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Osmotic and Activity Coefficients of Aqueous $(NH_4)_2SO_4$ as a Function of Temperature, and Aqueous $(NH_4)_2SO_4-H_2SO_4$ Mixtures at 298.15 K and 323.15 K

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Osmotic coefficients of $(NH_4)_2SO_{4(aq)}$, and aqueous $(NH_4)_2SO_4-H_2SO_4$ mixtures at 298.15 K and 323.15 K, and $H_2SO_{4(aq)}$ at 323.15 K have been determined by an isopiestic method. Using the Pitzer molality-based thermodynamic model, the measurements are combined with other literature data to obtain osmotic and activity coefficients of, first, $(NH_4)_2SO_{4(aq)}$ from <273 K to ~373 K and, second, aqueous $(NH_4)_2SO_4-H_2SO_4$ over the entire composition range at 298.15 K.

1. Introduction

Aqueous $(NH_4)_2SO_4$ and $(NH_4)_2SO_4-H_2SO_4$ mixtures are important components of atmospheric aerosols (Seinfeld, 1986; Clarke *et al*., 1987), and an understanding of their thermodynamic properties is needed to predict aerosol formation and behavior (Coffman and Hegg, 1995; Kim *et al*., 1993a,b).

The properties of aqueous H_2SO_4 have been studied extensively, with recent critical reviews by Clegg *et al*. (1994) (0−6 mol kg^{-1}, 278.15−328.15 K) and Clegg and Brimblecombe (1995a) (0−40 mol kg^{-1}, <200−328.15 K) covering a wide range of temperature and composition. Clegg *et al*. (1995) have combined new measurements of water vapor pressures of supersaturated aqueous $(NH_4)_2SO_4$ from 278.15 K to 313.15 K with existing boiling point, freezing point, osmotic coefficient, and thermal data to yield the thermodynamic properties of aqueous $(NH_4)_2SO_4$ to very high concentration (up to 25 mol kg^{-1}) as a function of temperature. However, the thermodynamic properties of aqueous $(NH_4)_2SO_4$ at moderate temperatures and concentrations below saturation are still poorly known compared to those of other important inorganic salts, chiefly due to the paucity of thermal measurements and the low quality of available freezing point depression data. Measurements for aqueous $(NH_4)_2SO_4-H_2SO_4$ mixtures are also lacking, the principal data sets being isopiestic determinations at 298.15 K (Park *et al*., 1989), and water vapor pressures for supersaturated solutions (at or near 298.15 K) obtained using electrodynamic balances (see Clegg and Brimblecombe (1995b)).

There is a need, first, for additional data for aqueous $(NH_4)_2SO_4$ solutions at undersaturated concentrations to define more accurately the variation of their thermodynamic properties with temperature. Second, measurements are required for aqueous $(NH_4)_2SO_4-H_2SO_4$ solutions at different temperatures and compositions to improve our understanding of the properties of these mixtures and constrain the thermodynamic (activity coefficient) models used in practical calculations.

In this work we present new isopiestic measurements of aqueous $(NH_4)_2SO_4$, H_2SO_4, and $(NH_4)_2SO_4-H_2SO_4$ mixtures over a range of molalities at 298.15 K and 323.15 K. The results are combined with other literature data using the Pitzer activity coefficient model (e.g., see Pitzer (1991)) to derive, first, thermodynamic properties of aqueous $(NH_4)_2SO_4$ for undersaturated molalities from the freezing temperature to the boiling temperature of the solutions and, second, thermodynamic properties of aqueous $(NH_4)_2SO_4-H_2SO_4$ mixtures at 298.15 K.

Table 1. Compositions of the Original Stock Solutions

solute	m/(mol kg^{-1})	solute	m/(mol kg^{-1})
NaCl	0.9987	H_2SO_4:$(NH_4)_2SO_4$	0.6653:0.3210
H_2SO_4	0.7305	H_2SO_4:$(NH_4)_2SO_4$	0.3330:0.6483
$(NH_4)_2SO_4$	0.9732		

2. Experiments

(a) Preparation of Solutions. The stock solutions of aqueous NaCl (Baker, Ultrex Ultrapure Reagent, lot no. A28344), H_2SO_4 (Baker, Ultrex Ultrapure Reagent, lot no. UA103), and $(NH_4)_2SO_4$ (Baker, Baker Analysed Reagent, lot no. E47340) were prepared as follows, using water that was first distilled and then passed through a four-stage ion-exchange system, and finally purged with helium. The NaCl crystals were dried at 433 K for 15 h under vacuum prior to preparing the stock solution, whereas the remaining reagents were used without further treatment. The concentrations of the five stock solutions (NaCl, H_2SO_4, $(NH_4)_2SO_4$, 2:1 $H_2SO_4-(NH_4)_2SO_4$, and 1:2 $H_2SO_4-(NH_4)_2SO_4$) were measured by acidimetric titration with weight burets containing standardized HCl and NaOH. The molalities of the titrants were established by similar potentiometric titrations against the primary standards Na_2CO_3 and $KHC_6H_4(COO)_2$ (Eastman, lot no. 054), respectively. The concentrations of HCl and NaOH were corrected for buoyancy and confirmed by titrating one against the other with a reproducibility of *ca*. ±0.05%. The acidimetric titrations of the four salt solutions and mixtures were carried out on the effluent formed by first passing a known mass of solution through a cation exchange column (Dowex 50X8-100 resin in H$^+$ form) and washing the column with approximately 100 cm^3 of water. The reproducibility of these analyses was <0.1%. The compositions of the stock solutions are given in Table 1.

(b) Equipment and Procedure. The isopiestic apparatus, which was described in some detail by Rush and Johnson (1966), was modified slightly for the present work.

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The Teflon covers on the 12 platinum dishes were replaced by individually tailored KELF covers to provide a tighter seal when the dishes were removed from the vessel for weighing. Nitrogen rather than dry air was used to pressurize the chamber before removing the dishes, and the inflow of gas was controlled at six evenly-spaced positions around the inside rim of the chamber in order to minimize preferential evaporation at the original gas inlet port. The temperature was controlled to within ±0.003 K at 298.15 K and 323.15 K, with additional cooling provided at the former temperature by circulation of water through copper tubing from an external thermostat set at (297.85 ± 0.1) K.

The procedure for removing, weighing, and reinserting the dishes was similar to that described previously (Rush and Johnson, 1966). Note that, as in previous studies, the 12 dishes contained duplicate solutions of NaCl (standard) and the five salts under investigation, with the duplicates arranged opposite each other around the circumference of the copper block. The maximum concentration differences between the duplicates were <0.1% at equilibrium. Generally, at 298.15 K equilibrium was attained within 7 days after sealing the dishes inside the evacuated isopiestic apparatus. At 323.15 K, only 3 days were required to reach equilibrium.

Aqueous $(NH_4)_2SO_4$ and $(NH_4)_2SO_4-H_2SO_4$ Mixtures. The stoichiometric concentrations of the solutions at each equilibration are given in Tables 2 and 3. Five sets of isopiestic experiments are listed, indicating that for each set the solutions in the dishes were discarded and fresh stock solutions added in order to minimize cumulative uncertainties due to solution loss or contamination. It should be noted that for sets 4 and 5, the temperature was changed from 298.15 K to 323.15 K so that the results obtained at both temperatures were compatible.

Aqueous H_2SO_4 Solutions. These equilibrations were carried out in an independent series of measurements made only at 323.15 K, involving five loadings of the dishes with fresh stock solutions. The aqueous NaCl standard was placed in two dishes, and an aqueous H_2SO_4 sample in a single dish. The calculated molalities of the NaCl standards (mean value) and those of the samples, based on the measured masses of the dishes, are given in Table 2.

(c) Analysis and Results. The osmotic coefficient of the NaCl standard (ϕ_{NaCl}) and the stoichiometric osmotic coefficient of the sample solution (ϕ_{st}) are related by $\phi_{st} = \phi_{NaCl}(2/3)m(NaCl)/(m((NH_4)_2SO_4) + m(H_2SO_4))$, where m denotes molality. Note that while this expression yields an osmotic coefficient on the basis of complete dissociation of H_2SO_4 the thermodynamic modeling of the properties of the solution mixtures (section 3) requires explicit recognition of bisulfate (HSO_4^-) formation. The symbol ϕ is used in this work for the osmotic coefficient of pure aqueous $(NH_4)_2SO_4$, but is calculated from the same formula as that given for ϕ_{st} above. Values of ϕ_{NaCl} were calculated using the equations of Archer (1992), and including the corrections noted in Table 1 of Clegg *et al.* (1994). The resulting values of ϕ and ϕ_{st} are listed in Tables 2 and 3 for the pure aqueous solutions and mixtures, respectively.

During the development of the thermodynamic model (section 3), it was noted that some of the measured osmotic coefficients deviated significantly from the general trends of the data and were apparently in error (values in parentheses in Tables 2 and 3). The reason for this is unclear, though we note that several of these determinations came from the same equilibrations, notably sets 5-13 to 5-15 at low molality. Insufficient equilibration time is not thought to be a factor for these particular samples, since 2−3 weeks was allowed where only about 4 days is required to equilibrate a ~1 mol kg^{-1} solution at 323.15 K.

Measurements for the pure aqueous solutions (Table 2, excluding parenthesized values) were compared with other available data in order to test consistency. Osmotic coefficients of pure aqueous $(NH_4)_2SO_4$ at 298.15 K (Table 2) were found to be greater than those determined by Wishaw and Stokes (1954) by an average of about 0.0011, with the largest deviations occurring at or below 1 mol kg^{-1}. The scatter in the two data sets is of approximately the same magnitude (±0.001). Differences from the results of Filippov *et al.* (1986) average +0.0029, with a slightly larger degree of random error (about ±0.0015) in this data set. These deviations between the results of different studies are similar to those found for aqueous H_2SO_4 at 298.15 K (Clegg *et al.*, 1994), and constitute a satisfactory level of agreement. Osmotic coefficients of aqueous H_2SO_4 at 323.15 K cannot be compared directly to other measurements. However, Clegg *et al.* (1994) included these data in a model of the thermodynamic properties of aqueous H_2SO_4, which was also constrained by emf measurements to 328.15 K and heat capacities to 313.15 K. The rms deviation of the osmotic coefficients listed in Table 2 (excluding values in parentheses) from those calculated using the model is only 0.000 77. We conclude that the osmotic coefficients determined in this study are generally accurate to within ±0.002.

3. A Thermodynamic Model of Aqueous $(NH_4)_2SO_4-H_2SO_4$ Solutions

A principal aim of the present study is to combine the measurements presented here with other literature data to produce a model of the thermodynamic properties of aqueous $(NH_4)_2SO_4-H_2SO_4$ mixtures, enabling the calculation of osmotic and activity coefficients over the entire composition range. As noted in the Introduction, previous studies have examined the properties of pure aqueous $(NH_4)_2SO_4$ as a function of temperature (Clegg *et al.*, 1995) and aqueous $(NH_4)_2SO_4-H_2SO_4$ at 298.15 K (Clegg and Brimblecombe, 1995b), both focusing on supersaturated solutions and utilizing a mole-fraction-based model (Pitzer and Simonson, 1986; Clegg *et al.*, 1992). Here we develop a model of the subsaturated system only, incorporating the new data presented here and using Pitzer's molality-based equations. This is intended for use in calculating the properties of mixtures at low to moderate concentrations, and to provide reference values of osmotic and activity coefficients as the basis for a more extended treatment relevant to problems in atmospheric chemistry. The results are also of direct interest to the electric power industry in reference to the formation of corrosive condensates in the turbines of plants using AVT (all volatile treatment) water chemistry (Palmer *et al.*, 1996).

