

Isopiestic Determination of the Osmotic Coefficients of $\text{Na}_2\text{SO}_4(\text{aq})$ at 25 and 50°C, and Representation with Ion-Interaction (Pitzer) and Mole Fraction Thermodynamic Models¹

Joseph A. Rard,^{2,*} Simon L. Clegg,³ and Donald A. Palmer⁴

Received May 20, 1999; revised August 11, 1999

Isopiestic vapor-pressure measurements were made for $\text{Na}_2\text{SO}_4(\text{aq})$ from 0.11 to 3.74 mol·kg⁻¹ at 25.00°C and from 0.12 to 3.57 mol·kg⁻¹ at 50.00°C, using NaCl(aq) as the reference standard. Published isopiestic data, direct vapor pressures, emfs of reversible cells, freezing temperature depressions, boiling temperature elevations, heat capacities, and dilution enthalpies for this system have been critically assessed and recalculated in a consistent manner. Parameters for Pitzer's model and a mole fraction-based thermodynamic model were evaluated. The mole fraction-based thermodynamic model for $\text{Na}_2\text{SO}_4(\text{aq})$ is valid from the freezing temperatures of the solutions to 150.5°C. Pitzer's model represents the osmotic coefficients and emfs essentially to experimental accuracy at 25 and 50°C provided that the third virial coefficient was ionic-strength dependent.

KEY WORDS: Isopiestic measurements, sodium sulfate, osmotic coefficient, thermodynamics, Pitzer's model.

¹ Some parts of this work were presented at the 217th American Chemical Society National Meeting in Anaheim, California, March 21–25, 1999, at the Symposium to Honor Frank Millero.

² Geosciences and Environmental Technologies, Earth and Environmental Sciences Directorate, Lawrence Livermore National Laboratory, University of California, Livermore, California 94550. Email: rardl@llnl.gov.

³ School of Environmental Sciences, University of East Anglia, Norwich NR4 7TJ, U.K. Email: s.clegg@uea.ac.uk.

⁴ Chemical and Analytical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831-6110. Email: ddp@ornl.gov.

1. INTRODUCTION

The electrolyte Na_2SO_4 is present at significant concentrations in seawater and most natural brines. Alkaline sulfate lakes are known that contain high concentrations of both MgSO_4 and Na_2SO_4 . For example, the Basque Lakes of British Columbia have total sulfate concentrations of about 1.6–1.7 mol-L⁻¹ and pHs ranging up to 8.3.⁽¹⁾ Matthes⁽²⁾ cited the analysis of one natural brine from New Mexico, which contained 302.5 g-L⁻¹ (3.15 mol-L⁻¹) of sulfate and one mine water from oxidation of sulfide minerals from the Comstock Lode with 209.1 g-L⁻¹ of sulfate. Both mirabilite and thenardite, $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ and Na_2SO_4 , along with double salts such as bloedite $\text{Na}_2\text{Mg}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$, aphthitalite $\text{K}_3\text{Na}(\text{SO}_4)_2$, and burkeite $2\text{Na}_2\text{SO}_4 \cdot \text{Na}_2\text{CO}_3$, and triple salts such as hanksite $9\text{Na}_2\text{SO}_4 \cdot 2\text{Na}_2\text{CO}_3 \cdot \text{KCl}$, are present in some evaporate deposits.^(1,3,4) In addition, soluble sulfate salts affect the solubility and precipitation of $\text{SrSO}_4(\text{s})$ and $\text{BaSO}_4(\text{s})$ mineral scale from oil field brines.⁽⁵⁾ A quantitative understanding of the diagenetic processes leading to the precipitation of these sulfate salts and scale formation requires a reliable thermodynamic equation of state for $\text{Na}_2\text{SO}_4(\text{aq})$ that is valid over wide ranges of molality and temperature.

Rard and Miller⁽⁶⁾ and Goldberg⁽⁷⁾ critically assessed the available ambient temperature thermodynamic activity data for $\text{Na}_2\text{SO}_4(\text{aq})$ and gave correlating equations for the osmotic and activity coefficients at 25°C. Shortly thereafter, Rogers and Pitzer⁽⁸⁾ reported heat capacities for this system from 31.47 to 201.53°C and, in combination with selected literature data, obtained an ion-interaction (Pitzer) model valid from 25 to 200°C. In 1986, Holmes and Mesmer⁽⁹⁾ reported high-temperature isopiestic data from 110 to 225°C, and used these and a larger selection of critically assessed literature data to produce a Pitzer model valid from freezing temperatures to 225°C.⁽¹⁰⁾ In 1988, Pabalan and Pitzer⁽¹¹⁾ reported additional high temperature heat capacities for temperatures up to 299.6°C at pressures of 20 MPa and used these and other newer data to revise the parameters of their earlier model. More recently, Hovey *et al.*⁽¹²⁾ reevaluated the parameters for Pitzer's model for the temperature range 0 to 100°C, but because of errors in the temperature dependences of the ion-interaction parameters, their model yields correct results only at 25°C.

Sufficient thermodynamic data have become available for $\text{Na}_2\text{SO}_4(\text{aq})$ since 1988 to warrant a new critical examination. In addition to the isopiestic data at 25 and 50°C reported here, there are isopiestic studies of Baabor *et al.*^(13–15) at 25 and 40°C, emf studies at 10–70°C and 25°C,^(16,17) enthalpy of dilution studies at 100°C and at 40–100.2°C,^(18,19) and heat capacities covering the temperature ranges of 50 to 200°C and 60 to 220°C.^(18,20) There are

also some earlier thermodynamic data, which were not considered in the previous reviews.

