰ enthalpies of reaction^{81,108} and the heat capacities of HSO₄⁻ and SO₄²⁻ at infinite dilution as extrapolated by Hovey and Hepler⁸⁰ and Hovey *et al.*,¹⁰⁹ respectively, and other thermal data referenced by them. Dickson *et al.*¹⁰⁴ obtained $K_{\text{HSO}_4} = 0.010865 \pm 0.0005$ mol kg⁻¹ at 298.15 K, in satisfactory agreement with other estimates considering that their analysis is probably biased toward high temperatures. They also determined $\Delta_r H^\circ = -22.8 \pm 0.8$ kJ mol⁻¹ and $\Delta_r C_p^\circ = -275 \pm 17$ J mol⁻¹ K⁻¹ for the dissociation reaction, both at 298.15 K. The variation of the heat capacity change ($\Delta_r C_p^\circ$) with temperature can be derived from eqn. (6) of Dickson *et al.*:¹⁰⁴

$$\Delta_r C_p^\circ = -1962.617711 + 9.48630148692T - 0.01283109903T^2 \quad (18)$$

[The constants in eqn. (18) are specified so as to retain close numerical agreement with the equation of Dickson *et al.*, and do not reflect the actual accuracy to which $\Delta_r C_p^\circ$ can be determined.] The quantity $\Delta_r C_p^\circ$ is related to the infinite dilution values of the apparent molal heat capacities of the ions:

$$\Delta_r C_p^\circ = C_p^\circ(\text{SO}_4^{2-}) + C_p^\circ(\text{H}^+) - C_p^\circ(\text{HSO}_4^-) \quad (19)$$

By definition $C_p^\circ(\text{H}^+)$ is equal to zero, hence:

$$\Delta_r C_p^\circ = C_p^\circ(\text{SO}_4^{2-}) - C_p^\circ(\text{HSO}_4^-) \quad (20a)$$

$$\equiv C_p^\phi - C_p^\circ(\text{HSO}_4^-) \quad (20b)$$

where C_p^ϕ is the infinite dilution value of the apparent molal heat capacity of the acid, on the basis of complete dissociation, given in eqn. (9a).

We have chosen to include C_p^ϕ , and its variation with temperature, as unknowns in our model. However, values of C_p^ϕ can also be obtained from data for other electrolytes, since the apparent molal properties of ions are additive at infinite dilution. Gardner *et al.*¹¹⁰ have done this, using integral enthalpies of solution, and tabulate C_p^ϕ of H₂SO₄ from 273 to 373 K (their 298.15 K value is -295.4 J mol⁻¹ K⁻¹). The analysis by Hovey and Hepler⁸⁰ of their own heat capacity data, and using C_p^ϕ (-282.3 J mol⁻¹ K⁻¹ at 298.15 K) obtained by the same method in an earlier paper by Hovey *et al.*,¹⁰⁹ yielded -17.8 J mol⁻¹ K⁻¹ for $C_p^\circ(\text{HSO}_4^-)$ at 298.15 K. Combining these two values gives $\Delta_r C_p^\circ$ for the dissociation reaction equal to $-282.3 - (-17.8) = -264.5$ J mol⁻¹ K⁻¹, which agrees well with the value of Dickson *et al.*¹⁰⁴ (-275 ± 17 J mol⁻¹ K⁻¹) referred to above.

In developing the model fits described below, we have adopted the temperature variation of K_{HSO_4} as determined by Dickson *et al.*,¹⁰⁴ combined with our choice of the 298.15 K value of the dissociation constant of 0.01050 mol kg⁻¹, as stated above. These yield the following expression for K_{HSO_4} as a function of temperature:

$$\begin{aligned} \log(K_{\text{HSO}_4}) &= 562.69486 - 102.5154 \ln(T) \\ &\quad - 1.117033 \times 10^{-4} T^2 \\ &\quad + 0.2477538T - 13273.75/T \end{aligned} \quad (21)$$

where the first constant was adjusted slightly to give agreement with our choice of K_{HSO_4} . Note that the above equation, adapted from eqn. (6) of Dickson *et al.*¹⁰⁴ yields 298.15 K values of $\Delta_r H^\circ$ and $\Delta_r C_p^\circ$ of -22.7554 kJ mol⁻¹ and -274.8772 J mol⁻¹ K⁻¹, respectively.

3.8 Weights

Relative weights (w_r) assigned in Sections 3.1–3.5 above are internal to each dataset and do not take into account the differing magnitudes of experimental error typical of each kind of measurement, for example about $1.5 \text{ J mol}^{-1} \text{ K}^{-1}$ in the case of C_p^ϕ compared with only $1.3 \times 10^{-4} \text{ V}$ for the emf measurements. The absolute weight given to an individual data point in the model fit is therefore set equal to the relative weight multiplied by a characteristic weight (w_c) for each type of data. Initially these characteristic weights were set so as to give contributions to the total sum of squared deviations approximately in the ratio 3:2:1:1:0.25 (ϕ : emf: $\Delta_{\text{dil}}H$: C_p^ϕ : α). As the fit of the model was refined, the characteristic weights for each type of property were recalculated as:

$$w_c = [10(1/N) \sum w_r(y-f)^2]^{-1} \quad (22)$$

where y and f are observed and fitted quantities, respectively, and N is the number of points (for which $w_r \neq 0$) in each dataset. Some minor adjustments to w_c were later made to reflect the consistency of the individual thermodynamic properties with the overall data set, reducing the characteristic weight given to degree of dissociation data (by 50%) and increasing that for $\Delta_{\text{dil}}H$ (by 25%). The characteristic weights, w_c , finally assigned to each dataset are as follows: ϕ , 4.3×10^4 ; emf, 4.4×10^6 ; $\Delta_{\text{dil}}H$, 5.8×10^{-4} ; C_p^ϕ , 3.7×10^{-2} ; α , 60. The standard errors equivalent to these w_c values are $\sigma(\phi) = 0.0015$, $\sigma(E) = 1.5 \times 10^{-4} \text{ V}$, $\sigma(\Delta_{\text{dil}}H) = 13.13 \text{ J mol}^{-1}$, $\sigma(C_p^\phi) = 1.64 \text{ J K}^{-1} \text{ mol}^{-1}$ and $\sigma(\alpha) = 0.041$.

4. Method

The sets of parameters $\beta_{\text{ca}}^{(0)}$, $\beta_{\text{ca}}^{(1)}$, $C_{\text{ca}}^{(0)}$, $C_{\text{ca}}^{(1)}$, ω_{ca} and α_{ca} must be determined as functions of temperature for the two ionic interactions $\text{H}^+ - \text{SO}_4^{2-}$ and $\text{H}^+ - \text{HSO}_4^-$, so as to minimise the total weighted sum of squared deviations for the five measured properties ϕ , emf, $\Delta_{\text{dil}}H$, C_p^ϕ and α . This was done using a generalised non-linear least-squares fitting routine (E04FDF¹¹¹), first obtaining estimates of the parameters at 298.15 K from ϕ and emf data, then extending the fit to 298.15 K thermal data and finally to emf and C_p^ϕ measurements at other temperatures. The use of different temperature functionalities for the parameters was explored.