(a) Theoretical Background. The basis of the Pitzer ion-interaction model is given by Pitzer (1991) and references therein. In this study we adopt the extended form presented in Appendix I of Clegg *et al.* (1994). Briefly, for mixed electrolyte solutions the equations involve two types of interactions. First, and most important, are those between pairs of ions of opposite sign which are described by parameters $\beta_{ca}^{(i)}$ and $C_{ca}^{(i)}$ (i = 0 and 1 for the system considered here). Parameter $C_{ca}^{(0)}$ corresponds to C_{ca} in the original formulation of the model, and $C_{ca}^{(1)}$ is the additional term employed by Archer (1992) and then generalized by Clegg *et al.* (1994). Second, there are parameters $\theta_{ii'}$ and $\psi_{ii'j}$ for interactions between two dissimilar ions of one sign (i and i') and between two ions of one sign and with one of opposite sign (j), respectively.

Table 2. Solution Molalities for Each Equilibration, and Osmotic Coefficients of Aqueous $(NH_4)_2SO_4$ (1) and H_2SO_4 (2)

m(NaCl)/(mol kg^{-1})	m_1/(mol kg^{-1})	set[a]	t/°C	ϕ[b]	m(NaCl)/(mol kg^{-1})	m_2/(mol kg^{-1})	set[a]	t/°C	ϕ_{st}[b]
1.0801	1.0538	1-1	25	0.6426	0.5158	0.4835	1	50	0.6570
0.8999	0.8616	1-2	25	0.6499	0.4425	0.4164	1	50	0.6532
0.9248	0.8874	1-3	25	0.6491	0.3782	0.3579	1	50	0.6488
0.7672	0.7207	1-4	25	0.6591	0.3218	0.3037	1	50	(0.6503)
0.7360	0.6882	1-5	25	0.6614	0.2721	0.2576	1	50	(0.6482)
0.6915	0.6449	1-6	25	0.6622	0.2708	0.2575	1	50	0.6452
0.6686	0.6197	1-7	25	0.6658	0.2002	0.1894	1	50	(0.6500)
0.6321	0.5812	1-8	25	0.6705	0.8242	0.7543	0	50	0.6812
0.6052	0.5541	1-9	25	0.6728	0.5338	0.4987	0	50	0.6597
0.5680	0.5179	1-10	25	0.6750	0.5490	0.5133	0	50	0.6594
0.5345	0.4841	1-11	25	0.6790	0.6739	0.6243	0	50	0.6686
0.4457	0.3997	1-12	25	(0.6847)	0.9516	0.8631	0	50	0.6915
0.4939	0.4423	2-1	25	0.6862	1.1242	1.0072	0	50	0.7062
0.4087	0.3600	2-2	25	0.6968	1.3331	1.1774	0	50	0.7246
0.3433	0.2973	2-3	25	0.7086	1.6146	1.4017	0	50	0.7490
0.2439	0.2070	2-5	25	(0.7241)	1.7106	1.4785	0	50	0.7566
0.9930	0.9607	3-1	25	0.6456	1.8119	1.5530	0	50	0.7675
1.0530	1.0262	3-2	25	0.6426	2.1108	1.7816	0	50	0.7935
1.2021	1.1906	3-3	25	0.6366	2.7041	2.2166	0	50	0.8473
1.3054	1.3060	3-4	25	0.6334	2.5520	2.1157	0	50	(0.8299)
1.5580	1.5894	3-5	25	0.6292	3.1655	2.5416	0	50	0.8899
3.5650	3.9076	3-6	25	0.6611	5.1822	3.9014	0	50	1.0702
1.5540	1.5890	4-1	25	0.6277	5.0978	3.8479	0	50	1.0622
1.7418	1.8037	4-2	25	0.6261	5.6057	4.1755	0	50	1.1077
1.7658	1.8314	4-3	25	0.6260	4.6834	3.5740	0	50	1.0258
1.8568	1.9359	4-4	25	0.6259	4.5995	3.5183	0	50	1.0184
2.1514	2.2750	4-5	25	0.6277	3.9817	3.1028	0	50	0.9636
2.6961	2.9050	4-6	25	0.6367	2.2137	1.8552	0	50	0.8042
2.9137	3.1566	4-7	25	0.6418	0.8279	0.7573	0	50	0.6817
3.0707	3.3390	4-8	25	0.6458	0.8550	0.7800	2	50	0.6843
3.6732	4.0425	4-9	25	0.6630	1.1374	1.0175	3	50	0.7078
3.5451	3.8930	4-10	25	0.6591	1.8654	1.5932	3	50	0.7728
3.7132	4.0904	4-11	25	0.6641	2.0961	1.7676	3	50	0.7935
4.5972	5.1463	4-12	25	0.6917	1.5248	1.3292	3	50	0.7421
5.0305	5.6834	4-13	25	0.7046	1.7372	1.4951	3	50	0.7610
5.1748	5.8586	4-14	25	0.7096	2.3003	1.9191	3	50	0.8121
3.5148	3.8586	4-16	25	0.6580	3.0908	2.4883	3	50	0.8835
1.0629	1.0354	5-1	25	0.6431	3.8715	3.0272	3	50	0.9540
1.1793	1.1686	5-2	50	0.6404	4.7151	3.5946	3	50	1.0288
1.1464	1.1350	5-3	50	0.6399	5.1462	3.8761	3	50	1.0675
0.9325	0.9005	5-4	50	0.6489	4.1271	3.1911	3	50	(0.9797)
0.8608	0.8232	5-5	50	0.6530	4.2138	3.2590	3	50	0.9845
0.7423	0.7039	5-6	50	(0.6550)	3.6749	2.8928	3	50	0.9364
0.6388	0.5907	5-7	50	0.6689	2.6764	2.1928	3	50	0.8463
0.5799	0.5308	5-8	50	0.6743					
0.5041	0.4551	5-9	50	0.6820					
0.4360	0.3885	5-10	50	0.6897					
0.3852	0.3395	5-11	50	0.6966					
0.3346	0.2925	5-12	50	0.7020					
0.1703	0.1441	5-13	50	(0.7276)					
0.1584	0.1319	5-14	50	(0.7400)					
0.1645	0.1373	5-15	50	(0.7379)					
3.4727	3.8870	4-17	50	0.6505					
3.2682	3.6411	4-18	50	0.6454					
4.1170	4.6835	4-19	50	0.6655					
3.3488	3.7385	4-20	50	0.6473					
4.5249	5.2017	4-21	50	0.6747					
4.8398	5.6098	4-22	50	0.6816					
5.1664	6.0414	4-23	50	0.6884					
4.0909	4.6785	4-26	50	0.6609					
3.1565	3.5260	4-27	50	0.6393					
2.8608	3.1680	4-28	50	0.6333					
2.5396	2.7780	4-29	50	0.6285					
2.2917	2.4825	4-30	50	0.6251					
2.0164	2.1541	4-31	50	0.6234					
1.6892	1.7670	4-32	50	0.6244					
1.4471	1.4848	4-33	50	0.6277					
1.2614	1.2824	4-34	50	(0.6220)					

[a] Series number followed by the sequence number which specifies the order in which solutions from each series were weighed following equilibration. Values for $(NH_4)_2SO_4$ (m_1) refer to the same equilibrations as listed in Table 3, while those for H_2SO_4 (m_2) are for different experiments. [b] Osmotic coefficients of the test solutions, calculated using the equations of Archer (1992) for the thermodynamic properties of aqueous NaCl (section 2). Values in parentheses are judged to be in error, and were therefore omitted from the analysis of the results.

Table 3. Solution Molalities for Each Equilibration, and Osmotic Coefficients of Aqueous $(NH_4)_2SO_4$ (1)−H_2SO_4 (2) Mixtures