The existing temperature-dependent thermodynamic models for $\text{Na}_2\text{SO}_4(\text{aq})$ ^(8,10–12) are based on the standard three parameter version of Pitzer's ion-interaction model.⁽²¹⁾ However, Archer^(22,23) found that allowing the third virial coefficient of this model to have an ionic-strength dependence, which introduces a fourth parameter, virtually eliminated the systematic deviations which were otherwise present for $\text{NaCl}(\text{aq})$ and $\text{NaBr}(\text{aq})$. Subsequently, Archer and Rard⁽²⁴⁾ applied this extension to $\text{MgSO}_4(\text{aq})$ and Clegg *et al.*⁽²⁵⁾ to the associated electrolyte $\text{H}_2\text{SO}_4(\text{aq})$ and the new models represent the available thermodynamic data essentially to within experimental accuracy. We find that including the ionic strength dependence of the third virial coefficient yields a significantly improved representation for $\text{Na}_2\text{SO}_4(\text{aq})$ at 25 and 50°C.

In this report, we present a critical analysis of the available thermodynamic data for $\text{Na}_2\text{SO}_4(\text{aq})$, recalculate them in a consistent manner, and use the more reliable results to evaluate the parameters of both an Archer-type modified Pitzer model and a similar model using mole fraction compositions. The mole fraction concentration model was able to represent these data accurately for the temperature region -0.88 to 150.50°C , which is the region where osmotic coefficients, dilution enthalpies, and heat capacities are all available. Although the modified Pitzer model was able to represent these thermodynamic data at 25 and 50°C to full experimental accuracy, there were systematic deviations between experiment and model at higher temperatures.

2. EXPERIMENTAL

The isopiestic experiments were performed at Oak Ridge National Laboratory (ORNL) using a modified version of the apparatus described by Rush and Johnson.⁽²⁶⁾ The techniques used for operating this apparatus were described by Clegg *et al.*,⁽²⁷⁾ as was a modification of the caps used to seal the isopiestic sample dishes. Rard and Platford⁽²⁸⁾ give a detailed description of the general isopiestic method with an emphasis on the experimental aspects.

In brief, the isopiestic apparatus at ORNL is constructed from a Lucite desiccator and contains a gold-plated copper heat-transfer block with recesses machined into it to hold a maximum of 12 isopiestic sample dishes (cups). The 12 platinum dishes have individually fitted covers, which are used to cap them at the end of an experiment while the apparatus is still inside the constant temperature bath, thus avoiding molality changes due to solvent loss or gain from the samples after the apparatus is removed from this bath and opened to remove the dishes for weighing. This feature becomes more important at the higher temperature of 50°C where, in the absence of internal

capping, the amounts of solvent loss and thus the molality errors from uncapped dishes are greater because of the higher solvent vapor pressures.

Stock solutions were prepared from samples of Baker Ultrex Ultrapure Reagent or Alfa Ultrapure NaCl(cr), or from Aldrich Gold Label or Alfa Ultrapure Reagent $\text{Na}_2\text{SO}_4 \cdot n\text{H}_2\text{O}(\text{cr})$, and purified water. Most of these NaCl(cr) samples were dried either under vacuum at 100 or 115°C or in air at 175°C, prior to being used for solution preparation, whereas only three of the $\text{Na}_2\text{SO}_4 \cdot n\text{H}_2\text{O}(\text{cr})$ samples were dried before use. The water for solution preparations was purified first by distillation, then using a four-stage ion-exchange system, and finally by purging with helium to remove dissolved air. Based on dehydration experiments reported by Rard,⁽²⁹⁾ NaCl(s) dried in air around 175°C can contain about 0.15 mass-% residual water. However, samples dried under vacuum presumably will retain significantly less water than those dried in air. The samples of $\text{Na}_2\text{SO}_4 \cdot n\text{H}_2\text{O}(\text{cr})$ were not analyzed for their water content nor were they usually dried. Assumed molar masses are 58.4428 g·mol⁻¹ for NaCl, 142.044 g·mol⁻¹ for Na_2SO_4 , and 18.0153 g·mol⁻¹ for H₂O. All apparent masses were converted to masses using buoyancy corrections.

Molalities of most of the NaCl(aq) and $\text{Na}_2\text{SO}_4(\text{aq})$ stock solutions were determined by passing a known mass of solution through a cation-exchange column, which replaced the Na⁺ originally present with an equivalent amount of H⁺, followed by potentiometric pH mass titration of the eluted H⁺ with standardized NaOH(aq). The molalities of these NaOH(aq) solutions were determined by mass titration against known masses of primary standard $\text{KHC}_6\text{H}_4(\text{COO})_2$ (potassium hydrogen phthalate). In addition, the molality of one $\text{Na}_2\text{SO}_4(\text{aq})$ stock solution was determined gravimetrically by precipitation of the sulfate as BaSO₄(s). Stock solution molality determinations were done in duplicate and were reproducible to ≤0.1%. However, since the molalities of most of the $\text{Na}_2\text{SO}_4(\text{aq})$ and the reference standard NaCl(aq) stock solutions were determined in an identical manner, any systematic errors in their determinations will partially cancel when osmotic coefficients are calculated from the isopiestic molality ratios.