Sulfate–hydrogensulfate speciation is, of course, not known *a priori* and is calculated for every data point for each successive set of parameter estimates. This was done by determining the zero of the following function f , which describes the distribution of the total molality of hydrogen ion [$\equiv 2m(\text{H}_2\text{SO}_4)$] between free H^+ [$m(\text{H}^+)$] and HSO_4^- [$m(\text{HSO}_4^-)$]:

$$f = m(\text{H}^+)m(\text{SO}_4^{2-})/[K_{\text{HSO}_4}^* + m(\text{H}^+)] - m(\text{HSO}_4^-) \quad (23)$$

where $m(\text{SO}_4)^{\text{T}}$ is the total sulfate molality [$\equiv m(\text{H}_2\text{SO}_4)$] and $K_{\text{HSO}_4}^*$ is the stoichiometric dissociation product of the hydrogensulfate ion (and not the thermodynamic constant). Because the incremental change in parameter estimates may be very small from one cycle of the calculation to the next, and the fact that enthalpies of dilution, and especially heat capacities, are calculated as numerical differentials [eqn. (8) and (9)] it was necessary to determine speciation to full machine precision (typically one part in 10^{16}) in the fitting program.

5. Results

A general equation for the temperature variation of model parameter P (where $P = \beta_{\text{ca}}^{(0)}$, $\beta_{\text{ca}}^{(1)}$, $C_{\text{ca}}^{(0)}$, $C_{\text{ca}}^{(1)}$) that was found to

be satisfactory is:

$$P = q_1 + (T - T_r)\{10^{-3}q_2 + (T - T_r) \times [10^{-3}q_3/2 + (T - T_r)10^{-3}q_4/6]\} \quad (24)$$

where T is in K and the reference temperature, T_r , is 328.15 K. The equation for the temperature variation of E°/V , the standard emf of cells I, II and IV, is:

$$E^\circ = r_1 + 10r_2(1/T - 1/T_0) + 10^{-3}r_3 \times [T \ln(T) - T_0 \ln(T_0)] \quad (25)$$

where $T_0 = 298.15 \text{ K}$. The equation used to represent the infinite dilution value of the apparent molal heat capacity, $C_p^\phi/\text{J mol}^{-1} \text{ K}^{-1}$, is:

$$C_p^\phi = s_1 + (T - T_0)s_2 + 0.1(T - T_0)^2s_3 \quad (26)$$

All parameters determined in the model fit are listed in Table 6, together with their temperature ranges of validity and the standard errors for the parameters for eqn. (25) and (26) above. Assigned values of the coefficients α_{ca} and ω_{ca} are also given in Table 6: note that $\alpha_{\text{H}, \text{SO}_4}$ varies with temperature. For convenience, 298.15 K values of all parameters are listed in Table 7. Fig. 8–12 show the residuals for each dataset, and indicate the deviations of the fit from the weighted data. Note that it was not necessary to include the mixing parameters $\theta_{\text{HSO}_4, \text{SO}_4}$ and $\psi_{\text{HSO}_4, \text{SO}_4, \text{H}}$ to represent accurately the experimental data.

While some ‘cycling’ of the residuals is evident in the fit to the emf (Fig. 9) and $\Delta_{\text{dil}}H$ data below 1.4 mol kg^{-1} (Fig. 10), most observations are fitted substantially within experimental error. Note that the patterns of residuals for the emf data are essentially random for cell I at 328.15 K and for cells II and III at 298.15 K, and systematic trends for other temperatures and cells are $\leq 2.5 \times 10^{-4} \text{ V}$. As a test, to determine whether activity data and thermal properties not taken at 298.15 K were biasing the results at 298.15 K, a separate fit to osmotic and emf data at 298.15 K only was carried out. There was no decrease in the sum of squared deviations, confirming the quality of the fit. For measurements of α at 273.15 and 323.15 K¹⁴ we note a trend towards positive deviations at low molalities. However, the α data are too few in number to determine whether this reflects real errors in the fitted model, and 298.15 K data from the same source show a similar pattern of residuals.

The residuals of the osmotic coefficients are random for the direct vapour pressure measurements [Fig. 8(c)], as they are for isopiestic data at 273.15 and 323.15 K [Fig. 8(d)]. There are slightly different trends in the residuals for data at 298.15 K depending on whether NaCl [Fig. 8(a)] or KCl [Fig. 8(b)] was used as standard. However, taken together, the results are essentially random above 0.4 mol kg^{-1} [Fig. 8(e)], which confirms the accuracy of our model fit. The standard deviation of $\Delta\phi$ (unweighted) at 298.15 K is 0.0024.

The standard potentials of cells I, II and IV at 298.15 K (Table 7) agree with results obtained earlier by Pitzer *et al.*¹⁰ to within 0.62 mV (cell I) and 0.063 mV (cells II and IV). Gardner *et al.*¹¹² have calculated mean activity coefficients of H_2SO_4 from the emf data of Covington *et al.*³² and third-law potentials for cell II from 0.1 to 4.0 mol kg^{-1} and 273.15 to 328.15 K. These mean activity coefficients agree with values calculated using the present model to within 0.001₄ at 298.15 K, 0.006 at 273.15 K and 0.002 at 328.15 K.

Rard *et al.*,³ and later Rard,²⁶ have evaluated osmotic coefficient data at 298.15 K independently of other activity measurements, for the use of aqueous H_2SO_4 as an isopiestic standard. Osmotic coefficients generated by the present model agree with the most recent values presented by Rard,²⁶

Table 6 Fitted model parameters for aqueous H_2SO_4

(a)								
	$\beta_{\text{H}_2\text{SO}_4}^{(0)}$	$\beta_{\text{H}_2\text{SO}_4}^{(1)}$	$C_{\text{H}_2\text{SO}_4}^{(1)}$					
q_1	0.227 784 933	0.372 293 409	-0.002 800 325 20					
q_2	-3.786 677 18	1.50	18.172 894 6					
q_3	-0.124 645 729	0.207 494 846	0.382 383 535					
q_4	-0.002 357 478 06	0.004 485 264 92	0.002 5					
(b)								
	$\beta_{\text{HSO}_4}^{(0)}$	$\beta_{\text{HSO}_4}^{(1)}$	$C_{\text{HSO}_4}^{(1)}$					
q_1	0.034 892 535 1	-1.066 412 31	0.0					
q_2	4.972 078 03	-74.684 042 9	-0.176 776 695					
q_3	0.317 555 182	-2.262 689 44	-0.731 035 345					
q_4	0.008 225 803 41	-0.035 296 854 7	0.0					
(c)								
	cell I ^a	standard error	cell II ^a	standard error	cell III ^{a,b}	standard error	cell IV ^a	standard error
r_1	1.690 998	3.68×10^{-5}	0.612 357 3	3.3×10^{-5}	1.077 553	6.99×10^{-5}	0.352 767 9	6.3×10^{-5}
r_2	8.883 153	0.18	-7.273 884	0.20	---	---	6.844 643 9	0.38
r_3	0.202 140 7	2.97×10^{-3}	-0.248 245 9	3.3×10^{-3}	---	---	0.266 346 36	6.4×10^{-3}
(c)								
	$C_p^{\phi,a}$	standard error						
s_1	-286.175	2.6						
s_2	3.677 433	0.16						
s_3	-0.471 039 1	0.069						

Both $\omega_{\text{H}_2\text{SO}_4}$ and ω_{HSO_4} are equal to $2.5 \text{ mol}^{-1/2} \text{ kg}^{1/2}$; the coefficient $\alpha_{\text{H}_2\text{SO}_4}$ is set to $2.0 \text{ mol}^{-1/2} \text{ kg}^{1/2}$, while α_{HSO_4} was allowed to vary with temperature according to the equation $\alpha_{\text{HSO}_4} = 2 - 1842.843(1/T - 1/298.15)$. As is the case for earlier treatments,^{11,12} the mixture parameters $\theta_{\text{HSO}_4, \text{SO}_4}$ and $\psi_{\text{HSO}_4, \text{SO}_4, \text{H}}$ were found not to be needed and are set to zero. ^a Parameters are valid for the temperature ranges: cell I, 278.15–328.15 K; cell II, 278.15–328.15 K; cell III, 298.15 K; cell IV, 273.15–323.15 K; C_p^{ϕ} , 283.15–328.15 K. ^b At 298.15 K, E° (cell I) – E° (cell II) = 1.690998 – 0.6123573 = 1.077553 = 0.001088 V, whereas it should be exactly zero if all of the cell potentials were internally consistent. This suggests that the standard potential of the lead sulfate/lead dioxide electrode is known only to within about 1 mV.