m(NaCl)/(mol kg^{-1})	set[a]	t/°C	m_1/(mol kg^{-1})	m_2/(mol kg^{-1})	ϕ_{st}[b]	m_1/(mol kg^{-1})	m_2/(mol kg^{-1})	ϕ_{st}[b]
1.0801	1-1	25	0.3401	0.7051	0.6479	0.7318	0.3759	0.6114
0.8999	1-2	25	0.2835	0.5878	0.6426			
0.9248	1-3	25	0.2915	0.6044	0.6429	0.6185	0.3176	0.6153
0.7672	1-4	25	0.2412	0.4999	0.6409	0.5042	0.2590	0.6224
0.7360	1-5	25	0.2311	0.4790	0.6410			
0.6915	1-6	25	0.2171	0.4501	0.6401	0.4513	0.2318	0.6252
0.6686	1-7	25	0.2099	0.4350	0.6398	0.4345	0.2232	0.6274
0.6321	1-8	25	0.1980	0.4106	0.6403	0.4084	0.2098	0.6303
0.6052	1-9	25	0.1893	0.3924	0.6409	0.3893	0.2000	0.6326
0.5680	1-10	25	0.1776	0.3683	0.6404	0.3640	0.1870	0.6344
0.5345	1-11	25	0.1671	0.3465	0.6400	0.3411	0.1752	0.6367
0.4457	1-12	25	0.1392	0.2886	(0.6397)	0.2793	0.1435	0.6473
0.4939	2-1	25	0.1537	0.3187	0.6424	0.3120	0.1603	0.6426
0.4086	2-2	25	0.1267	0.2625	0.6444	0.2544	0.1307	0.6512
0.3433	2-3	25	0.1056	0.2190	0.6490	0.2108	0.1083	0.6602
0.2541	2-4	25	0.07859	0.1629	(0.6464)	0.1556	0.07991	(0.6629)
0.2439	2-5	25	0.07442	0.1543	(0.6554)	0.1469	0.07543	(0.6743)
0.9930	3-1	25	0.3126	0.6481	0.6456	0.6676	0.3428	0.6138
1.0530	3-2	25	0.3316	0.6874	0.6471	0.7120	0.3656	0.6119
1.2021	3-3	25	0.3786	0.7847	0.6515	0.8229	0.4227	0.6085
1.3053	3-4	25	0.4110	0.8520	0.6549	0.9008	0.4626	0.6067
1.5580	3-5	25	0.4892	1.0140	0.6653	1.0925	0.5611	0.6048
3.5650	3-6	25	1.1011	2.2825	0.7635	2.7108	1.3922	0.6296
1.5540	4-1	25	0.4890	1.0138	0.6637	1.0920	0.5609	0.6034
1.7418	4-2	25	0.5472	1.1344	0.6716	1.2371	0.6354	0.6031
1.7658	4-3	25	0.5547	1.1499	0.6725	1.2559	0.6450	0.6031
1.8568	4-4	25	0.5827	1.2079	0.6767	1.3265	0.6813	0.6035
2.1514	4-5	25	0.6730	1.3950	0.6905	1.5577	0.8000	0.6057
2.6961	4-6	25	0.8386	1.7384	0.7177	1.9936	1.0239	0.6129
2.9137	4-7	25	0.9046	1.8752	0.7288	2.1709	1.1149	0.6166
3.0707	4-8	25	0.9524	1.9744	0.7368	2.3005	1.1815	0.6193
3.6732	4-9	25	1.1349	2.3526	0.7686	2.8101	1.4432	0.6302
3.5451	4-10	25	1.0962	2.2723	0.7617	2.6999	1.3866	0.6279
3.7132	4-11	25	1.1474	2.3786	0.7704	2.8450	1.4611	0.6309
4.5972	4-12	25	1.4209	2.9456	0.8152	3.6449	1.8720	0.6452
5.0305	4-13	25	1.5581	3.2299	0.8364	4.0679	2.0892	0.6504
5.1748	4-14	25	1.6043	3.3257	0.8433	4.2140	2.1642	0.6518
5.2080	4-15	25	1.6147	3.3473	0.8450	4.2474	2.1814	0.6522
3.5148	4-16	25	1.0859	2.2511	0.7608	2.6712	1.3719	0.6280
1.0629	5-1	25	0.3334	0.6912	(0.6499)	0.7167	0.3681	(0.6138)
1.1793	5-2	50	0.3797	0.7870	0.6415	0.8208	0.4215	0.6024
1.1464	5-3	50	0.3694	0.7657	0.6398	0.7953	0.4084	0.6033
0.9325	5-4	50	0.3001	0.6221	0.6336	0.6337	0.3254	0.6092
0.8608	5-5	50	0.2768	0.5739	0.6319	0.5801	0.2980	0.6122
0.7423	5-6	50	0.2393	0.4960	0.6271	0.4997	0.2566	(0.6096)
0.6388	5-7	50	0.2047	0.4242	0.6283	0.4189	0.2152	0.6231
0.5799	5-8	50	0.1856	0.3846	0.6277	0.3771	0.1936	0.6271
0.5041	5-9	50	0.1608	0.3332	0.6283	0.3239	0.1664	0.6330
0.4360	5-10	50	0.1385	0.2872	0.6295	0.2772	0.1424	0.6386
0.3852	5-11	50	0.1220	0.2529	0.6309	0.2429	0.1247	0.6434
0.3346	5-12	50	0.1057	0.2190	0.6324	0.2105	0.1081	(0.6445)
0.1703	5-13	50	0.05311	0.1101	(0.6425)	0.1060	0.05443	(0.6537)
0.1584	5-14	50	0.04888	0.1013	0.6498	0.09593	0.04927	(0.6722)
0.1644	5-15	50	0.05090	0.1055	0.6474	0.1001	0.05141	(0.6684)
3.4727	4-17	50	1.1139	2.3091	0.7387	2.7342	1.4043	0.6110
3.2682	4-18	50	1.0482	2.1728	0.7296	2.5533	1.3114	0.6081
4.1170	4-19	50	1.3214	2.7392	0.7676	3.3275	1.7089	0.6189
3.3488	4-20	50	1.0735	2.2255	0.7335	2.6224	1.3468	0.6097
4.5249	4-21	50	1.4549	3.0161	0.7850	3.7210	1.9110	0.6231
4.8398	4-22	50	1.5594	3.2326	0.7979	4.0361	2.0729	0.6259
5.1664	4-23	50	1.6691	3.4600	0.8108	4.3744	2.2466	0.6281
5.4963	4-24	50	1.7797	3.6893	0.8242	4.7249	2.4266	0.6303
5.6912	4-25	50	1.8462	3.8273	0.8316	4.9368	2.5354	0.6314
4.0909	4-26	50	1.3144	2.7247	0.7656	3.3047	1.6973	0.6182
3.1565	4-27	50	1.0137	2.1015	0.7236	2.4557	1.2612	0.6065
2.8608	4-28	50	0.9196	1.9064	0.7099	2.1988	1.1293	0.6028
2.5396	4-29	50	0.8170	1.6935	0.6955	1.9240	0.9881	0.5996
2.2917	4-30	50	0.7385	1.5310	0.6838	1.7174	0.8820	0.5970
2.0164	4-31	50	0.6507	1.3489	0.6716	1.4900	0.7653	0.5954
1.6892	4-32	50	0.5452	1.1301	0.6585	1.2235	0.6283	0.5958
1.4471	4-33	50	0.4678	0.9697	0.6484	1.0319	0.5299	0.5968
1.2614	4-34	50	0.4079	0.8457	0.6414	0.8837	0.4538	0.6012

[a] Series number followed by the sequence number which specifies the order in which solutions from each series were weighed following equilibration. [b] Stoichiometric osmotic coefficients of the test solutions, calculated using the equations of Archer (1992) for the thermodynamic properties of aqueous NaCl (section 2). Values in parentheses are judged to be in error, and were therefore omitted from the analysis of the results.

Values of all parameters, which vary as functions of temperature and pressure, are determined by fitting to thermodynamic data—osmotic and activity coefficients and thermal properties in the present case.

Here, parameters are required first for the two limiting cases: pure aqueous $(NH_4)_2SO_4$ and pure aqueous H_2SO_4. Using these values, the additional interactions—principally between NH_4^+ and HSO_4^-—are obtained by fitting to data for the mixed system. In this work we adopt parameters determined for pure aqueous H_2SO_4 presented by Clegg *et al.* (1994). The Pitzer model equation for the osmotic coefficient of pure aqueous $(NH_4)_2SO_4$ is given below:

$$\phi - 1 = 2A_\phi I^{1/2}/(1 + bI^{1/2}) + (4/3)mB^{\phi}_{NH_4SO_4} + (16/3)m^2C^{T\phi}_{NH_4SO_4} \quad (1)$$

where:

$$B^{\phi}_{NH_4SO_4} = \beta^{(0)}_{NH_4SO_4} + \beta^{(1)}_{NH_4SO_4}\exp(-\alpha I^{1/2}) \quad (2)$$

$$C^{T\phi}_{NH_4SO_4} = C^{(0)}_{NH_4SO_4} + C^{(1)}_{NH_4SO_4}\exp(-\omega I^{1/2}) \quad (3)$$

In eqs 1−3 A_ϕ is the Debye−Hückel constant (0.3915 at 298.15 K), I (mol kg^{-1}) is the ionic strength, m (mol kg^{-1}) is the molality of $(NH_4)_2SO_4$, b is a constant (1.2), and $\beta^{(0)}_{NH_4SO_4}$, $\beta^{(0)}_{NH_4SO_4}$, $C^{(0)}_{NH_4SO_4}$, and $C^{(1)}_{NH_4SO_4}$ are interaction parameters whose values are to be determined. Symbols α and ω represent constants with values 2.0 and 2.5, respectively. The corresponding model equations for the apparent molar enthalpy and heat capacity of aqueous $(NH_4)_2SO_4$ are

$$^{\phi}L = 6(A_H/2b)\ln(1 + bI^{1/2}) - 4RT^2(mB^{L}_{NH_4SO_4} + 2m^2C^{TL}_{NH_4SO_4}) \quad (4)$$

$$^{\phi}C_p = {}^{\phi}C_p{}^{\circ} + 6(A_C/2b)\ln(1 + bI^{1/2}) - 4RT^2(mB^{J}_{NH_4SO_4} + 2m^2C^{TJ}_{NH_4SO_4}) \quad (5)$$

where

$$B^{L}_{NH_4SO_4} = \beta^{(0)L}_{NH_4SO_4} + \beta^{(1)L}_{NH_4SO_4}\exp(-\alpha I^{1/2}) \quad (6)$$

$$C^{TL}_{NH_4SO_4} = C^{(0)L}_{NH_4SO_4} + C^{(1)L}_{NH_4SO_4}\exp(-\omega I^{1/2}) \quad (7)$$

$$B^{J}_{NH_4SO_4} = \beta^{(0)J}_{NH_4SO_4} + \beta^{(1)J}_{NH_4SO_4}\exp(-\alpha I^{1/2}) \quad (8)$$

$$C^{TJ}_{NH_4SO_4} = C^{(0)J}_{NH_4SO_4} + C^{(1)J}_{NH_4SO_4}\exp(-\omega I^{1/2}) \quad (9)$$

In eqs 4 and 5 A_H and A_C are the Debye−Hückel constants for enthalpy and heat capacity, respectively, R (8.3144 J mol^{-1} K^{-1}) is the gas constant, and T (K) is temperature. $^{\phi}C_p{}^{\circ}$ is the infinite dilution value of the apparent molar heat capacity at temperature T. Values of the Debye−Hückel constants used in this study are derived from the work of Archer and Wang (1990). Each parameter p with superscripts L (eqs 6 and 7) and J (eqs 8 and 9) is related to those in eqs 2 and 3 by

$$p^{L} = \partial p/\partial T \quad (10)$$

$$p^{J} = \partial^2 p/\partial T^2 + (2/T)(\partial p/\partial T) \quad (11)$$

Within the Pitzer model the mixed system $(NH_4)_2SO_4$−H_2SO_4−H_2O is treated as containing the dissolved species H^+, NH_4^+, HSO_4^-, and SO_4^{2-}, with NH_4^+ dissociation neglected in these mostly very acidic solutions. Molalities of HSO_4^- and SO_4^{2-} are related by the equilibrium $HSO_4^- \rightleftharpoons H^+ + SO_4^{2-}$, and an expression for the equilibrium constant as a function of temperature is given by Clegg *et al.* (1994). Model equations for the osmotic and activity coefficients in aqueous $(NH_4)_2SO_4$−H_2SO_4 mixtures are not given here, but can readily be derived from the generalized expressions given by Clegg *et al.* (1994).

The dissociation equilibrium of the HSO_4^- ion must be determined for any solution mixture by iteration of the activity coefficient equations. Speciation varies as a function of temperature, and therefore, thermal properties such as heats of dilution ($\Delta_{dil}H$) are most easily obtained by numerical differentiation of the excess Gibbs energy expressed in terms of stoichiometric osmotic and activity coefficients (e.g., see Clegg *et al.* (1994)). Equations for the apparent molar enthalpy ($^{\phi}L$) (Clegg *et al.*, 1994) of pure aqueous H_2SO_4 and the expressions for aqueous NH_4HSO_4 are analogous but with stoichiometric osmotic and activity coefficients defined by

$$\phi_{st} = \phi^*(m(H^+) + m(NH_4{}^+) + m(HSO_4{}^-) + m(SO_4{}^{2-}))/(m(H^+) + m(NH_4{}^+) + 2m(HSO_4{}^-) + m(SO_4{}^{2-})) \quad (12)$$

$$\gamma_\pm(NH_4HSO_4) = (\gamma_{NH_4}\gamma_H(m(H^+)/m(H^+{}_T))\gamma_{SO_4}m(SO_4{}^{2-})/m(SO_4{}^{2-}{}_T))^{1/3} \quad (13)$$

where ϕ^* is the osmotic coefficient calculated by the model for the equilibrium speciation, and the stoichiometric value (ϕ_{st}) is used when complete dissociation of HSO_4^- is assumed (hence, the factor of 2 in the denominator of eq 12). In eq 13, γ_H and γ_{SO_4} are the activity coefficients calculated by the model for the free ions (present at molalities $m(H^+)$ and $m(SO_4^{2-})$), and the subscript T denotes total quantities, i.e., including the amounts of H^+ and SO_4^{2-} present as HSO_4^-.