A total of nine NaCl(aq) stock solutions and seven $\text{Na}_2\text{SO}_4(\text{aq})$ stock solutions were used for the isopiestic measurements. Three of these $\text{Na}_2\text{SO}_4(\text{aq})$ solutions were prepared by mass from dried $\text{Na}_2\text{SO}_4(\text{s})$ and purified water, and the calculated molalities and those from cation exchange analyses agree to 0.02 to 0.22%. For six of the eight NaCl(aq) or $\text{Na}_2\text{SO}_4(\text{aq})$ stock solutions for which comparisons are possible, the molalities calculated from the masses of water and salt agree to ≤0.11% with the molalities obtained by direct analysis. Table I contains a summary of the stock solution molalities obtained by molality analysis along with those calculated from the masses of reagent and water. Isopiestic results from the different series of experiments, which involved many different stock solutions prepared from

Table I. Molalities of NaCl(aq) and Na₂SO₄(aq) Stock Solutions

Series	<i>m</i> (NaCl) ^a	<i>m</i> (NaCl) ^b	Drying (°C)	<i>m</i> (Na ₂ SO ₄)	<i>m</i> (Na ₂ SO ₄) ^b	Drying (°C)
1,2,3	0.9987	0.9998	not dried	0.8575 ^a	—	—
4	5.5073	—	—	0.8575 ^{a,c}	—	—
5	1.0030 ^d	1.0004	100 (vacuo)	0.8590 ^a	—	—
— ^h	0.1958	0.1954	100 (vacuo)	0.2011 ^a	0.2013	100 (vacuo)
— ^h	—	0.9748 ^e	115 (vacuo)	0.8273 ^a	0.8255	100 (vacuo)
— ^h	0.9852	—	—	0.9878 ^f	—	—
— ^h	—	0.9869 ^e	175 (air)	1.2173 ^{a,g}	1.2171 ^g	175 (air)
— ^h	1.0922	1.0926	— ⁱ	0.9060 ^a	—	—
— ^h	1.1228	1.1230	— ⁱ	1.2173 ^{a,g}	1.2171 ^g	175 (air)

^a Molality obtained by cation-exchange chromatography followed by mass titration of the eluted H⁺ with NaOH(aq). This stock solution molality was accepted for isopiestic molality calculations.

^b Molality calculated from masses of salt and water used to prepare the solution assuming that the salt was completely anhydrous.

^c Same solution as the one immediately above.

^d This solution was prepared approximately 10 years before the molality analysis was performed. The 0.26% difference between the two molalities presumably resulted from a small amount of solvent evaporation. Since the molality analysis using the cation-exchange method was performed as the Series 5 isopiestic experiments were being started, it is the appropriate concentration to use for molality calculations.

^e This molality was accepted for isopiestic molality calculations.

^f Molality obtained by gravimetric analysis as BaSO₄(s). This concentration was accepted for isopiestic molality calculations.

^g These stock solutions are identical.

^h Older series.

ⁱ Not recorded.

two different sources each of commercial Na₂SO₄ and NaCl and several different methods of molality determination, were generally quite consistent. However, some individual results were discrepant.

Isopiestic experiments were performed both at 25.00±0.00₃°C and at 50.00±0.00₃°C. Equilibration times for the experiments at 25.00°C were typically about 1 week for molalities (*m*) > 0.5 mol·kg⁻¹ and about 2 weeks at lower molalities. In contrast, at 50.00°C equilibration times of about 4 days were adequate for molalities > 0.5*m*, but about 1 week was necessary at lower molalities. There are several previous reports that generally isopiestic equilibrium is reached more rapidly as the temperature is increased.⁽²⁸⁾

The isopiestic experiments were performed at various times between 1985 and 1993. Tables II and III list the equilibrium molalities for the experiments at 25.00 and 50.00°C, respectively. The mean molalities for

Table II. Isopiestic Molalities of NaCl(aq) and Na₂SO₄(aq) and the Osmotic Coefficients of Na₂SO₄(aq) at 25.00°C (298.15 K)^a