Table 7 Model parameters and standard potentials at 298.15 K^a

$\beta_{\text{H, HSO}_4}^{(0)}$	0.295 903 322	$\beta_{\text{H, SO}_4}^{(0)}$	-0.008 386 089 24
$\beta_{\text{H, HSO}_4}^{(1)}$	0.400 482 398	$\beta_{\text{H, SO}_4}^{(1)}$	0.314 734 575
$C_{\text{H, HSO}_4}^{(0)}$	-0.005 657 866 56	$C_{\text{H, SO}_4}^{(0)}$	0.010 192 247 4
$C_{\text{H, HSO}_4}^{(1)}$	-0.409 364 246	$C_{\text{H, SO}_4}^{(1)}$	-0.323 662 605
$\alpha_{\text{H, HSO}_4}$	2.0	$\alpha_{\text{H, SO}_4}$	2.0
$\omega_{\text{H, HSO}_4}$	2.5	$\omega_{\text{H, SO}_4}$	2.5
C_p°	-286.2	A_ϕ^b	0.391 475
E° (cell I)	1.691 00	$A_H/(RT)^b$	0.801 844
E° (cell II)	0.612 357	A_C/R^b	3.836 018
E° (cell III)	1.077 55		
E° (cell IV)	0.352 768	K_{HSO_4}	0.0105

^a Units are as follows: $\beta_{\text{ca}}^{(0)}$ and $\beta_{\text{ca}}^{(1)}/\text{kg mol}^{-1}$; $C_{\text{ca}}^{(0)}$ and $C_{\text{ca}}^{(1)}/\text{kg}^2 \text{mol}^{-2}$; A_ϕ , α_{ca} and $\omega_{\text{ca}}/\text{kg}^{1/2} \text{mol}^{-1/2}$; $C_p^\circ/\text{J K}^{-1} \text{mol}^{-1}$; E°/V ; $K_{\text{HSO}_4}/\text{mol kg}^{-1}$. ^b Debye-Hückel limiting slopes were calculated from the polynomial function equation given in Appendix II.

and by Rard and Platford,²⁷ to within +0.0032/-0.0015 for $m(\text{H}_2\text{SO}_4) \leq 6.0 \text{ mol kg}^{-1}$.

Comparisons are also made with thermal data. Wu and Young's⁷¹ tabulated L^ϕ deviate from model calculated values by about 300 J mol^{-1} above 0.5 mol kg^{-1} . However, because this difference is roughly constant, and arises from differences between the model and Wu and Young's graphical integration of $\partial L^\phi/\partial \sqrt{m}$ below 0.5 mol kg^{-1} , there is little effect on the calculated differentials of activity with respect to temperature. The value of C_p° at 298.15 K ($-286.2 \pm 2.6 \text{ J mol}^{-1} \text{ K}^{-1}$) determined in the fit, is consistent with $-295.4 \text{ J mol}^{-1} \text{ K}^{-1}$ estimated by Gardner *et al.*¹¹⁰ from integral enthalpy of solution data for Na_2SO_4 , and $-282.3 \text{ J mol}^{-1} \text{ K}^{-1}$ adopted by Hovey and Hepler.⁸⁰ At temperatures other than 298.15 K, C_p° calculated from eqn. (26) agrees with the values of Gardner *et al.*¹¹⁰ to within $33 \text{ J mol}^{-1} \text{ K}^{-1}$ from 283.15 to 323.15 K.

Reardon and Beckie¹² have also fitted the Pitzer model to thermodynamic data for aqueous H_2SO_4 (excluding C_p° and using a much smaller database) over a similar range of temperature and molality to that used here. A comparison of their calculated values with the data yields sums of squared deviations (measured minus calculated) that exceed those obtained using the present model by factors of 5 and 2.3 for ϕ and $\Delta_{\text{dil}}H$, respectively. Thus, our model better represents the properties of aqueous H_2SO_4 by a large margin, although it is more complex than that used by Reardon and Beckie. We also believe that our model equation represents the osmotic coefficient with sufficient accuracy for it to be used as an isopiestic standard over its range 0-6.1 mol kg^{-1} and 273.15-328.15 K.

Values of activities, degrees of dissociation and thermal properties of aqueous H_2SO_4 , calculated with the present model, are listed in Tables 8-10 for 273.15, 298.15 and 323.15 K. At 298.15 K we have included calculated relative partial molal enthalpies [$\bar{L}(\text{H}_2\text{O})$, $\bar{L}(\text{H}_2\text{SO}_4)/\text{J mol}^{-1}$] and heat capacities [$\bar{J}(\text{H}_2\text{O})$, $\bar{J}(\text{H}_2\text{SO}_4)/\text{J mol}^{-1} \text{ K}^{-1}$]. Values of $\bar{L}(\text{H}_2\text{SO}_4)$ calculated by the present model average about 1.25% greater than those listed in Table 5 of Wu and Young,⁷¹ with cyclic deviations between the two studies of the same order below 1 mol kg^{-1} , corresponding to those in the residual plot in Fig. 10. However, our model equations represent the input values of $\Delta_{\text{dil}}H$ to within about 50 J mol^{-1} in this region, which is 0.2-0.4% of $\bar{L}(\text{H}_2\text{SO}_4)$. There is no systematic difference between the relative partial molal enthalpies of water calculated in the two studies, though the maximum deviations from Wu and Young ($\pm 9\%$ between 0.2 and $1.5 \text{ mol kg}^{-1} \text{ H}_2\text{SO}_4$) are greater on a percentage basis than for $\bar{L}(\text{H}_2\text{SO}_4)$. We have not tabulated apparent or rela-