The thermodynamic properties of aqueous $(NH_4)_2SO_4$ and $(NH_4)_2SO_4$−H_2SO_4 mixtures are considered below.

(b) Aqueous $(NH_4)_2SO_4$. Sources of available data for the thermodynamic properties of pure aqueous $(NH_4)_2SO_4$ have been discussed by Clegg *et al.* (1995) and are listed in their Table 2. Those data sets relevant to the present study are summarized here in Table 4.

Osmotic coefficient data at 298.15 K (sets 1−3 in Table 4) were first fitted with eq 1 to establish values of the model parameters at this temperature. Data from the different sources were given unit weight. As in a previous study (Clegg and Brimblecombe, 1995b), values of the osmotic coefficient of K_2SO_4 for $(0.001 \le m \le 0.1)$ mol kg^{-1} were included at a reduced weight of 0.2 since no data are available for $(NH_4)_2SO_4$ below 0.1294 mol kg^{-1}. The results of the fit are shown in Figure 1a with fitted parameters listed in Table 5. We note that differences between the best fit values of ϕ and those calculated using parameters given by Pitzer (1991), based upon osmotic coefficients from the evaluation of Robinson and Stokes (1965), are within −0.004 to +0.007 for molalities less than 5.5 mol kg^{-1}.

The variation of the thermodynamic properties of aqueous ammonium sulfate with temperature can be determined from enthalpies and heat capacities together with data yielding osmotic coefficients at temperatures other than 298.15 K: the measurements at 323.15 K given in Table 2, freezing point depressions (see Table 2 of Clegg *et al.* (1995)), boiling point elevations (Table 4), and direct determinations of vapor pressures (Table 4). We note first of all that enthalpy data at 298.15 K (data set 7 in Table

Table 4. Sources of Thermodynamic Data for Pure Aqueous $(NH_4)_2SO_4$[a]

m/(mol kg^{-1})	t/°C	type[b]	N	ref
0.129−5.83	25	iso	1	Wishaw and Stokes (1954)
0.583−5.714	25	iso	2	Filippov *et al.* (1986)
0.132−6.041	25, 50	iso	3	this study
0−3.096	31.97−100.09	vp[c]	4	Tammann (1885)
0−8.809	91.16−108.09	bp	5	Buchanan (1899)
0.025−7.33	100.04−106.26	bp[d]	6	Johnston (1906)
0−5.55	25	$\Delta_f H°$ [e]	7	Wagman *et al.* (1982)
0.1388	18−88.2	$\Delta_{sol}H$[e,f]	8	Beggerow (1976)
24.6−40 wt %	23−92	C_p[g]	9	Schneider *et al.* (1982)
0.28−3.70	19−21	C_p	10	D'ans *et al.* (1977)

[a] See also Table 2 of Clegg *et al.* (1995) for sources of data for saturation with respect to solid phases (ice and $(NH_4)_2SO_{4(cr)}$), and vapor pressures of saturated and supersaturated solutions. [b] Data types are as follows: iso, isopiestic measurement; vp, direct vapor pressure measurement; bp, boiling point; $\Delta_f H°$, tabulated heat of formation; $\Delta_{sol}H$, heat of solution; C_p, heat capacity or specific heat. [c] As tabulated by Timmermans (1960), though note that concentrations are in grams of solute per 100 grams of H_2O and not weight percent as listed. [d] Data tabulated for normalities were not used, but some results given in Johnston's Figure 3 were included. [e] Notes concerning the original sources of data are given in Table 2 of Clegg *et al.* (1995). [f] These values were used to obtain an estimate of $^{\phi}C_p$ at 298.15 K. [g] Data presented graphically. Values at 25 °C were estimated for three molalities from Schneider *et al.*'s Figure 2.

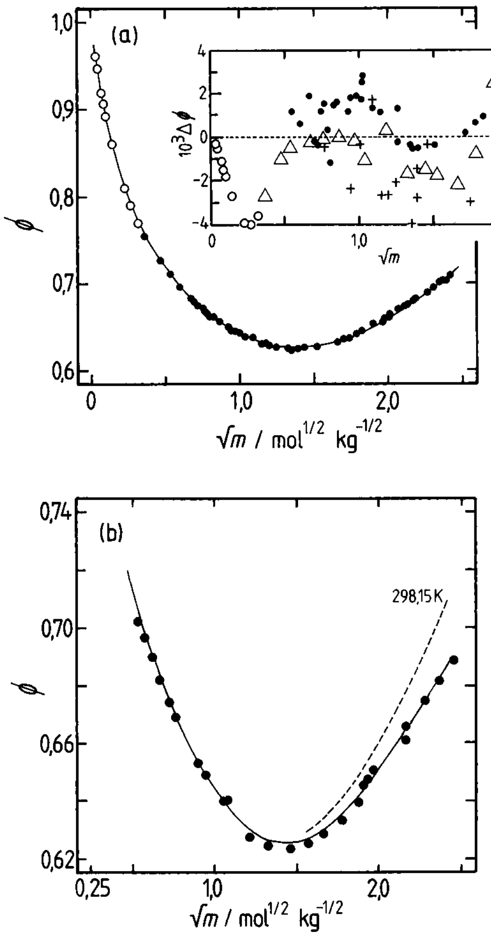

Figure 1. Measured and fitted osmotic coefficients (ϕ) of aqueous $(NH_4)_2SO_4$. (a) Results at 298.15 K, with deviations of the fitted model from measured values (inset). Symbols (main plot): (○) osmotic coefficients of aqueous K_2SO_4 (Goldberg, 1981), (•) data for $(NH_4)_2SO_{4(aq)}$ from sources listed in Table 4. Symbols (inset): (○) as in main plot, (△) source 1, (+) source 2, (•) source 3. (b) Results at 323.15 K. All data are from this study (source 3).

4) are evaluations from very early measurements and provide only 10 values of $^{\phi}L$ to 5.55 mol kg^{-1}. It is clear from Figure 9 of Clegg *et al.* (1995) that these are of limited accuracy. The same is true of the apparent molar heat capacities, with only nine values (data sets 8−10 in Table 4) in addition to the infinite dilution value of −133.1 J mol^{-1} K^{-1} (Wagman *et al.*, 1982). Measurements that yield ϕ directly at temperatures other than 298.15 K are therefore important for constraining the model.

Clegg *et al.* (1995) have shown that, whereas measurements of the freezing point depression of aqueous $(NH_4)_2SO_4$ are quite scattered, their model treatment of the system agrees satisfactorily with the data. We therefore adopt values of osmotic coefficients at the freezing temperature calculated using that model. Osmotic coefficients at the boiling points of the solutions were calculated from the measurements of Johnston (1906) for molalities below 1 mol kg^{-1} (with the adjustments described by Clegg *et al.* (1995)) and from those of Buchanan (1899). In both cases vapor pressures of pure water from the equation of state of Hill (1990) were used, with fugacity corrections carried out as described by Rard and Platford (1991). Values of $p°(H_2O)$ were obtained by extrapolation for temperatures above 373.15 K.

Data were first checked for overall consistency by fitting values of $^{\phi}L$ and $^{\phi}C_p$ at 298.15 K using eqs 4 and 5, and osmotic coefficients at temperatures other than 298.15 K based on the assumption that the partial molar heat capacity of water in the solutions had a simple linear variation with temperature. (As was the case in our previous work (Clegg *et al.*, 1995), the vapor pressure measurements of Tammann (1885) were not fitted but were retained for later comparisons.) Our measurements at 323.15 K and the osmotic coefficients derived from both the freezing temperatures and boiling points were all represented satisfactorily. It was concluded from this that the data were consistent.

Initial attempts to fit the Pitzer model to the full data set were only partially successful, mainly due to the paucity of data at the temperature extremes. Consequently, some additional values of ϕ were generated over a range of temperatures using the result of the consistency test. The final fit is shown in Figures 1b to 5, and the model parameters are listed in Table 5. The osmotic coefficients at 323.15 K are represented well (Figure 1b), as are those derived from the boiling point elevations (Figure 4) and freezing temperatures (Figure 5). The fitted values of the enthalpies and heat capacities, shown in Figures 2 and 3, are similar to those obtained by Clegg *et al.* (1995). Water activities for aqueous $(NH_4)_2SO_4$ at four molalities, and for temperatures from 31.97 to 100.09 °C, are compared in Figure 6 with values derived from the vapor pressure measurements of Tammann (1885). The observed trend in water activity with temperature is predicted adequately by the model, although calculated values tend to be slightly greater than those measured close to 100 °C.

Thus far it has been assumed that NH_4^+ does not dissociate in solution. Test calculations were therefore carried out to determine the effect of including the equilibria $NH_4^+ \rightleftarrows H^+ + NH_3$ and $HSO_4^- \rightleftarrows H^+ + SO_4^{2-}$ in the model and using parameters and equilibrium constants given by Clegg *et al.* (1994) and Clegg and Whitfield (1995). It was found that the maximum difference in the calculated value of the osmotic coefficient was 0.000 35 at 0.001 mol kg^{-1} and 298.15 K. At molalities greater than 0.01 mol kg^{-1} differences were <0.000 05 in ϕ at both 298.15 K and 323.15 K. For temperatures around 373.15 K osmotic coefficients were higher than those obtained when assuming no dissociation by <0.001 for molalities greater than 0.1 mol kg^{-1}—still substantially less than the uncertainty

Table 5. Fitted Model Parameters[a]

parameter	p(298.15 K)	$\partial p/\partial T$	$\partial^2 p/\partial T^2$	$\partial^3 p/\partial T^3$
$\beta^{(0)}_{NH_4SO_4}$	0.0374028	3.47309×10^{-4}	-5.71929×10^{-6}	0.0
$\beta^{(1)}_{NH_4SO_4}$	0.534514	4.62287×10^{-3}	-2.16307×10^{-4}	-1.62030×10^{-6}
$C^{(0)}_{NH_4SO_4}$ [b]	-2.17617×10^{-4}	-1.37077×10^{-5}	1.67896×10^{-7}	1.96550×10^{-9}
$C^{(1)}_{NH_4SO_4}$ [b]	0.164263	8.03072×10^{-3}	0.0	0.0
$\beta^{(0)}_{NH_4HSO_4}$	0.0327514			
$\beta^{(1)}_{NH_4HSO_4}$	0.468421			
$C^{(0)}_{NH_4HSO_4}$ [G]	1.153446×10^{-3}			
$C^{(1)}_{NH_4HSO_4}$ [G]	-0.3487185			
ψ_{H,NH_4,HSO_4}	-8.646×10^{-3}			
ψ_{H,NH_4,SO_4}	-0.02245			
ψ_{HSO_4,SO_4,NH_4}	-8.423×10^{-3}			

[a] This table lists values of the parameters at 298.15 K and first, second, and third differentials with respect to temperature (also at 298.15 K). The corresponding equation for any parameter p at temperature T (K) is $p = p(298.15\text{ K}) + (T - T_r)(\partial p/\partial T - T_r\partial^2 p/\partial T^2 - (1/2)TT_r\partial^3 p/\partial T^3) + (1/2)(T^2 - T_r^2)\partial^2 p/\partial T^2 + (1/6)(T^3 - T_r^3)\partial^3 p/\partial T^3$, where T_r is the reference temperature of 298.15 K. For the acid sulfate mixtures the parameter θ_{H,NH_4} has a value of -0.019 at 298.15 K. Other parameters, apart from those given here, are set to zero. [b] Parameters C above are related to the commonly-used C^ϕ by $C^\phi = 2|z_M z_X|^{1/2}C$.