$m(\text{NaCl})$	$m(\text{Na}_2\text{SO}_4)$	ϕ	$m(\text{NaCl})$	$m(\text{Na}_2\text{SO}_4)$	ϕ
Series 1					
1.0801±0.0001	1.0550±0.0002	0.6419	0.6321±0.0002	0.5704±0.0001	0.6831
0.9248±0.0002	0.8821±0.0002	0.6529	0.6052±0.0004	0.5425±0.0001	0.6872
0.7672±0.0001	0.7110±0.0002	0.6681	0.5680±0.0001	0.5054±0.0006*	0.6917
0.7360±0.0002	0.6782±0.0001	0.6712	0.5345±0.0002	0.4720±0.0004	0.6964
0.6915±0.0006	0.6324±0.0005	0.6753	0.4457±0.0014*	0.3865±0.0010*	0.7080
0.6686±0.0001	0.6077±0.0003	0.6790			
Series 2					
0.4939±0.0001	0.4317±0.0002	0.7030	0.2541±0.0022**	0.2111±0.0011**	0.7396†
0.4086±0.0003	0.3499±0.0002	0.7168	0.2439±0.0002	0.1998±0.0003	0.7503
0.3433±0.0000	0.2888±0.0000	0.7295			
Series 3					
1.5580±0.0010	1.6065±0.0037*	0.6226	1.0530±0.0000	1.0250±0.0001	0.6433
1.3053±0.0001	1.3112±0.0001	0.6308	0.9930±0.0001	0.9576±0.0003	0.6477
1.2021±0.0001	1.1935±0.0000	0.6351			
Series 4					
3.6732±0.0006	3.7003±0.0001	0.7244	2.1514±0.0002	2.2577±0.0001	0.6325
3.5148±0.0003	3.5653±0.0003	0.7121	1.8568±0.0002	1.9383±0.0000	0.6251
3.0707±0.0003	3.1687±0.0003	0.6805	1.7658±0.0001	1.8373±0.0001	0.6239
2.9137±0.0002	3.0217±0.0002	0.6705	1.7418±0.0001	1.8109±0.0000	0.6236
2.6961±0.0000	2.8142±0.0001	0.6572	1.5540±0.0001	1.5986±0.0000	0.6239
Series 5					
1.0629±0.0003	1.0337±0.0002	0.6442			
Older combined series					
3.7111±0.0003	3.7355±0.0011	0.7267	0.8836±0.0002	0.8377±0.0002	0.6559
3.6821±0.0024	3.7100±0.0008	0.7246	0.8672±0.0005	0.8180±0.0003	0.6588
3.5272±0.0025	3.5773±0.0007	0.7128	0.8279±0.0003	0.7771±0.0001	0.6610
3.3805±0.0000	3.5235±0.0001	0.6871†	0.7686±0.0003	0.7113±0.0007	0.6690
3.3795±0.0010	3.5233±0.0001	0.6869†	0.7054±0.0001	0.6469±0.0000	0.6737
3.2480±0.0000	3.3944±0.0002	0.6796†	0.6828±0.0004	0.6211±0.0000	0.6787
3.2471±0.0009	3.3942±0.0002	0.6794†	0.6407±0.0002	0.5794±0.0000	0.6818
3.1782±0.0023	3.2682±0.0005	0.6876	0.6304±0.0004	0.5699±0.0000	0.6819
2.9130±0.0003	3.0237±0.0005	0.6699	0.6150±0.0004	0.5538±0.0001	0.6843
2.7324±0.0012	2.8499±0.0004	0.6592	0.5942±0.0001	0.5329±0.0001	0.6867
2.4924±0.0003	2.6278±0.0001	0.6426†	0.5176±0.0002	0.4562±0.0005	0.6975
2.4919±0.0001	2.6277±0.0001	0.6425†	0.5046±0.0001	0.4426±0.0001	0.7007
2.4151±0.0001	2.5343±0.0004	0.6426	0.4946±0.0003	0.4323±0.0005	0.7030
2.0315±0.0009	2.1287±0.0001	0.6290	0.4630±0.0001	0.4029±0.0000	0.7058
1.9843±0.0005	2.0769±0.0005	0.6280	0.4231±0.0007	0.3650±0.0005	0.7116
1.7736±0.0002	1.8451±0.0003	0.6244	0.4177±0.0001	0.3590±0.0003	0.7142
1.6418±0.0009	1.6896±0.0001	0.6266†	0.3913±0.0003	0.3344±0.0002	0.7182
1.5937±0.0019*	1.6337±0.0016	0.6274†	0.3776±0.0003	0.3193±0.0001	0.7257†

Table II. Continued.

$m(\text{NaCl})$	$m(\text{Na}_2\text{SO}_4)$	ϕ	$m(\text{NaCl})$	$m(\text{Na}_2\text{SO}_4)$	ϕ
1.4164 \pm 0.0004	1.4389 \pm 0.0003	0.6272	0.3047 \pm 0.0005	0.2542 \pm 0.0002	0.7357
1.3439 \pm 0.0056**	1.3573 \pm 0.0025*	0.6286	0.2959 \pm 0.0005	0.2456 \pm 0.0001	0.7396
1.3167 \pm 0.0001	1.3295 \pm 0.0005	0.6279†	0.2931 \pm 0.0004	0.2440 \pm 0.0002	0.7375
1.2454 \pm 0.0004	1.2367 \pm 0.0002	0.6362†	0.2876 \pm 0.0005	0.2415 \pm 0.0005	0.7311†
1.2399 \pm 0.0010	1.2374 \pm 0.0004	0.6329	0.2731 \pm 0.0001	0.2244 \pm 0.0005*	0.7474†
1.2080 \pm 0.0010	1.1950 \pm 0.0010	0.6375†	0.2564 \pm 0.0000	0.2109 \pm 0.0002	0.7469
1.2016 \pm 0.0002	1.1862 \pm 0.0004	0.6387†	0.2522 \pm 0.0001	0.2071 \pm 0.0001	0.7482
1.1943 \pm 0.0004	1.1859 \pm 0.0005	0.6347	0.2520 \pm 0.0003	0.2070 \pm 0.0002	0.7480
1.1854 \pm 0.0005	1.1802 \pm 0.0010	0.6328†	0.2500 \pm 0.0004	0.2050 \pm 0.0001	0.7493
1.0872 \pm 0.0004	1.0643 \pm 0.0004	0.6407	0.2300 \pm 0.0003	0.1875 \pm 0.0001	0.7542
1.0843 \pm 0.0001	1.0558 \pm 0.0001	0.6440†	0.2104 \pm 0.0003	0.1706 \pm 0.0002	0.7589
1.0457 \pm 0.0001	1.0181 \pm 0.0002	0.6430	0.2021 \pm 0.0003	0.1634 \pm 0.0000	0.7614
1.0377 \pm 0.0001	1.0025 \pm 0.0001	0.6478†	0.2006 \pm 0.0003	0.1621 \pm 0.0003	0.7618
1.0286 \pm 0.0003	0.9985 \pm 0.0009	0.6444	0.1395 \pm 0.0001	0.1103 \pm 0.0004*	0.7820
0.9500 \pm 0.0000	0.9101 \pm 0.0002	0.6508	0.1394 \pm 0.0002	0.1098 \pm 0.0000	0.7850