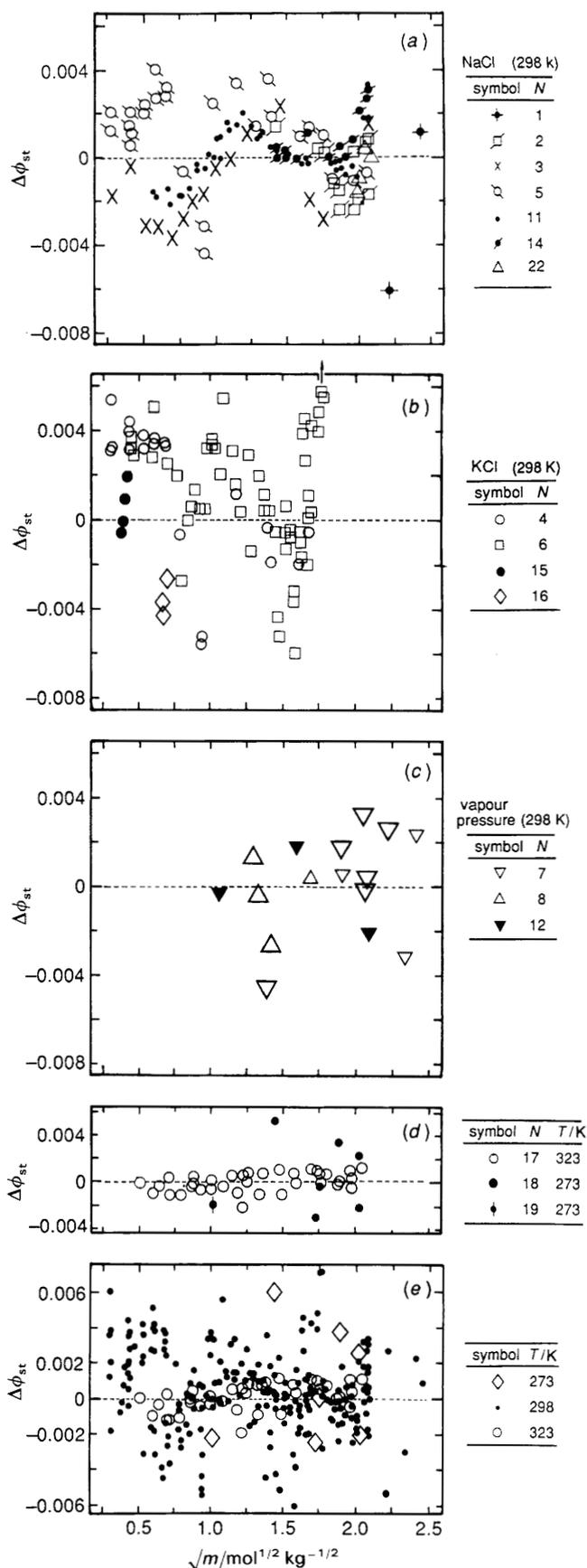


Fig. 8 Deviations between the measured and fitted stoichiometric osmotic coefficients (ϕ_{st}) of aqueous H_2SO_4 at 298.15 K (a)-(c), 273.15 and 323.14 K (d), and all temperatures (e). (a) Aqueous NaCl used as isopiestic standard (except NaOH for $N = 1$); (b) aqueous KCl used as isopiestic standard; (c) direct vapour pressure measurement; (d) see Table 1 for isopiestic standards. (e) All data. Keys for (a)-(d): symbols are related to the dataset numbers N in Table 1.

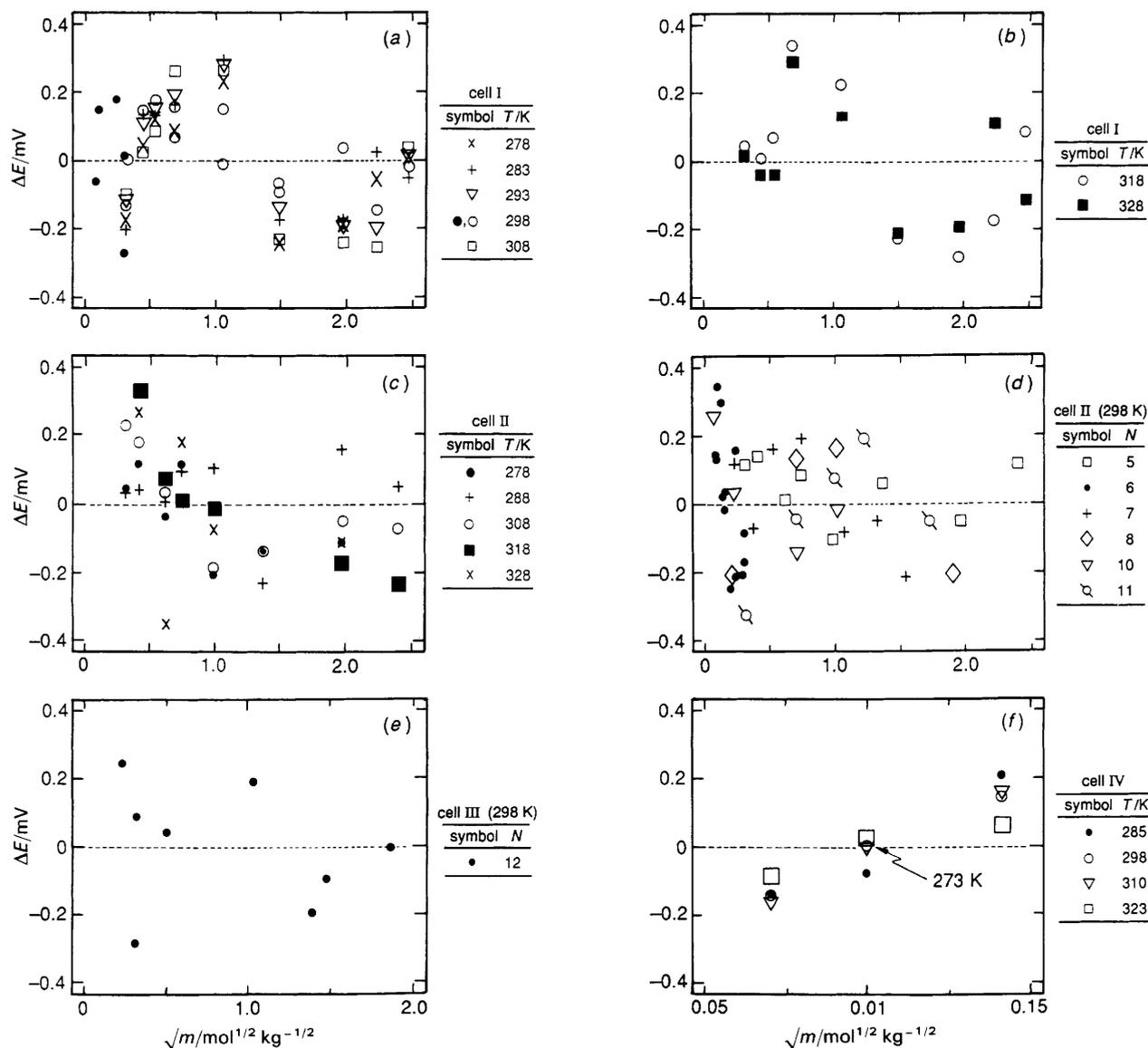


Fig. 9 Deviations between measured and fitted emfs of cells I–IV. Keys give cell type, with (rounded) temperature of measurement (T) and/or dataset number (N) in Table 2. (a), (b) $N = 1$ for all data, except filled circles ($N = 2$); (c) $N = 5$ for all data; (f) $N = 13$ for all data.

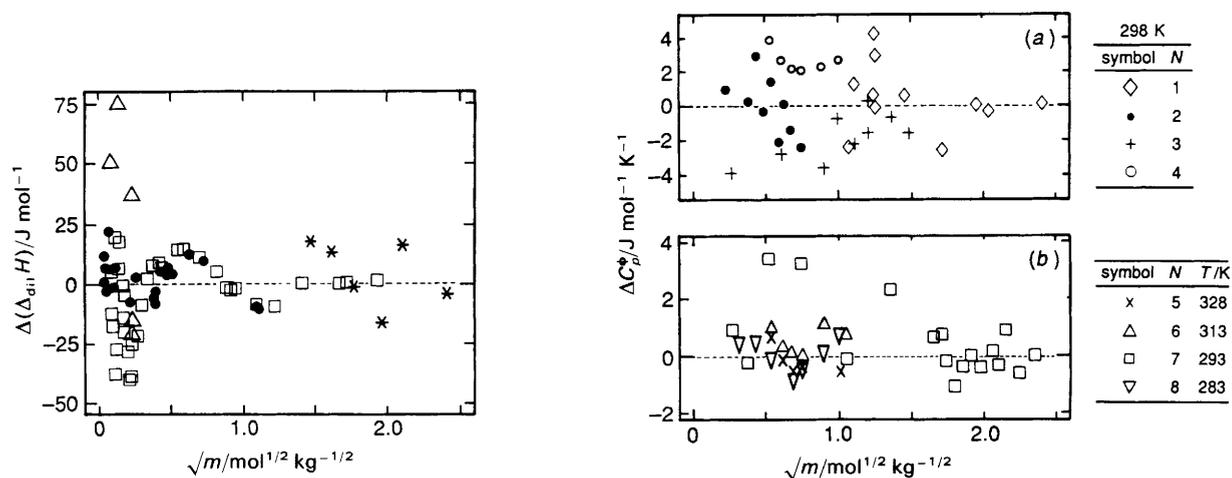


Fig. 10 Deviations between measured and fitted differential enthalpies of dilution at 298.15 K, plotted against the square root of the initial molality, m_1 . The dataset numbers (N) of Table 3 are: (*) 1, (\bullet) 2, (\square) 3, (Δ) 4.