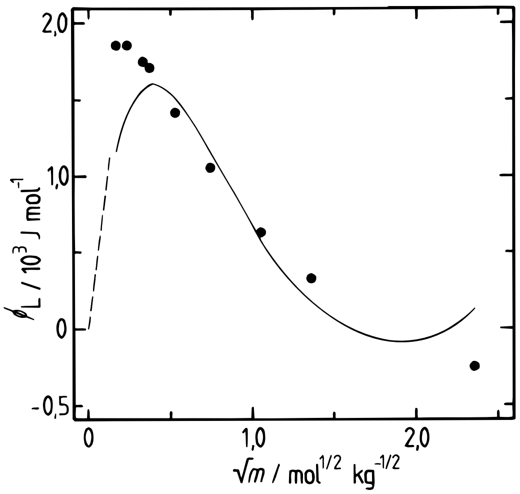

Figure 2. Enthalpies of dilution ($^\phi L$/(J mol^{-1})) of aqueous $(NH_4)_2SO_4$ at 298.15 K: symbols, data from source 7 in Table 4; solid line, fitted model; dashed line, limiting slope (equivalent to the first term in eq 4).

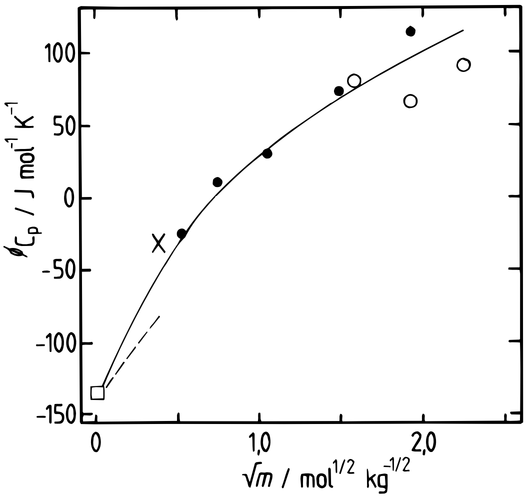

Figure 3. Apparent molar heat capacities ($^\phi C_p$/(J mol^{-1} K^{-1})) of aqueous $(NH_4)_2SO_4$ at 298.15 K. Symbols: (□) $^\phi C_p°$ from Wagman *et al.* (1982), (×) source 8, (○) source 9, (•) source 10 in Table 4. Lines: (solid) fitted model, (dashed) limiting slope (equivalent to the second term in eq 5).

in the measurements. It was concluded that neglecting NH_4^+ dissociation does not significantly affect the results obtained above.

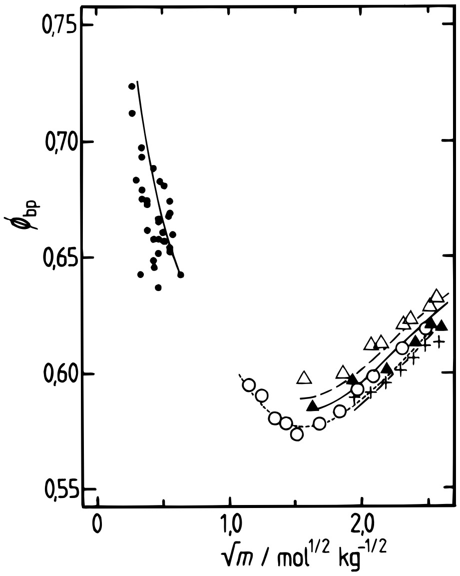

Figure 4. Osmotic coefficients of aqueous $(NH_4)_2SO_4$ (ϕ_{bp}) at the boiling points of the solutions. Symbols: (— • —) source 6 (100.0 °C), (--△--) source 5 (91.3 and 91.16 °C), (—▲—) source 5 (94.41 °C and 94.24 °C), (··○··) source 5 (99.4 °C), (—+—) source 5 (100.28 °C). The Celsius temperatures given in parentheses above are the boiling temperatures of pure water for each set of observations. Lines represent the fitted model.

(c) Aqueous $(NH_4)_2SO_4$–H_2SO_4 Mixtures. Sources of data for the acid sulfate mixtures considered in this study are listed in Table 6.

Properties at 298.15 K. The principal set of osmotic coefficient measurements for the mixed system, in addition to the values presented here, is that of Park *et al.* (1989). Clegg and Brimblecombe (1995b), in their study of aqueous $(NH_4)_2SO_4$–H_2SO_4 to high supersaturation at 298.15 K, used the measurements of Park *et al.* (1989) for comparison only. They are included here because the aim here is to represent the thermodynamic properties of more dilute solutions to high accuracy, and the measurements of Park *et al.* are an important supplement to those presented in Table 3, covering a range of compositions intermediate to the two $(NH_4)_2SO_4$:H_2SO_4 ratios treated here. Furthermore, it was found that the Pitzer model could not be satisfactorily constrained over the full range of composition from pure aqueous $(NH_4)_2SO_4$ to pure aqueous H_2SO_4 using only the data in Table 3. This is due to the fact that osmotic and activity coefficient measurements do not

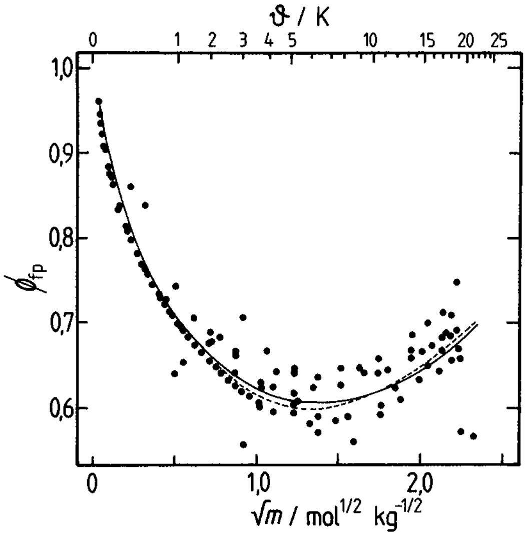

Figure 5. Calculated osmotic coefficients (ϕ_{fp}) of aqueous $(NH_4)_2SO_4$ at the freezing temperatures of the solutions, compared with available measurements and predictions using the model of Clegg *et al.* (1995): symbols, data sets 1–9 from Table 2 of Clegg *et al.* (1995); solid line, the fitted model; dashed line, predicted using the results of Clegg *et al.* (1995).

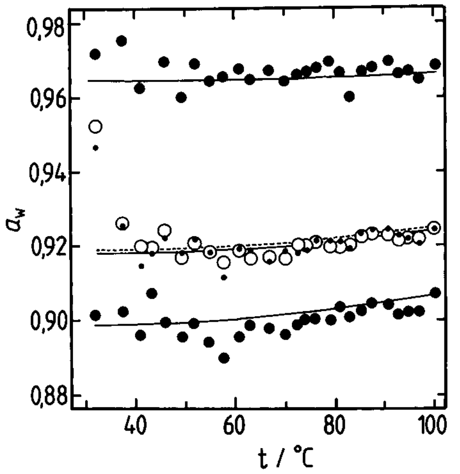

Figure 6. Water activities (a_w) of aqueous $(NH_4)_2SO_4$ for four molalities, from direct vapor pressure determinations (source 4 in Table 4). Symbols: (●) 1.054 mol kg^{-1} (uppermost portion of the graph), (○) 2.489 mol kg^{-1}, (•) 2.513 mol kg^{-1}, (●) 3.096 mol kg^{-1} (lower portion of graph). Lines: predicted values (in center portion of the plot the dashed line is for 2.489 mol kg^{-1}, and the solid line for 2.513 mol kg^{-1}).

directly constrain the degree of dissociation of HSO_4^- calculated by the model.

The measurements of Park *et al.* (1989) are presented as equilibrium molalities of a series of test solutions and three isopiestic standards: aqueous $(NH_4)_2SO_4$ and duplicate samples of aqueous H_2SO_4. The equilibration of the standards was tested by comparing their water activities (a_w) using the model of Clegg *et al.* (1994) for aqueous H_2SO_4 and parameters given in Table 5 for aqueous $(NH_4)_2SO_4$. The two aqueous H_2SO_4 standards agreed with one another to within -1×10^{-4} to $+2 \times 10^{-4}$ in a_w, while the $(NH_4)_2SO_4$ standard was consistent with the others to within -3×10^{-4} to $+4 \times 10^{-4}$ apart from two larger deviations of about 7×10^{-4} and 15×10^{-4} for the 2.481 mol kg^{-1} and 4.767 mol kg^{-1} solutions, respectively. Stoichiometric osmotic coefficients of the test solutions were calculated using the mean molalities of the two aqueous H_2SO_4 standards (except for the lowest molality where the 0.251 mol kg^{-1} standard was assumed to be more nearly correct), and were then compared with other available data to test consistency. First, although the measurements of Park *et al.* (1989) are of lower precision than those listed in Table 3, there was generally satisfactory agreement except for the two lowest sets of molalities. In these cases osmotic coefficients derived from the Park *et al.* data appeared consistently high (by about 0.0075) compared to other measurements and, later, to fits using the model. The determinations of Park *et al.* (1989) for a_w equal to 0.992 and 0.983 (their Table 1) were therefore rejected, and are not further considered. Second, the measurements of Park *et al.* for higher molalities agreed with the data of Tang and Munkelwitz (1977) for aqueous NH_4HSO_4 and for compositions corresponding to letovicite (Tang *et al.*, 1978; Tang and Munkelwitz, 1994; Tang, unpublished data). We have not included these data in the fit of the present model because they were obtained from determinations of droplet size as a function of relative humidity, and from electrodynamic balance experiments. Both of these techniques are inherently less precise than isopiestic equilibria, and consequently the data are quite scattered.

Table 6. Sources of Thermodynamic Data for Aqueous $(NH_4)_2SO_4$–H_2SO_4 Mixtures[a]

m^b/(mol kg^{-1})	comp	t/°C	type^c	N	ref
0.145–7.472	mix	25, 50	iso	11	this study
0.234–6.845	mix	25^d	iso	12	Park *et al.* (1989)
0.010–2.10	*e*	25	emf	13	Crockford and Simmons (1934)
6.380–7.274^f	mix	0–25	sol	14	Silcock (1979)
0.139–2.775^g	NH_4HSO_4	18	$\Delta_{dil}H$	15	Beggerow (1976)
0.209–10.13	NH_4HSO_4	0–50	α	16	Young *et al.* (1959)
0.655–8.610	NH_4HSO_4	25, 50	α^h	17	Dawson *et al.* (1986)
3.382–18.21	mix	20	α	18	Balej *et al.* (1984)

[a] See also Tables 2 and 3 of Clegg and Brimblecombe (1995b) for other sources of data, in particular electrodynamic balance measurements of vapor pressures of concentrated (including supersaturated) solutions. Since that paper was prepared, Tang and Munkelwitz have published much of their water activity data (Tang and Munkelwitz, 1994). Degree of dissociation data of Irish and Chen (1970) and Kruus *et al.* (1985) were rejected by Clegg and Brimblecombe (1995b) and are not considered here. [b] Molality of the listed species, or total molality ($m((NH_4)_2SO_4) + m(H_2SO_4)$) for mixtures. [c] Data types are as follows: iso, isopiestic measurement; emf, electromotive force (leading to the mean activity coefficient of sulfuric acid); sol, solubility of $(NH_4)_2SO_4$ in aqueous H_2SO_4; $\Delta_{dil}H$, heat of dilution; α, degree of dissociation of the HSO_4^- ion. [d] Given by Park *et al.* (1989) as 298 K, and assumed to be 25 °C exactly. [e] 0.01 mol kg^{-1} H_2SO_4 and 0.10 mol kg^{-1} H_2SO_4 in 0–2.0 mol kg^{-1} $(NH_4)_2SO_4$. [f] For total molalities less than 7.5 mol kg^{-1} (the limit of the model fit) and excluding a few points rejected as being in error. [g] Range of initial molalities before dilution. [h] Measured at 10 MPa of total pressure.