^aOsmotic coefficients of the reference standard $\text{NaCl}(\text{aq})$ were calculated using the equation and parameters of Archer (Ref. 23). Tabulated values of the molalities are denoted with a single asterisk if the scatter of the isopiestic molalities slightly exceeds that normally obtained for isopiestic experiments, and with two asterisks for those experiments with even larger scatter. Molalities without asterisks are from experiments that meet the criteria for high-quality experiments, namely, the uncertainty of the average molalities is $\leq 0.1\%$ for $m > 0.5$ and $\leq 0.2\%$ for $m < 0.5$. Osmotic coefficients denoted with a dagger (†) were given zero weight in our modeling calculations and those denoted with a double dagger (‡) were given a reduced relative weight of 0.5 or 0.25.

duplicate samples and the deviation from each mean are reported. The more recent experiments are labeled by series number, where each series represents sequential equilibrations using the same pair of duplicate samples of $\text{NaCl}(\text{aq})$ and of $\text{Na}_2\text{SO}_4(\text{aq})$, where $\text{NaCl}(\text{aq})$ is the reference standard. In one of the experiments at 50.00°C, only a single $\text{Na}_2\text{SO}_4(\text{aq})$ molality is reported because of crystallization in the replicate sample. The experiments performed in the 1980s are grouped together as the “older series” and represent numerous different series of experiments. The equilibrium molalities for each series are given from the highest to the lowest molality rather than the actual order of their determination. Several of the series involved measurements at both temperatures, where several temperature changes were made on a more or less random basis to check the reproducibility of the experiments. Although about 22% of the experimental results show moderate to large discrepancies from the remaining experiments, most (5/6) of these individual discrepant experiments occurred during the “older series” of measurements where some experimental techniques were being tested and varied, and many of those probably resulted from an inadequate equilibration time following a tempera-

Table III. Isopiestic Molalities of NaCl(aq) and Na₂SO₄(aq) and the Osmotic Coefficients of Na₂SO₄(aq) at 50.00°C (323.15 K)^a

$m(\text{NaCl})$	$m(\text{Na}_2\text{SO}_4)$	ϕ	$m(\text{NaCl})$	$m(\text{Na}_2\text{SO}_4)$	ϕ
Series 4					
3.4727±0.0030	3.5686±0.0088**	0.7086	2.0164±0.0001	2.0547±0.0002	0.6535
2.8608±0.0001	2.9539±0.0006	0.6792	1.6892±0.0008	1.6874±0.0012	0.6538
2.5396±0.0008	2.6179±0.0005	0.6670	1.4471±0.0003	1.4211±0.0001	0.6559
2.2917±0.0001	2.3546±0.0003	0.6591	1.2614±0.0070**	1.2002±0.0100**	0.6700†
Series 5					
1.1793±0.0005	1.1246±0.0008	0.6655	0.4360±0.0001	0.3700±0.0002	0.7242‡
1.1464±0.0003	1.0891±0.0003	0.6669	0.3852±0.0001	0.3235±0.0002	0.7311‡
0.9325±0.0003	0.8614±0.0002	0.6783‡	0.3346±0.0000	0.2786±0.0002	0.7370‡
0.8608±0.0001	0.7866±0.0003	0.6834‡	0.2429±0.0000	0.1970±0.0000	0.7570‡
0.7423±0.0007	0.6683±0.0003	0.6899†	0.1703±0.0005*	0.1385±0.0009**	0.7570†
0.6388±0.0001	0.5631±0.0001	0.7017‡	0.1644±0.0000	0.1318±0.0004*	0.7683†
0.5799±0.0001	0.5059±0.0001	0.7075‡	0.1584±0.0000	0.1272±0.0005*	0.7673†
0.5041±0.0001	0.4335±0.0000	0.7159‡			
Older combined series					
3.4601±0.0043*	3.5494 ^b	0.7092	1.1036±0.0005	1.0449±0.0000	0.6676
2.9849±0.0020	3.0805±0.0002	0.6847	1.0740±0.0003	1.0112±0.0006	0.6703
2.7751±0.0024	2.8648±0.0003	0.6758	1.0332±0.0016*	0.9903±0.0114**	0.6704‡
2.4414±0.0010	2.5139±0.0002	0.6637	0.9032±0.0004	0.8326±0.0001	0.6788‡
2.3691±0.0017	2.4362±0.0000	0.6617	0.9010±0.0019*	0.8283±0.0008	0.6806‡
2.3322±0.0049*	2.3933±0.0002	0.6615	0.7190±0.0002	0.6441±0.0000	0.6927‡
2.3160±0.0036*	2.3767±0.0005	0.6609	0.6667±0.0011*	0.5901±0.0013	0.6996‡
2.2597±0.0008	2.3184±0.0003	0.6588	0.5896±0.0003	0.5163±0.0002	0.7051‡
1.9897±0.0010	2.0235±0.0003	0.6538	0.5290±0.0093 ^c	0.4534±0.0002	0.7189†
1.7695±0.0005	1.7791±0.0001	0.6527	0.5222±0.0003	0.4545±0.0001	0.7078†
1.6460±0.0005	1.6417±0.0001	0.6532	0.5186±0.0014*	0.4500±0.0002	0.7098†
1.4902±0.0000	1.4677±0.0001	0.6556	0.4959±0.0005	0.4255±0.0000	0.7174‡
1.4686±0.0005	1.4446±0.0009	0.6556	0.4751±0.0006	0.4072±0.0001	0.7178‡
1.4466±0.0031*	1.4160±0.0005	0.6580†	0.4468±0.0002	0.3792±0.0003	0.7243‡
1.4074±0.0023*	1.3759±0.0008	0.6573	0.4201±0.0001	0.3545±0.0003	0.7281‡
1.3760±0.0020*	1.3415±0.0007	0.6580	0.4177±0.0126**	0.3489±0.0006	0.7355†
1.3349±0.0000	1.2944±0.0004	0.6600	0.3691±0.0004	0.3083±0.0001	0.7349†
1.2809±0.0009	1.2482±0.0007	0.6549†	0.2775±0.0002	0.2264±0.0001	0.7521†
1.2019±0.0007	1.1608±0.0005	0.6579†	0.2653±0.0001	0.2159±0.0001	0.7542†
1.1762±0.0005	1.1221±0.0004	0.6651	0.1981±0.0005*	0.1588±0.0001	0.7670‡
1.1080±0.0006	1.0580±0.0001	0.6621†	0.1477±0.0003	0.1166±0.0000	0.7811†
1.1079±0.0006	1.0579±0.0001	0.6621†			