Fig. 11 Deviations between measured and fitted apparent molal heat capacities in H_2SO_4 . (a) 298.15 K; (b) other temperatures. Keys give the (rounded) temperature of measurement (T) and dataset number (N) in Table 4.

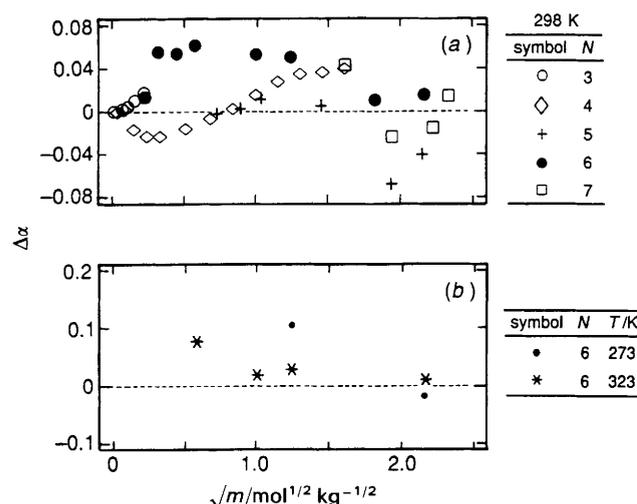


Fig. 12 Deviations between measured and fitted degrees of dissociation of the hydrogensulfate ion. (a) 298.15 K; (b) other temperatures. Keys give the (rounded) temperature of measurement (T) and dataset number (N) in Table 5.

tive partial molal heat capacities at 273.15 or 323.15 K in Tables 9 and 10, as the model is unlikely to be as well constrained with respect to these quantities at the extremes of the temperature range over which it has been applied.

6. Conclusions

A generalised, extended formulation of the molality-based Pitzer thermodynamic model has been presented here and applied to measured properties of aqueous H_2SO_4 , yielding a self-consistent representation of activities, apparent molal enthalpies and heat capacities of aqueous H_2SO_4 from 0 to 6.1 mol kg^{-1} , for the temperature range 273.15–328.15 K. The extension to the model provides a more flexible framework for calculating the properties of both single- and multi-component electrolyte solutions at low and moderate molalities, and its application to sulfuric acid will lead to improved calculations of thermodynamic properties of acidic sulfate mixtures.

The work of S.L.C. was supported by a grant from the Leverhulme Trust. The contributions of J.A.R. and K.S.P. were

Table 8 Thermodynamic properties of aqueous H_2SO_4 at 298.15 K

molality/mol kg^{-1}	γ_{\pm}	ϕ_{st}	α^a	L^{\dagger}	C_p^{\dagger}	$\bar{L}(\text{H}_2\text{O})$	$\bar{L}(\text{H}_2\text{SO}_4)$	$\bar{J}(\text{H}_2\text{O})$	$\bar{J}(\text{H}_2\text{SO}_4)$
(0.0001)	0.9500	0.9813	0.982 86	497.3	-267.9	-7.5689×10^{-4}	917.5	-2.895×10^{-5}	34.35
(0.0002)	0.9253	0.9712	0.967 55	890.9	-252.9	-2.6763×10^{-3}	1 633.6	-1.006×10^{-4}	61.16
(0.0005)	0.8737	0.9493	0.928 18	1 874.6	-217.2	-1.3211×10^{-2}	3 341.3	-4.625×10^{-4}	120.3
(0.0010)	0.8152	0.9236	0.876 21	3 150.9	-174.8	-4.0382×10^{-2}	5 392.5	-1.270×10^{-3}	181.9
(0.0020)	0.7384	0.8890	0.800 41	4 997.0	-121.2	-0.11087	8 074.0	-2.956×10^{-3}	247.0
0.0050	0.6146	0.8325	0.667 58	8 224.4	-47.4	-0.34858	12 094	-6.719×10^{-3}	313.4
0.0100	0.5145	0.7867	0.555 11	10 978	-2.11	-0.72091	14 980	-9.873×10^{-3}	338.9
0.0200	0.4189	0.7440	0.447 04	13 679	27.9	-1.3468	17 417	-1.160×10^{-2}	346.3
0.0500	0.3098	0.6987	0.328 95	16 807	46.4	-2.7538	19 864	-9.222×10^{-3}	342.8
0.1000	0.2436	0.6759	0.265 25	18 734	50.6	-4.5207	21 243	-5.837×10^{-3}	340.0
0.2000	0.1916	0.6647	0.224 99	20 299	52.5	-7.2577	22 313	-1.139×10^{-2}	341.8
0.3000	0.1672	0.6647	0.212 26	21 059	54.1	-9.3826	22 795	-2.741×10^{-2}	345.3
0.4000	0.1525	0.6685	0.208 14	21 530	55.8	-11.088	23 069	-5.021×10^{-2}	349.0
0.5000	0.1425	0.6744	0.207 81	21 857	57.6	-12.528	23 248	-7.890×10^{-2}	352.5
0.6000	0.1353	0.6816	0.209 47	22 100	59.3	-13.856	23 382	-0.1135	356.0
0.7000	0.1300	0.6898	0.212 26	22 292	61.1	-15.216	23 498	-0.1543	359.5
0.8000	0.1259	0.6990	0.215 74	22 450	62.8	-16.740	23 611	-0.2016	363.0
0.9000	0.1228	0.7088	0.219 65	22 585	64.6	-18.546	23 729	-0.2552	366.5
1.0000	0.1204	0.7194	0.223 86	22 706	66.3	-20.736	23 857	-0.3150	370.0
1.2000	0.1173	0.7420	0.232 78	22 922	69.8	-26.602	24 152	-0.4507	376.8
1.4000	0.1157	0.7663	0.242 08	23 122	73.3	-34.878	24 505	-0.6012	383.3
1.6000	0.1153	0.7920	0.251 57	23 320	76.6	-45.928	24 913	-0.7548	389.0
1.8000	0.1157	0.8188	0.261 13	23 522	79.8	-59.993	25 372	-0.8963	393.6
2.0000	0.1169	0.8464	0.270 66	23 732	82.7	-77.234	25 875	-1.0081	396.9
2.2000	0.1186	0.8746	0.280 07	23 951	85.3	-97.777	26 418	-1.0723	398.6
2.4000	0.1209	0.9034	0.289 23	24 180	87.6	-121.74	26 996	-1.0732	398.6
2.6000	0.1237	0.9327	0.297 96	24 420	89.5	-149.28	27 607	-1.0011	397.0
2.8000	0.1269	0.9624	0.306 09	24 671	90.9	-180.56	28 250	-0.8549	394.0
3.0000	0.1306	0.9926	0.313 39	24 931	91.9	-215.79	28 924	-0.6446	390.0
3.2000	0.1347	1.0232	0.319 64	25 203	92.5	-255.18	29 629	-0.3914	385.5
3.4000	0.1393	1.0542	0.324 66	25 485	92.8	-298.88	30 364	-0.1240	381.0
3.6000	0.1443	1.0856	0.328 26	25 777	92.8	-346.94	31 126	0.1264	377.0
3.8000	0.1498	1.1172	0.330 34	26 079	92.6	-399.28	31 912	0.3331	373.9
4.0000	0.1556	1.1490	0.330 85	26 391	92.3	-455.64	32 714	0.4799	371.8
4.2000	0.1620	1.1807	0.329 80	26 711	91.9	-515.62	33 526	0.5641	370.7
4.4000	0.1687	1.2123	0.327 27	27 039	91.6	-578.70	34 340	0.5963	370.2
4.6000	0.1758	1.2436	0.323 37	27 374	91.3	-644.30	35 149	0.5977	370.2
4.8000	0.1833	1.2745	0.318 25	27 715	91.0	-711.81	35 947	0.5966	370.2
5.0000	0.1912	1.3047	0.312 09	28 060	90.7	-780.66	36 727	0.6241	369.9
5.2000	0.1994	1.3343	0.305 05	28 408	90.4	-850.37	37 485	0.7115	369.0
5.4000	0.2080	1.3630	0.297 30	28 758	90.1	-920.51	38 220	0.8878	367.1
5.6000	0.2168	1.3908	0.289 00	29 108	89.7	-990.79	38 929	1.179	364.2
5.8000	0.2259	1.4177	0.280 31	29 459	89.2	-1061.0	39 613	1.608	360.0
6.0000	0.2352	1.4437	0.271 35	29 809	88.6	-1131.0	40 272	2.194	354.5