Crockford and Simmons (1934) have measured emfs of the cell $Pt(H_2)|H_2SO_{4(aq)}, (NH_4)_2SO_{4(aq)}|Hg_2SO_4, Hg(Pt)$ at 298.15 K, which yield stoichiometric activity coefficients of H_2SO_4 ($\gamma_\pm$) according to the equation

$$E = E° - (RT/2F)\ln([m(H^+_T)]^2 m(SO_4^{2-}{}_T)\gamma_\pm^3) \quad (14)$$

where E (V) is the emf of the cell, $E°$ is the standard potential at temperature T (K), and F (96 484.6 C mol^{-1}) is Faraday's constant. Values of $\gamma_\pm$ were derived from the measured emfs using eq 14, after first calculating $E°$ (0.612 08$_5$ V) from the emfs of two molalities of pure aqueous H_2SO_4 (0.01 mol kg^{-1} and 0.1 mol kg^{-1}) together with $\gamma_\pm$ from Table 8 of Clegg *et al.* (1994). The two individual values of $E°$ agreed to within 7 μV, an excellent result, with a difference (bias potential) from the value of $E°$ derived by Clegg *et al.* (1994) from the data of other researchers of −0.27 mV. While there are no other

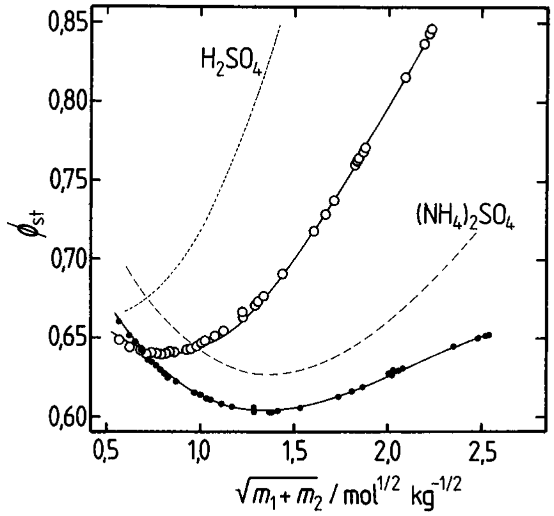

Figure 7. Stoichiometric osmotic coefficients (ϕ_{st}) of aqueous $(NH_4)_2SO_4-H_2SO_4$ mixtures at 298.15 K, plotted against the square root of total molality. Symbols: (•) 2:1 $(NH_4)_2SO_4$:H_2SO_4, (○) 1:2 $(NH_4)_2SO_4$:H_2SO_4. All data are from Table 3, with values in parentheses omitted from the plot. Lines: (solid) fitted model, (dashed, dotted) values for pure aqueous $(NH_4)_2SO_4$ and H_2SO_4, respectively.

measurements with which the results of Crockford and Simmons can be compared, the two determinations for pure aqueous H_2SO_4 suggest that their work is accurate.

Solubility measurements (saturation of the mixtures with respect to $(NH_4)_2SO_{4(cr)}$) are extensive, but only of minor use as thermodynamic constraints on the modeled properties due to the upper concentration limit of the fit being set at 7.5 mol kg^{-1}. Nevertheless, it was possible to include a few of the data compiled by Silcock (1979). The quantity fitted by the model is the activity product of the NH_4^+ and SO_4^{2-} ions in the saturated solution $[(m(NH_4^+))^2 m(SO_4^{2-})\gamma_{NH_4}{}^2\gamma_{SO_4}]$. The value of this quantity (1.008 at 298.15 K) was calculated from the known solubility of $(NH_4)_2SO_4$ in pure aqueous solution (Broul *et al.*, 1981) and the Pitzer model using parameters listed in Table 5.

Measured degrees of dissociation of HSO_4^- can also be used to constrain the model. Three sources of available measurements for aqueous NH_4HSO_4 and one for mixtures of other compositions are given in Table 6. The measurements of Young *et al.* (1959) and Dawson *et al.* (1986) were used by Clegg and Brimblecombe (1995b) in their treatment of aqueous $(NH_4)_2SO_4-H_2SO_4$ at 298.15 K. However, in this work using the Pitzer molality-based model it was found that predicted values of the degree of dissociation were consistently lower than measured values (see section 4), even when the data were used partially to constrain the model. The reason for this is unclear, but is presumably related to differences between the models. For example, the two sets of equations represent accurately both the osmotic coefficients and degrees of dissociation of HSO_4^- in pure aqueous H_2SO_4 at 298.15 K (Clegg *et al.*, 1994; Clegg and Brimblecombe, 1995a). However, osmotic coefficients of aqueous NH_4HSO_4 calculated by the present model, which agree closely with the osmotic coefficient measurements of Park *et al.* (1989) for mixtures close to this composition, differ from those obtained by Clegg and Brimblecombe (1995b) by up to 0.013 in ϕ_{st} (with values calculated by the present model being lower). Because our primary aim is to represent solute and solvent activities, rather than species concentrations, we have not used available degree of dissociation data to constrain the model, although some comparisons are presented in section 4.

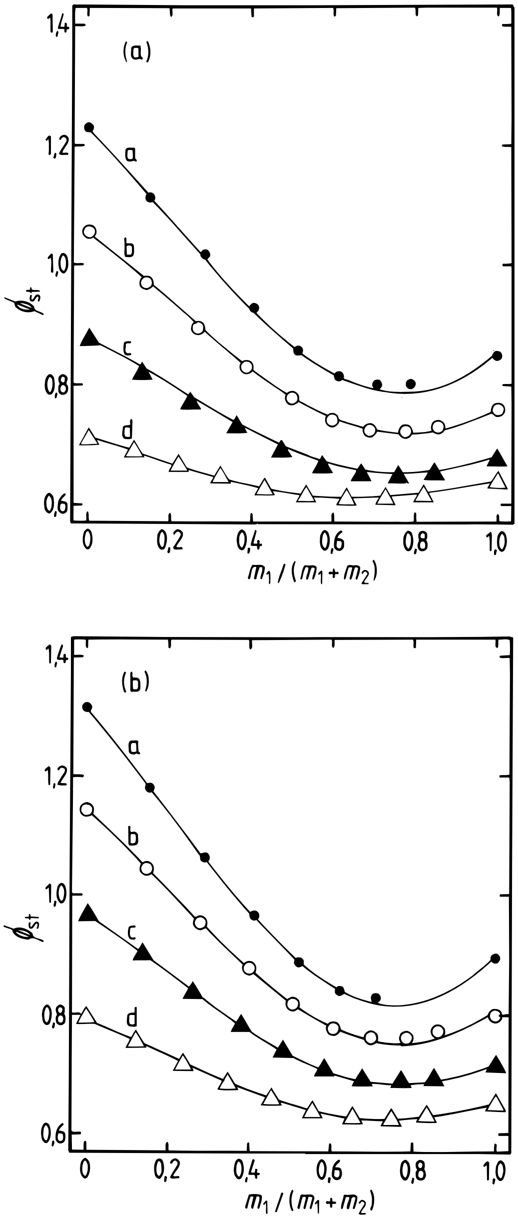

Figure 8. Stoichiometric osmotic coefficients (ϕ_{st}) of aqueous $(NH_4)_2SO_4-H_2SO_4$ mixtures at 298.15 K, plotted against the molality fraction of $(NH_4)_2SO_4$ in the mixture. All data are from Park *et al.* (1989) (source 12 in Table 6). Each symbol represents measurements at the following fixed water activities: (a) (●) 0.812, (○) 0.868, (▲) 0.920, (△) 0.965; (b) (●) 0.785, (○) 0.841, (▲) 0.895, (△) 0.943. Lines show the fitted model. For clarity, each set of measurements is offset vertically by the following amounts: (a) a, +0.15, b, +0.10, c, +0.05, d, 0.0; (b) a, +0.175, b, +0.125, c, +0.075, d, +0.025.

Osmotic coefficients, emfs, and $(NH_4)_2SO_4$ solubilities at 298.15 K were fitted using the model, with unknown parameters $\beta^{(0)}$, $\beta^{(1)}$, $C^{(0)}$, and $C^{(1)}$ for $NH_4^+-HSO_4^-$ interactions, and also ψ_{H,NH_4,HSO_4}, ψ_{H,NH_4,SO_4}, and ψ_{HSO_4,SO_4,NH_4}. The parameter θ_{H,NH_4} was fixed to the value of -0.019 given in Table 16 of Pitzer (1991). Osmotic coefficients listed in Table 3 were given a weight of 1.0 and the measurements of Park *et al.* (1989) a weight of 0.05, resulting in contributions to the total sum of squared deviations of 49% and 31%, respectively. The emfs of Crockford and Simmons (1934) were assigned a weight of 25, and contributed 17.5% to the sum of squares. There were only two measured salt solubilities within the fitted molality range of 0−7.5 mol kg^{-1}, and these points (with a weight of 1.6×10^{-3}) yielded a contribution of only 2.25% to the sum of squared

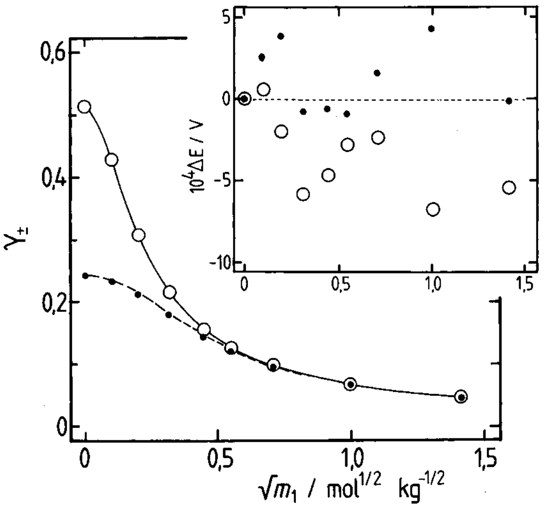

Figure 9. Stoichiometric activity coefficients ($\gamma_\pm$) of H_2SO_4 in aqueous $(NH_4)_2SO_4-H_2SO_4$ mixtures at 298.15 K, plotted against the square root of $(NH_4)_2SO_4$ molality ($m_1^{1/2}$). Measurements are from Crockford and Simmons (1934) (source 13 in Table 6). Symbols: (○) 0.01 $m(H_2SO_4)$, and (●) 0.1 $m(H_2SO_4)$ in the mixture. Lines represent the fitted model. Inset: deviations (observed − fitted) in emf (ΔE).