^a See footnote for Table II.^b Single sample since crystallization occurred in the replicate sample.^c The isopiestic unit was accidentally bumped, and part of one of the NaCl(aq) samples may have spilt, thus making questionable the calculated molality.

ture change, or from splattering of one or more solutions while air was being removed from the isopiestic apparatus. If splattering occurs, it is the more serious problem, because it affects the reliability of all subsequent equilibrations with the same sample.

Samples of $(\text{NH}_4)_2\text{SO}_4(\text{aq})$ were also present during many of the isopiestic equilibrations of Series 1–5, those results were reported previously.⁽²⁷⁾

3. ANALYSIS OF PUBLISHED THERMODYNAMIC DATA FOR $\text{Na}_2\text{SO}_4(\text{aq})$

3.1. Isopiestic Measurements

In addition to the isopiestic results given in Tables II and III, there are many previous isopiestic studies for $\text{Na}_2\text{SO}_4(\text{aq})$, especially at 25°C, which span the temperature range of 0.00 to 225.04°C. However, there are relatively few such data at temperatures below 25°C and no previous investigation at 50°C. Table IV summarizes these studies and lists their molality ranges and temperature, reference standard(s), and number of isopiestic equilibrations if known. The reference standard used for the majority of these studies was $\text{NaCl}(\text{aq})$,^(9,14,15,31–45) but Rard and Miller⁽⁶⁾ used $\text{KCl}(\text{aq})$, Patterson, Soldano, and co-workers^(31–36,40) and Moore *et al.*⁽⁴⁰⁾ used both $\text{NaCl}(\text{aq})$ and $\text{KCl}(\text{aq})$, Platford⁽⁴¹⁾ used $\text{KCl}(\text{aq})$ and $\text{H}_2\text{SO}_4(\text{aq})$ for one experiment, and Majima *et al.*⁽⁴⁶⁾ used $\text{H}_2\text{SO}_4(\text{aq})$. Childs and Platford⁽⁴⁷⁾ used both $\text{H}_2\text{SO}_4(\text{aq})$ and aqueous urea as reference standards, but also included samples of $\text{NaCl}(\text{aq})$ and $\text{KCl}(\text{aq})$ in their equilibrations. The equilibrations of Baabor *et al.*⁽¹³⁾ at 25.00°C did not include any of the usual reference standards, and the osmotic coefficients of the only other binary solution included in these equilibrations, $\text{Li}_2\text{SO}_4(\text{aq})$, are not sufficiently well characterized for it to serve as one, so these data were not reanalyzed.

Molality-based or “practical” osmotic coefficients ϕ of $\text{Na}_2\text{SO}_4(\text{aq})$ were calculated from the fundamental equation for isopiestic equilibrium

$$\phi = \nu^* m^* \phi^* / \nu m \quad (1)$$

where m is the molality of $\text{Na}_2\text{SO}_4(\text{aq})$ and $\nu = 3$ its stoichiometric ionization number, and where ν^* , m^* , and ϕ^* denote the corresponding quantities for the isopiestic reference standard. Values of ϕ reported in Tables II and III were computed from the listed equilibrium molalities and from values of ϕ^* for $\text{NaCl}(\text{aq})$ calculated from the extended Pitzer equation of Archer.⁽²³⁾ Osmotic coefficients for $\text{Na}_2\text{SO}_4(\text{aq})$ from the published isopiestic studies listed in Table IV were recalculated on a consistent basis, with ϕ^* calculated from Archer’s evaluations^(23,48) for both $\text{NaCl}(\text{aq})$ and $\text{KCl}(\text{aq})$ and ϕ^* of $\text{H}_2\text{SO}_4(\text{aq})$ from the evaluation of Clegg *et al.*⁽²⁵⁾ As noted by Rard and Clegg,⁽⁴⁹⁾ it is not necessary to correct the published isopiestic molalities for changes in molar masses since