Values in parentheses are for molalities below the lower limit for which activity data (emf, ϕ) exist. Thermal properties L^{\dagger} , $\bar{L}(\text{H}_2\text{O})$ and $\bar{L}(\text{H}_2\text{SO}_4)$ are given in J mol^{-1} , and C_p^{\dagger} , $\bar{J}(\text{H}_2\text{O})$ and $\bar{J}(\text{H}_2\text{SO}_4)$ in $\text{J mol}^{-1} \text{ K}^{-1}$. ^a The use of α in conjunction with γ_{\pm} and K_{HSO_4} allows the species activity coefficients γ_{H^+} , $\gamma_{\text{HSO}_4^-}$ and $\gamma_{\text{SO}_4^{2-}}$ to be recovered.

Table 9 Thermodynamic properties of aqueous H₂SO₄ at 273.15 K^a

molality/mol kg ⁻¹	γ_{\pm}	ϕ_{st}	α^a	L^*	$\bar{L}(\text{H}_2\text{O})$	$\bar{L}(\text{H}_2\text{SO}_4)$
(0.0001)	0.9569	0.9845	0.991 36	202.1	-2.8804×10^{-4}	362.0
(0.0002)	0.9373	0.9770	0.983 45	351.3	-1.0150×10^{-3}	633.0
(0.0005)	0.8971	0.9609	0.962 23	729.6	-5.1713×10^{-3}	1303.7
(0.0010)	0.8515	0.9420	0.932 33	1 244	-1.6748×10^{-2}	2173.3
(0.0020)	0.7895	0.9154	0.884 81	2 044	-5.0203×10^{-2}	3437.3
0.0050	0.6827	0.8682	0.789 95	3 621	-0.18313	5653.8
0.0100	0.5888	0.8260	0.697 32	5 158	-0.42698	7 528.4
0.0200	0.4923	0.7828	0.596 41	6 852	-0.89264	9 330.0
0.0500	0.3746	0.7324	0.469 96	9 057	-2.0532	11 337
0.1000	0.2994	0.7042	0.392 37	10 531	-3.5175	12 483
0.2000	0.2382	0.6872	0.338 22	11 740	-5.4711	13 258
0.3000	0.2089	0.6836	0.319 65	12 294	-6.5342	13 503
0.4000	0.1909	0.6847	0.313 11	12 607	-6.9415	13 570
0.5000	0.1787	0.6884	0.312 09	12 800	-6.8870	13 564
0.6000	0.1698	0.6939	0.314 02	12 925	-6.5613	13 532
0.7000	0.1632	0.7010	0.317 64	13 009	-6.1489	13 496
0.8000	0.1582	0.7093	0.322 26	13 068	-5.8226	13 472
0.9000	0.1544	0.7187	0.327 50	13 113	-5.7384	13 466
1.0000	0.1516	0.7291	0.333 11	13 149	-6.0342	13 484
1.2000	0.1479	0.7523	0.344 89	13 212	-8.2298	13 593
1.4000	0.1464	0.7783	0.356 92	13 280	-13.194	13 803
1.6000	0.1465	0.8064	0.368 85	13 364	-21.546	14 111
1.8000	0.1478	0.8362	0.380 51	13 468	-33.828	14 512
2.0000	0.1501	0.8676	0.391 73	13 596	-50.560	15 000
2.2000	0.1533	0.9001	0.402 34	13 749	-72.270	15 573
2.4000	0.1574	0.9337	0.412 15	13 928	-99.470	16 229
2.6000	0.1623	0.9683	0.420 93	14 133	-132.61	16 964
2.8000	0.1680	1.0037	0.428 45	14 364	-172.00	17 773
3.0000	0.1745	1.0400	0.434 49	14 620	-217.75	18 649
3.2000	0.1818	1.0771	0.438 84	14 900	-269.72	19 579
3.4000	0.1899	1.1148	0.441 34	15 204	-327.51	20 551
3.6000	0.1988	1.1530	0.441 89	15 529	-390.50	21 550
3.8000	0.2085	1.1916	0.440 47	15 872	-457.88	22 561
4.0000	0.2191	1.2302	0.437 10	16 233	-528.77	23 570
4.2000	0.2305	1.2687	0.431 88	16 605	-602.26	24 565
4.4000	0.2426	1.3069	0.424 95	16 989	-677.47	25 536
4.6000	0.2556	1.3445	0.416 50	17 381	-753.61	26 475
4.8000	0.2693	1.3813	0.406 72	17 779	-830.03	27 378
5.0000	0.2838	1.4172	0.395 84	18 180	-906.20	28 241
5.2000	0.2989	1.4521	0.384 07	18 583	-981.76	29 063
5.4000	0.3147	1.4858	0.371 61	18 986	-1056.5	29 846
5.6000	0.3310	1.5183	0.358 68	19 387	-1130.2	30 591
5.8000	0.3480	1.5496	0.345 44	19 786	-1203.1	31 300
6.0000	0.3656	1.5797	0.332 06	20 181	-1275.2	31 979

^a See footnotes to Table 8.