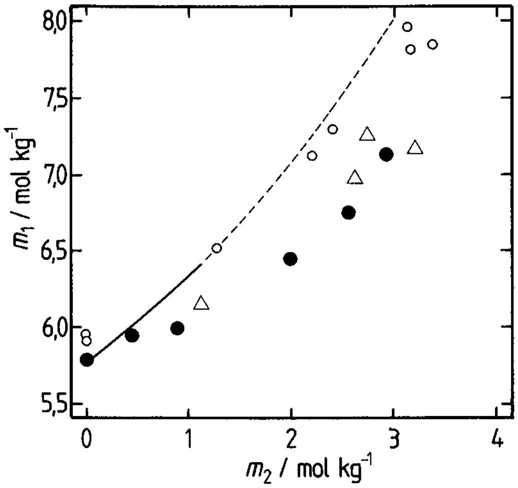

Figure 10. Solubilities of $(NH_4)_2SO_4$ (m_1) in aqueous H_2SO_4 (m_2). Data are from Silcock (1979) (source 14 in Table 6). Symbols: (●) 298.15 K, (○) 303.15 K, (△) 293.15 K. Lines: (solid) fitted solubilities at 298.15 K, (dashed) predicted solubilities at 298.15 K beyond the maximum molality of the fit (7.5 mol kg^{-1}).

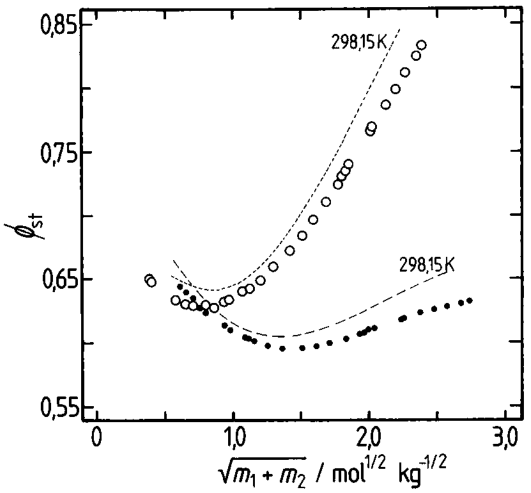

Figure 11. Stoichiometric osmotic coefficients (ϕ_{st}) of aqueous $(NH_4)_2SO_4-H_2SO_4$ mixtures at 323.15 K, plotted against the square root of total molality ($(m_1 + m_2)^{1/2}$). All data are from Table 3, with values in parentheses omitted from the plot. Symbols: (•) 2:1 $(NH_4)_2SO_4$:H_2SO_4, (○) 1:2 $(NH_4)_2SO_4$:H_2SO_4. Lines: (dashed, dotted) values for the same mixtures at 298.15 K, included for comparison.

deviations. The fitted parameters are listed in Table 5 and the results shown in Figures 7 to 10.

It is clear from Figures 7 and 8 that osmotic coefficients of mixtures containing more than about 50% $(NH_4)_2SO_4$ are lower than those for either pure aqueous $(NH_4)_2SO_4$ or pure aqueous H_2SO_4. Thus, for a given water activity in this region of composition, the mixed solution will have a higher total concentration of dissolved solute than either of the two end-member solutions. The results of Crockford and Simmons (1934) for the mean activity coefficient of H_2SO_4 are reproduced well by the model (Figure 9). We note that these measured values are consistently lower than those estimated by Park *et al.* (1989) using the McKay−Perring method, by up to about 0.016 at 2 mol kg^{-1} $(NH_4)_2SO_4$. Solubilities of $(NH_4)_2SO_4$ in aqueous H_2SO_4 from 293.15 K to 303.15 K are shown in Figure 10. The data are scattered, and values for 298.15 K do not fall between those for 293.15 K and 303.15 K, suggesting that they may be systematically in error by a small amount. Fitted solubilities show a clear trend toward higher values than measured solubilities (i.e., the calculated activity products of $(NH_4)_2SO_4$ are too low). However, total molalities in the mixture mostly exceed 6 mol kg^{-1}—the limits of the model fits for both pure components. Consequently, increases in the weighting in order to better represent the solubility measurements lead to a poorer fit to other data at lower concentrations. The model of Clegg and Brimblecombe (1995b) is to be preferred for calculations involving solubilities in aqueous $(NH_4)_2SO_4-H_2SO_4$ mixtures, as it is valid to very high concentration (approximately 40 mol kg^{-1} H_2SO_4) and treats saturation with respect to letovicite and NH_4HSO_4 in addition to $(NH_4)_2SO_4$.

Properties at Temperatures Other Than 298.15 K. The only activity data for the mixtures for temperatures other than 298.15 K appear to be those determined in this study for two $(NH_4)_2SO_4$:H_2SO_4 ratios at 323.15 K. These are compared in Figure 11 with 298.15 K values.

Heats of dilution ($\Delta_{dil}H$) for molalities m_a to m_b are equivalent to the difference in apparent molar enthalpies ${}^{\phi}L_b - {}^{\phi}L_a$. Six heats of dilution of aqueous NH_4HSO_4 at 291.15 K from 5.55 mol kg^{-1} to (2.77 to 0.0694) mol kg^{-1} are given in the *Landolt-Börnstein Tables* (Beggerow, 1976). These were converted to values for a series of sequential dilutions.

Extensions of the model to include the osmotic coefficients at 323.15 K (Table 3) and heats of dilution at 291.15 K showed that the data could be successfully represented. However, calculations of ϕ_{st} at 323.15 K for intermediate compositions between those measured by us (e.g., NH_4HSO_4) showed that the values were sensitive to the model parameters included. In addition, predicted thermodynamic properties between 323.15 K and 298.15 K, and extrapolations to lower temperatures, were influenced strongly by the heats of dilution—in particular the value for 5.55 mol kg^{-1} to 2.77 mol kg^{-1}. Where the model accurately fitted this thermal measurement, it was found that the trend in ϕ_{st} with temperature for compositions quite close to aqueous $(NH_4)_2SO_4$ appeared inconsistent with that for the pure salt. Also, calculated partial molar heat capacities of water for NH_4HSO_4 at high molalities were far outside the range of values for aqueous H_2SO_4 and aqueous $(NH_4)_2SO_4$ at the same molality. It was concluded that there are, at present, insufficient data yielding the

Table 7. Osmotic and Activity Coefficients of Pure Aqueous $(NH_4)_2SO_4$ Calculated Using the Fitted Model

	273.15 K		298.15 K		323.15 K		348.15 K		373.15 K	
m/(mol kg^{-1})	ϕ	$\gamma_\pm$	ϕ	$\gamma_\pm$	ϕ	$\gamma_\pm$	ϕ	$\gamma_\pm$	ϕ	$\gamma_\pm$
0.001	0.9618	0.8890	0.9605	0.8852	0.9586	0.8801	0.9561	0.8736	0.9530	0.8656
0.002	0.9475	0.8495	0.9458	0.8447	0.9433	0.8380	0.9398	0.8293	0.9353	0.8184
0.005	0.9216	0.7802	0.9195	0.7740	0.9157	0.7647	0.9103	0.7522	0.9030	0.7364
0.010	0.8957	0.7138	0.8933	0.7069	0.8885	0.6956	0.8810	0.6798	0.8705	0.6593
0.020	0.8640	0.6365	0.8617	0.6293	0.8557	0.6163	0.8455	0.5969	0.8306	0.5715
0.050	0.8135	0.5224	0.8127	0.5165	0.8056	0.5021	0.7912	0.4789	0.7687	0.4474
0.10	0.7701	0.4331	0.7723	0.4296	0.7654	0.4157	0.7483	0.3912	0.7198	0.3567
0.20	0.7240	0.3471	0.7309	0.3469	0.7263	0.3352	0.7084	0.3112	0.6758	0.2768
0.30	0.6966	0.3003	0.7069	0.3023	0.7045	0.2922	0.6875	0.2697	0.6545	0.2365
0.40	0.6774	0.2692	0.6901	0.2726	0.6895	0.2638	0.6736	0.2426	0.6412	0.2109
0.50	0.6630	0.2465	0.6774	0.2508	0.6780	0.2430	0.6632	0.2229	0.6316	0.1926
0.60	0.6519	0.2290	0.6673	0.2338	0.6688	0.2269	0.6548	0.2078	0.6240	0.1786
0.70	0.6430	0.2150	0.6591	0.2202	0.6611	0.2138	0.6477	0.1955	0.6176	0.1674
0.80	0.6359	0.2035	0.6523	0.2089	0.6547	0.2029	0.6416	0.1853	0.6120	0.1581
0.90	0.6302	0.1937	0.6467	0.1993	0.6492	0.1937	0.6363	0.1766	0.6071	0.1503
1.0	0.6255	0.1854	0.6420	0.1911	0.6445	0.1858	0.6317	0.1692	0.6027	0.1435
1.2	0.6189	0.1719	0.6350	0.1776	0.6371	0.1727	0.6241	0.1569	0.5953	0.1324
1.4	0.6148	0.1614	0.6305	0.1671	0.6319	0.1624	0.6185	0.1471	0.5895	0.1236
1.6	0.6127	0.1530	0.6278	0.1586	0.6285	0.1540	0.6144	0.1392	0.5851	0.1165
1.8	0.6121	0.1461	0.6266	0.1516	0.6265	0.1471	0.6117	0.1327	0.5819	0.1105
2.0	0.6127	0.1403	0.6266	0.1458	0.6257	0.1414	0.6101	0.1271	0.5798	0.1055
2.2	0.6143	0.1354	0.6275	0.1408	0.6259	0.1364	0.6095	0.1224	0.5787	0.1013
2.4	0.6167	0.1313	0.6293	0.1366	0.6269	0.1322	0.6097	0.1184	0.5783	0.0976
2.6	0.6198	0.1277	0.6317	0.1329	0.6285	0.1285	0.6106	0.1148	0.5787	0.0944
2.8	0.6234	0.1246	0.6347	0.1297	0.6307	0.1253	0.6120	0.1117	0.5796	0.0916
3.0	0.6276	0.1220	0.6382	0.1269	0.6333	0.1225	0.6139	0.1090	0.5810	0.0891
3.2	0.6322	0.1196	0.6421	0.1245	0.6363	0.1200	0.6161	0.1065	0.5829	0.0869
3.4	0.6371	0.1176	0.6462	0.1224	0.6396	0.1178	0.6187	0.1044	0.5850	0.0849
3.6	0.6424	0.1158	0.6507	0.1204	0.6431	0.1158	0.6214	0.1024	0.5874	0.0831
3.8	0.6481	0.1143	0.6553	0.1188	0.6468	0.1140	0.6243	0.1006	0.5900	0.0815
4.0	0.6540	0.1129	0.6602	0.1173	0.6506	0.1124	0.6273	0.0990	0.5927	0.0800
4.2	0.6601	0.1117	0.6652	0.1159	0.6545	0.1109	0.6303	0.0975	0.5956	0.0787
4.4	0.6665	0.1107	0.6704	0.1148	0.6584	0.1096	0.6334	0.0962	0.5985	0.0774
4.6	0.6731	0.1098	0.6756	0.1137	0.6624	0.1084	0.6365	0.0949	0.6014	0.0763
4.8	0.6800	0.1090	0.6809	0.1127	0.6663	0.1073	0.6396	0.0937	0.6043	0.0752
5.0	0.6870	0.1084	0.6863	0.1119	0.6703	0.1062	0.6426	0.0927	0.6071	0.0742
5.2	0.6942	0.1079	0.6918	0.1111	0.6742	0.1053	0.6455	0.0916	0.6099	0.0733
5.4	0.7015	0.1074	0.6972	0.1105	0.6780	0.1044	0.6483	0.0907	0.6127	0.0724
5.6	0.7091	0.1071	0.7027	0.1099	0.6818	0.1036	0.6510	0.0898	0.6153	0.0716
5.8	0.7168	0.1068	0.7082	0.1094	0.6854	0.1028	0.6535	0.0889	0.6178	0.0708
6.0	0.7246	0.1066	0.7138	0.1089	0.6890	0.1021	0.6559	0.0881	0.6202	0.0701