Table IV. Summary in Chronological Order of Available Isopiestic Results for $\text{Na}_2\text{SO}_4(\text{aq})$ at Various Temperatures

<i>m</i> Range	<i>t</i> (°C)	No. of points	Ref. std.	Rel. wt. ^a	Ref.
0.098–4.19	25.00	23	KCl	0	Robinson <i>et al.</i> (30)
0.891–3.18	99.65	5	NaCl/KCl	0	Patterson <i>et al.</i> (31)
0.594–2.70	121.1	9? ^b	NaCl/KCl	0	Soldano and Patterson (32)
0.30–0.60	140.3	7? ^b	NaCl/KCl	0	Soldano and Meek (33)
0.7–3.5	45.00	13? ^b	NaCl/KCl	0	Hellams <i>et al.</i> (34)
0.75–3.00	151.4	10? ^b	NaCl/KCl	0	Soldano and Bien (35)
0.50–2.75	165.0	10? ^b	NaCl/KCl	NA	Soldano and Bien (35)
0.91–3.4	59.98	13	NaCl/KCl	1(1)	Humphries <i>et al.</i> (36)
0.116–3.8	25.00	22	NaCl	1(5)	Platford (37)
0.36–4.4	25.0	10 ^c	NaCl	0	Wu <i>et al.</i> (38)
0.1–3.0	15.00	14? ^b	H ₂ SO ₄ /urea	0.025	Childs and Platford (47)
0.70–2.97	80.22	30	NaCl/KCl	0.67(3)	Moore <i>et al.</i> (40)
0.66–0.93	0.00	3	NaCl	0.1	Platford (41)
1.357	0.00	1	KCl/H ₂ SO ₄	0.1	Platford (41)
0.22–1.2	25.00	10	NaCl	1	Downes and Pitzer (42)
0.47–3.7	25.00	53	KCl	1	Rard and Miller (6)
1.01–1.8	25.00	4	NaCl	1(2)	Filippov <i>et al.</i> (43)
0.5571–2.8	109.99	28	NaCl	5	Holmes and Mesmer (9)
0.61–2.9	140.08	18	NaCl	5	Holmes and Mesmer (9)
0.56–2.8	170.01	14	NaCl	NA	Holmes and Mesmer (9)
0.65–3.1	200.02	25	NaCl	NA	Holmes and Mesmer (9)
0.65–3.4	225.04	18	NaCl	NA	Holmes and Mesmer (9)
0.58–1.7	25.0	5 ^d	H ₂ SO ₄	0	Majima <i>et al.</i> (46)
1.1737	25.00	1 ^e	NaCl	0	Filippov <i>et al.</i> (44)
0.14–3.3	40.00	19 ^f	NaCl	0	Baabor <i>et al.</i> (14)
0.21–3.3	40.00	18 ^f	NaCl	0	Baabor <i>et al.</i> (15)
0.11–3.7	25.00	98	NaCl	1(19)	Table II, this study
0.12–3.6	50.00	66	NaCl	2(17)	Table III, this study

^aA few data points from otherwise reliable data sets were given zero weights in the least-squares fits. The number of these rejected points is given in parentheses and their molalities are: 3.0337 with NaCl(aq) reference standard from the study of Humphries *et al.* (Ref. 36); 0.9217, 1.136, 2.045*m* from the study of Moore *et al.* (Ref. 40); 0.1156, 0.1626, 0.2106, 0.2826, and 3.64*m* from the study of Platford (Ref. 37); 1.008 and 1.481*m* from the study of Filippov *et al.* (Ref. 43); 0.1–0.5*m* (aqueous H₂SO₄ standard) from the study of Childs and Platford (Ref. 47). Data points from Tables II and III that were rejected or given reduced weights in the least-squares fits are identified in those tables. NA denotes that these data sets were not reanalyzed since they were measured outside of the temperature range being modeled. The smoothed isopiestic results of Childs and Platford (Ref. 47) were recalculated using their tabulated results for NaCl(aq), KCl(aq), and H₂SO₄(aq) reference standards. Their osmotic coefficient for each Na₂SO₄(aq) molality was assigned a total relative weight of 0.025, with one-third of that weight assigned to the results calculated with each reference standard for *m* > 0.5 and 1/2 of that weight to the NaCl(aq) and KCl(aq) results for *m* < 0.5. Similarly, the osmotic coefficients of Humphries *et al.* (Ref. 36) and Moore *et al.*, (Ref. 40) which involved both NaCl(aq) and KCl(aq) as reference standards, were assigned a total relative weight of 1 or 0.67 at each molality, respectively.

Table IV. Continued.