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Appendix I

The modified equation for excess Gibbs energy, from which expressions for activities and thermal and volumetric properties are derived, is given below for a solution containing an indefinite number of cations, c, and anions, a. For terms involving neutral species (unchanged by the extension to the model) see reviews by Pitzer⁹ or Clegg and Whitfield.¹³

$$\begin{aligned}
 G^{ex}/(n_w RT) = & -(4A_\phi I/1.2)\ln(1 + 1.2\sqrt{I}) \\
 & + \sum_c \sum_a m_c m_a (2B_{ca} + ZC_{ca}^T) \\
 & + \sum_{c < c'} \sum_a m_c m_{c'} \left[2\Phi_{cc'} + \sum_a m_a \psi_{cc'a} \right] \\
 & + \sum_{a < a'} \sum_c m_a m_{a'} \left[2\Phi_{aa'} + \sum_c m_c \psi_{aa'c} \right] \quad (\text{AI1})
 \end{aligned}$$

Definitions are given below. Equations for the activity coefficient of cation M, anion X and the osmotic coefficient follow:

$$\begin{aligned}
 \ln(\gamma_M) = & z_M^2 \mathcal{F} + \sum_a m_a (2B_{Ma} + ZC_{Ma}^T) \\
 & + \sum_c m_c \left(2\Phi_{Mc} + \sum_a m_a \psi_{Mca} \right) \\
 & + \sum_{a < a'} \sum_c m_a m_{a'} \psi_{Maa'} + z_M \sum_c \sum_a m_c m_a C_{ca}^T \quad (\text{AI2})
 \end{aligned}$$

$$\begin{aligned}
 \ln(\gamma_X) = & z_X^2 \mathcal{F} + \sum_c m_c (2B_{cX} + ZC_{cX}^T) \\
 & + \sum_a m_a \left(2\Phi_{Xa} + \sum_c m_c \psi_{Xac} \right) \\
 & + \sum_{c < c'} \sum_a m_c m_{c'} \psi_{Xcc'} + |z_X| \sum_c \sum_a m_c m_a C_{ca}^T \quad (\text{AI3})
 \end{aligned}$$

$$\begin{aligned}
 \phi - 1 = & \left(2 / \sum_i m_i \right) \left[-A_\phi I^{3/2} / (1 + 1.2\sqrt{I}) \right. \\
 & + \sum_c \sum_a m_c m_a (B_{ca}^* + ZC_{ca}^{T*}) \\
 & + \sum_{c < c'} \sum_a m_c m_{c'} \left(\Phi_{cc'}^* + \sum_a m_a \psi_{cc'a} \right) \\
 & \left. + \sum_{a < a'} \sum_c m_a m_{a'} \left(\Phi_{aa'}^* + \sum_c m_c \psi_{aa'c} \right) \right] \quad (\text{AI4})
 \end{aligned}$$

Table 10 Thermodynamic properties of aqueous H₂SO₄ at 323.15 K^a

molality/mol kg ⁻¹	γ_{\pm}	ϕ_{st}	α^a	L^*	$\bar{L}(\text{H}_2\text{O})$	$\bar{L}(\text{H}_2\text{SO}_4)$
(0.0001)	0.9353	0.9741	0.96280	1245.8	-1.9224×10^{-3}	2312.9
(0.0002)	0.9003	0.9588	0.93145	2227.8	-6.5493×10^{-3}	4045.5
(0.0005)	0.8273	0.9259	0.85736	4515.6	-2.9190×10^{-2}	7756.2
(0.0010)	0.7492	0.8900	0.77072	7169.7	-7.9164×10^{-2}	11564
(0.0020)	0.6547	0.8462	0.66074	10529	-0.18784	15743
0.0050	0.5192	0.7839	0.50002	15454	-0.48138	20799
0.0100	0.4213	0.7401	0.38634	18987	-0.86032	23763
0.0200	0.3346	0.7031	0.29217	22009	-1.4129	25930
0.0500	0.2416	0.6673	0.20479	25084	-2.5539	27919
0.1000	0.1875	0.6506	0.16546	26833	-4.0528	29083
0.2000	0.1458	0.6443	0.14596	28248	-6.6801	30102
0.3000	0.1266	0.6468	0.14292	28960	-8.9699	30619
0.4000	0.1151	0.6524	0.14440	29418	-10.998	30944
0.5000	0.1073	0.6595	0.14765	29748	-12.901	31180
0.6000	0.1018	0.6676	0.15167	30003	-14.840	31376
0.7000	0.0976	0.6764	0.15602	30212	-16.973	31558
0.8000	0.0944	0.6858	0.16048	30392	-19.445	31741
0.9000	0.0919	0.6956	0.16495	30552	-22.373	31932
1.0000	0.0900	0.7058	0.16936	30700	-25.854	32135
1.2000	0.0873	0.7271	0.17786	30976	-34.738	32583
1.4000	0.0857	0.7495	0.18583	31241	-46.440	33082
1.6000	0.0850	0.7727	0.19322	31504	-61.072	33623
1.8000	0.0849	0.7966	0.20001	31771	-78.614	34196
2.0000	0.0852	0.8211	0.20619	32043	-99.004	34791
2.2000	0.0860	0.8460	0.21175	32321	-122.21	35404
2.4000	0.0871	0.8714	0.21666	32604	-148.25	36033
2.6000	0.0886	0.8971	0.22090	32892	-177.25	36676
2.8000	0.0903	0.9232	0.22447	33186	-209.40	37337
3.0000	0.0923	0.9495	0.22733	33485	-244.95	38018
3.2000	0.0946	0.9760	0.22949	33790	-284.14	38719
3.4000	0.0971	1.0026	0.23093	34102	-327.13	39442
3.6000	0.0998	1.0294	0.23167	34419	-373.98	40185
3.8000	0.1027	1.0562	0.23171	34742	-424.58	40944
4.0000	0.1059	1.0831	0.23108	35072	-478.63	41714
4.2000	0.1093	1.1098	0.22982	35406	-535.60	42485
4.4000	0.1129	1.1364	0.22796	35745	-594.77	43249
4.6000	0.1167	1.1628	0.22556	36088	-655.26	43995
4.8000	0.1207	1.1890	0.22265	36432	-716.04	44713
5.0000	0.1248	1.2149	0.21930	36777	-776.00	45392
5.2000	0.1292	1.2404	0.21556	37121	-833.99	46024
5.4000	0.1338	1.2655	0.21148	37462	-888.83	46598
5.6000	0.1385	1.2902	0.20712	37797	-939.70	47109
5.8000	0.1434	1.3144	0.20252	38126	-984.61	47549
6.0000	0.1485	1.3381	0.19772	38446	-1023.4	47915

^a See footnotes to Table 8.The function \mathcal{F} in eqn. (AI2) and (AI3) is given by:

$$\begin{aligned} \mathcal{F} = & -A_{\phi}[\sqrt{I}/(1+1.2\sqrt{I}) + (2/1.2)\ln(1+1.2\sqrt{I})] \\ & + \sum_c \sum_a m_c m_a (B'_{ca} + ZC_{ca}^T/2) \\ & + \sum_{c < c'} \sum_c m_c m_{c'} \Phi'_{cc'} + \sum_{a < a'} \sum_a m_a m_{a'} \Phi'_{aa'} \end{aligned} \quad (\text{AI5})$$