variation of solution properties with temperature (activity or thermal measurements) adequately to constrain the model, even though the thermodynamic properties of aqueous solutions of the two pure components are known. Our tests have shown that in order to constrain the model it would be necessary to make assumptions concerning the reliability of the thermal measurements, and to introduce estimates of the osmotic coefficients at 323.15 K for compositions intermediate to those measured. We therefore have not extended the model of mixed solutions beyond 298.15 K. It is worth noting that such an extension may be easier when treating a larger range of concentration (such as that considered by Clegg and Brimblecombe (1995b) in their study of the acid sulfate mixture at 298.15 K), because measured solubilities with respect to $(NH_4)_2SO_4$, letovicite, and even NH_4HSO_4 can then be used as additional thermodynamic constraints.

4. Discussion

The model presented here enables osmotic and activity coefficients of pure aqueous $(NH_4)_2SO_4$ to be calculated from the freezing points to the boiling points of the solutions, and the properties of aqueous $(NH_4)_2SO_4-H_2SO_4$ mixtures to be calculated at 298.15 K. The measurements presented for 2:1 and 1:2 $(NH_4)_2SO_4-H_2SO_4$ mixtures at 323.15 K will in the future contribute toward the extension of the model to other temperatures. Calculated values of the osmotic and activity coefficients of pure aqueous $(NH_4)_2SO_4$ from 273.15 K to 323.15 K are listed in Table 7, and osmotic coefficients of aqueous $(NH_4)_2SO_4-H_2SO_4$ mixtures at 298.15 K are given in Table 8. The low precision and small number of data used to constrain the model at the temperature extremes should be borne in mind when using values from Table 7. Properties of pure aqueous $(NH_4)_2SO_4$ calculated by the model are likely to be most accurate between 298.15 K and 323.15 K.

We have compared the fitted model with that of Clegg and Brimblecombe (1995b), who used the mole-fraction-based equations of Pitzer, Simonson, and Clegg (Clegg *et al.*, 1992) to represent osmotic and activity coefficients in solutions to very high (supersaturated) concentrations at 298.15 K. Much of their work was based upon the water vapor pressure determinations of Spann (1984). The present work is likely to be more accurate for subsaturated solutions, due to both the restricted range of concentration being considered and the new data (Tables 2 and 3) that have been used to develop the model. A comparison of ϕ_{st} for aqueous NH_4HSO_4 to 6 mol kg^{-1} yields agreement between the two models to within +0.007 to −0.014, with the largest deviation occurring at about 5.3 mol kg^{-1}. While these differences are quite small, they may be related to those in predicted values of the degree of dissociation of HSO_4^- (α) in aqueous NH_4HSO_4, as noted earlier. Values of α predicted by the two models are compared in Figure 12 with the measurements of Young *et al.* (1959), and those of Dawson *et al.* (1986) which were obtained at 10 MPa of pressure. The molalities for which the mole-fraction-based

Table 8. Osmotic Coefficients of Aqueous $(NH_4)_2SO_4$ (1)−H_2SO_4 (2) Mixtures at 298.15 K Calculated Using the Fitted Model[a]

$(m_1 + m_2)$/(mol kg^{-1})	$\phi_{st}(0.75)$	$\phi_{st}(0.50)$	$\phi_{st}(0.25)$
0.001	0.9504	0.9410	0.9320
0.002	0.9296	0.9148	0.9013
0.005	0.8926	0.8695	0.8496
0.010	0.8584	0.8295	0.8059
0.020	0.8208	0.7881	0.7629
0.050	0.7696	0.7363	0.7132
0.100	0.7317	0.7016	0.6838
0.200	0.6948	0.6712	0.6623
0.300	0.6736	0.6551	0.6537
0.400	0.6588	0.6444	0.6496
0.500	0.6476	0.6368	0.6481
0.600	0.6387	0.6312	0.6482
0.700	0.6314	0.6270	0.6495
0.800	0.6255	0.6240	0.6519
0.900	0.6206	0.6219	0.6551
1.000	0.6165	0.6205	0.6589
1.200	0.6103	0.6195	0.6683
1.400	0.6062	0.6204	0.6793
1.600	0.6035	0.6225	0.6917
1.800	0.6020	0.6255	0.7049
2.000	0.6014	0.6293	0.7188
2.200	0.6014	0.6336	0.7332
2.400	0.6020	0.6383	0.7479
2.600	0.6031	0.6432	0.7628
2.800	0.6044	0.6483	0.7777
3.000	0.6061	0.6534	0.7926
3.200	0.6079	0.6586	0.8075
3.400	0.6099	0.6638	0.8222
3.600	0.6119	0.6690	0.8367
3.800	0.6141	0.6742	0.8510
4.000	0.6163	0.6792	0.8650
4.200	0.6185	0.6842	0.8788
4.400	0.6207	0.6890	0.8922
4.600	0.6229	0.6938	0.9052
4.800	0.6250	0.6984	0.9180
5.000	0.6271	0.7029	0.9303
5.200	0.6292	0.7073	0.9422
5.400	0.6311	0.7116	0.9538
5.600	0.6329	0.7157	0.9649
5.800	0.6347	0.7197	0.9756
6.000	0.6363	0.7235	0.9858

[a] Values are listed for three fractions of NH_4^+ [$m(NH_4^+)$/($m(NH_4^+)$ + $m(H^+_T)$)] corresponding to compositions $(NH_4)_{0.5}(H)_{1.5}SO_4$ (0.25), NH_4HSO_4 (0.5), and $(NH_4)_{1.5}(H)_{0.5}SO_4$ (0.75). For osmotic and activity coefficients of pure aqueous $(NH_4)_2SO_4$ (NH_4^+ fraction 1.0) and H_2SO_4 (NH_4^+ fraction 0), see Table 7 of this paper and Table 8 of Clegg *et al.* (1994).

equations predict a higher α than does the present model correspond to those for which higher values of ϕ_{st} are also predicted. It is unclear which model is more nearly correct, although the fact that the measured values of α at low molalities, where the models are likely to be most accurate, are significantly greater than predicted values may indicate a positive bias in the measurements.

The model can be used to calculate the equilibrium partial pressure of NH_3 ($p(NH_3)$) over aqueous $(NH_4)_2SO_4$ and its mixtures with H_2SO_4. The activity of dissolved NH_3 in equilibrium with NH_4^+ and H^+ is given by

$$a(\mathrm{NH_3}) = \gamma_{\mathrm{NH_3}} m(\mathrm{NH_3}) = K_{\mathrm{NH_4}} \gamma_{\mathrm{NH_4}} m(\mathrm{NH_4}^+)/(\gamma_{\mathrm{H}} m(\mathrm{H}^+)) \tag{15}$$

where K_{NH_4} (5.682×10^{-10} mol kg^{-1} at 25 °C; Bates and Pinching, 1949) is the acid dissociation constant of NH_4^+. The Henry's law constant of NH_3, K_H' (defined for the equilibrium $NH_{3(g)} \rightleftarrows NH_{3(aq)}$), is 60.72 mol kg^{-1} atm^{-1} at 298.15 K (Clegg and Brimblecombe, 1989). The equation for the Henry's law constant can be combined with eq 15 above to yield an expression for the equilibrium partial pressure of NH_3 over aqueous solutions:

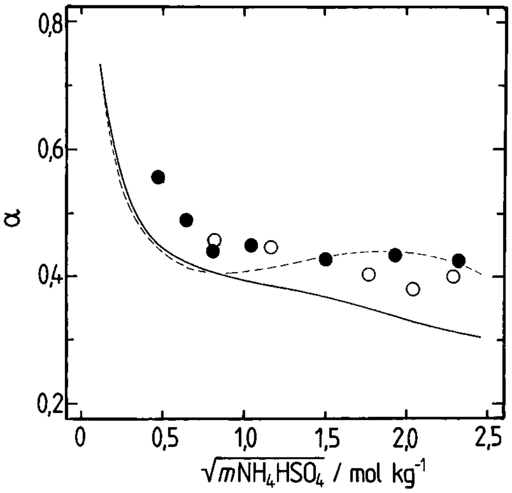

Figure 12. Degree of dissociation (α) of HSO_4^- in aqueous NH_4HSO_4 at 298.15 K. Symbols: (●) source 16 and (○) source 17 in Table 6. Lines: (solid) predicted using the present model, (dashed) calculated using the model of Clegg and Brimblecombe (1995b).

$$p(\mathrm{NH_3}) = (K_{\mathrm{NH_4}}/K_{\mathrm{H}}')\gamma_{\mathrm{NH_4}} m(\mathrm{NH_4}^+)/(\gamma_{\mathrm{H}} m(\mathrm{H}^+)) \tag{16}$$

We have compared equilibrium partial pressures of NH_3 calculated using the present model and that of Clegg and Brimblecombe (1995b) for solutions of NH_4HSO_4, and 9:1 $(NH_4)_2SO_4$−H_2SO_4, to 6 mol kg^{-1} total molality. In the first case there is agreement to within 5% (the mole fraction model yielding the lower partial pressures), and for the other mixture 19% (again with the mole-fraction-based model predicting lower values). We note that Koutrakis and Aurian-Blajeni (1993) have carried out some determinations of $p(NH)_3$ for $(NH_4)_2SO_4$−H_2SO_4 solutions at 293.15 K. However, Clegg and Brimblecombe (1995b) have pointed out that their calibration appears to be in error, and the experimental partial pressures disagree with calculated values by about an order of magnitude. Further measurements of equilibrium partial pressures of NH_3 over aqueous $(NH_4)_2SO_4$ and its mixtures with H_2SO_4 would be valuable.

Representation of the thermodynamic properties of electrolyte mixtures using models such as those of Pitzer or Pitzer, Simonson, and Clegg has significant advantages over more empirical methods in that the properties of complex mixtures can generally be predicted using parameters determined from data for binary solutions or ternary mixtures (e.g., see Harvie and Weare (1980)). Thus, the parameters determined in this study can be combined with others available in the literature to predict the properties of multicomponent acid sulfate mixtures containing the NH_4^+ ion.

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