In the above equations, I is the molality based ionic strength, and summations $c < c'$ and $a < a'$ are over all distinguishable pairs of cations and anions, respectively. The symbol $\psi_{cc'a}$ is a ternary parameter for the interaction of an anion and two distinct cations, and similarly for $\psi_{aa'c}$. The equations also contain the following functions:

$$Z = \sum_i m_i |z_i| \quad (\text{AI6})$$

$$B_{ca} = \beta_{ca}^{(0)} + \beta_{ca}^{(1)} g(\alpha_{ca} \sqrt{I}) \quad (\text{AI7})$$

$$B'_{ca} = \beta_{ca}^{(1)} g'(\alpha_{ca} \sqrt{I})/I \quad (\text{AI8})$$

$$B_{ca}^{\Phi} = \beta_{ca}^{(0)} + \beta_{ca}^{(1)} \exp(-\alpha_{ca} \sqrt{I}) \quad (\text{AI9})$$

$$C_{ca}^T = C_{ca}^{(0)} + 4C_{ca}^{(1)} h(\omega_{ca} \sqrt{I}) \quad (\text{AI10})$$

$$C_{ca}^T = 4C_{ca}^{(1)} h'(\omega_{ca} \sqrt{I})/I \quad (\text{AI11})$$

$$C_{ca}^{\Phi} = C_{ca}^{(0)} + C_{ca}^{(1)} \exp(-\omega_{ca} \sqrt{I}) \quad (\text{AI12})$$

where

$$g(x) = 2[1 - (1+x)\exp(-x)]/x^2 \quad (\text{AI13})$$

$$g'(x) = \exp(-x) - g(x) \quad (\text{AI14})$$

and two new functions are defined for the extended model:

$$h(x) = \{6 - [6 + x(6 + 3x + x^2)]\exp(-x)\}/x^4 \quad (\text{AI15})$$

$$h'(x) = \exp(-x)/2 - 2h(x) \quad (\text{AI16})$$

Note that $g'(\alpha_{ca} \sqrt{I})$ is equivalent to $Id[g(\alpha_{ca} \sqrt{I})]/dI$, and a corresponding relationship applies for $h'(\omega_{ca} \sqrt{I})$. Other functions for the standard model involve interactions between pairs of ions (i, j) of like sign:

$$\Phi_{ij} = \theta_{ij} + \theta_{ij}^E(I) \quad (\text{AI17})$$

$$\Phi'_{ij} = \theta_{ij}^E(I) \quad (\text{AI18})$$

$$\Phi_{ij}^{\Phi} = \theta_{ij} + \theta_{ij}^E(I) + I\theta_{ij}^E(I) \quad (\text{AI19})$$

The value of parameter θ_{ij} is obtained by fitting, whereas the unsymmetrical mixing term $\theta_{ij}^E(I)$ and its derivative are obtained from theory,^{11,13} and are equal to zero where the charges on ions i and j are equal in magnitude. These mixing

terms are given by:

$$\theta_{ij}^E = (z_i z_j / 4I) [J(x_{ij}) - 1/2J(x_{ii}) - 1/2J(x_{jj})] \quad (\text{AI20})$$

$$\begin{aligned} \theta_{ij}^{E'} &= \partial \theta_{ij}^E / \partial I \\ &= -\theta_{ij}^E / I + (z_i z_j / 8I^2) [x_{ij} J'(x_{ij}) \\ &\quad - (1/2)x_{ii} J'(x_{ii}) - (1/2)x_{jj} J'(x_{jj})] \end{aligned} \quad (\text{AI21})$$

and

$$J'(x_{ij}) = \partial J(x_{ij}) / \partial x_{ij} \quad (\text{AI22})$$

The molality-dependent variable x_{ij} is given by:

$$x_{ij} = 6z_i z_j A_\phi I^{1/2} \quad (\text{AI23})$$

The function $J(x_{ij})$ is an integral which has been evaluated numerically. The following approximating equation is used here to obtain values of $J(x_{ij})$ and $J'(x_{ij})$:¹¹³

$$J(x_{ij}) = x_{ij} / [4 + C_1 x_{ij}^2 \exp(C_3 x_{ij}^4)] \quad (\text{AI24})$$

with $C_1 = 4.581$, $C_2 = -0.7237$, $C_3 = -0.0120$ and $C_4 = 0.528$. More accurate (but complicated) methods are available.⁹ However, in the present application the alternative Chebychev polynomial representation of $J(x_{ij})$ and $J'(x_{ij})$ (used by Harvie *et al.*, for example¹¹) offers no improvement over eqn. (AI24).

Appendix II

Values of the Debye–Hückel coefficient, A_ϕ , used here (at 1 atm, and different temperatures) are those determined by Archer and Wang,¹⁶ calculated using a program supplied by Archer.¹¹⁴ The Debye–Hückel constants of Archer and Wang¹⁶ were obtained from least-squares equations for the relative permittivity of water as a function of temperature, pressure and water density. Since we are interested in the Debye–Hückel limiting law slopes as a function of temperature only, at a single pressure of 1 atm, we decided to represent A_ϕ with one equation valid over the temperature range 234.15–373.15 K. We use a polynomial in Chebychev series form involving the normalised variable x [$x = (2X - X_{\max} - X_{\min}) / (X_{\max} - X_{\min})$], where X is the temperature (in K). X_{\max} (373.15 K) and X_{\min} (234.15 K) are the upper and lower limits of the fit, respectively. The polynomial, with 19 ($N + 1$) coefficients, is given by:

$$\begin{aligned} A_\phi &= 0.5a_0 T_0(x) + a_1 T_1(x) + a_2 T_2(x) \\ &\quad + a_3 T_3(x) \cdots + a_N T_N(x) \end{aligned} \quad (\text{AII1})$$

where $T_0(x) = 1$, $T_1(x) = x$, and for $n \geq 2$:

$$T_n(x) = 2xT_{n-1}(x) - T_{n-2}(x) \quad (\text{AII2})$$

The polynomial coefficients, a_i , are listed in Table 11. Fitted values of A_ϕ agree with those calculated from the original program to within 0.5×10^{-7} below 250 K, and to within $0.95 \times 10^{-8} \text{ mol}^{-1/2} \text{ kg}^{1/2}$ at higher temperatures.

Table 11 Chebychev polynomial coefficients for A_ϕ , $234.15 \leq T/\text{K} \leq 373.15$

a_0	0.797 256 081 240	a_{10}	$-0.388 189 392 385 \times 10^{-4}$
a_1	$0.573 389 669 896 \times 10^{-1}$	a_{11}	$0.164 245 088 592 \times 10^{-4}$
a_2	$0.977 632 177 788 \times 10^{-3}$	a_{12}	$-0.686 031 972 567 \times 10^{-5}$
a_3	$0.489 973 732 417 \times 10^{-2}$	a_{13}	$0.283 455 806 377 \times 10^{-5}$
a_4	$-0.313 151 784 342 \times 10^{-2}$	a_{14}	$-0.115 641 433 004 \times 10^{-5}$
a_5	$0.179 145 971 002 \times 10^{-2}$	a_{15}	$0.461 489 672 579 \times 10^{-6}$
a_6	$-0.920 584 241 844 \times 10^{-3}$	a_{16}	$-0.177 069 754 948 \times 10^{-6}$
a_7	$0.443 862 726 879 \times 10^{-3}$	a_{17}	$0.612 464 488 231 \times 10^{-7}$
a_8	$-0.203 661 129 991 \times 10^{-3}$	a_{18}	$-0.175 689 013 085 \times 10^{-7}$
a_9	$0.900 924 147 948 \times 10^{-4}$		

This level of precision was chosen to ensure accuracy in the calculated second differential of A_ϕ with respect to temperature, because it appears in the expression for the apparent molal heat capacity, obtained here by numerical differentiation (Section 2). The very low minimum temperature of fit was needed in order to use the same polynomial in a second study of the $\text{H}_2\text{SO}_4\text{--H}_2\text{O}$ system over a more extended range of temperature and composition.⁵³

For program validation, the polynomial yields the following values: 273.15 K, $A_\phi = 0.376 421 452 \text{ mol}^{-1/2} \text{ kg}^{1/2}$; 298.15 K, $A_\phi = 0.391 475 238 \text{ mol}^{-1/2} \text{ kg}^{1/2}$.

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