- ^bThe results were presented as smoothed values of ϕ or isopiestic molality ratio at selected molalities, although Soldano and Patterson (Ref. 32) gave two actual molality ratios along with the smoothed results. The number of experimental measurements is unknown for these studies.
- ^cThe same molality pairs for five of these experiments (Ref. 38) are also given by Wu *et al.* (Ref. 39) in a later paper.
- ^dThese results were presented graphically in the 1983 paper along with some analysis, but the equilibrium molalities are tabulated only in the 1988 report (Ref. 46).
- ^eThis same experiment was reported previously by Filippov and Kalinkin (Ref. 45) but the NaCl(aq) reference solution molality was not given there.
- ^fBased on the reported reference molalities of NaCl(aq) and the identical experimental temperature, the results for the eleven highest-molality experiments reported in the 1996 and 1998 papers by Baabor *et al.* (Refs. 14 and 15) represent the same experiments, but with large revisions to the Na₂SO₄(aq) molalities. However, at lower concentrations the equilibrium molalities of both solutions are quite different and obviously represent separate experiments. We assumed that the revised results in the 1998 paper are to be preferred.

the original studies were published, because these corrections are considerably smaller than the typical experimental uncertainty.

The experimental equilibrium molalities were not reported for five of these studies. Childs and Platford⁽⁴⁷⁾ only listed smoothed values of ϕ at rounded molalities, so it was not possible to correct their results directly for revision of the ϕ^* values. However, approximate corrections could be applied to the results of Soldano and Bien,⁽³⁵⁾ Soldano and Patterson,⁽³²⁾ Soldano and Meek,⁽³³⁾ and of Hellams *et al.*,⁽³⁴⁾ since they reported the smoothed equilibrium molality ratios at rounded molalities.

The smoothed isopiestic results of Childs and Platford⁽⁴⁷⁾ at 15.00°C were corrected in an approximate manner for changes in the isopiestic reference standards by the following method. The authors listed smoothed values of m and ϕ for Na₂SO₄(aq) and various other electrolytes including NaCl(aq), KCl(aq), or H₂SO₄(aq). From the condition for isopiestic equilibrium, Eq. (1), $m^*\phi^* = \nu m\phi/\nu^*$, where the symbols with asterisks now denote NaCl(aq), KCl(aq), or H₂SO₄(aq). From each $m\phi$ value for Na₂SO₄(aq), we calculated the corresponding $m^*\phi^*$ for each reference standard. We then represented m^* for each of the reference standards as a function of $m^*\phi^*$ using the tabulated values of Childs and Platford,⁽⁴⁷⁾ and used the reported values of $m\phi$ for Na₂SO₄(aq) to obtain the corresponding molalities of the reference standard m^* . These m^* were then used to determine ϕ^* for each reference standard from the more recent evaluations,^(23,25,48) and hence ϕ . For molalities ≥ 0.5 the calculated values ϕ of Na₂SO₄(aq) using the three different standards agree fairly well at each molality, with a maximum difference of 0.4%. However, below 0.5 m , values of ϕ using H₂SO₄(aq) as reference standard differ by up to 1% from those calculated using NaCl(aq) or KCl(aq). This

implies either that the precision of their measurements is significantly worse at the lowest molalities, or that these three standards were not equilibrated against each other in this molality region. The discrepant results below 0.5 *m* with H₂SO₄(aq) as reference standard were thus given zero weight in our thermodynamic models.

A preliminary graphical examination was made of all of the isopiestic data sets to test for internal consistency, agreement with other data sets at the same temperature (if available), and consistency between independent studies at other temperatures. We were also influenced by Rard and Miller's⁽⁶⁾ comparison of the isopiestic results at 25°C, and the discussion and plot given by Holmes and Mesmer.⁽⁹⁾ These comparisons indicated that the early measurements from the high-temperature isopiestic unit at Oak National Laboratory^(31–33,35) are inaccurate, especially those of Soldano and Meek⁽³³⁾ at 140.3°C and of Soldano and Bien⁽³⁵⁾ at 151.4°C. As discussed by Rard and Platford,⁽²⁸⁾ the source of this error was a combination of a relatively large temperature gradient across the heat-transfer block and the lack of adequate sensitivity in the electromagnetic balance used for *in situ* weighing of the sample dishes. The isopiestic results of Hellams *et al.*⁽³⁴⁾ at 45.00°C and of Majima *et al.*⁽⁴⁶⁾ at 25.0°C are quite badly scattered, with three of the five values of ϕ from the latter study being too high by 0.017 to 0.025 and one value being too low by 0.016. In the first of these studies, the problems resulted from the lack of internal capping and resulting solvent loss when the apparatus was opened to remove the sample cups and, in the second case, from their inadequate temperature control. The results of these six isopiestic studies^(31–35,46) were consequently rejected by us, and several of them were also rejected by Holmes and Mesmer.⁽¹⁰⁾

The comparison of the available isopiestic data at 25.00°C by Rard and Miller⁽⁶⁾ indicated that their results, Platford's,⁽³⁷⁾ and Downes and Pitzer's⁽⁴²⁾ are precise and highly consistent and a further comparison by us indicates that most of the new results given in Table II are likewise consistent. Values of ϕ calculated from the isopiestic molalities of Robinson *et al.*⁽³⁰⁾ are lower by up to $\Delta\phi \approx 0.012$ whereas those of Wu *et al.*⁽³⁸⁾ and some of the Filippov *et al.*⁽⁴³⁾ results are higher by ≈ 0.004 – 0.005 . Although these discrepancies are much smaller than for some of the data sets mentioned in the preceding paragraph, they are significant and thus the results of these studies^(30,38) are rejected.

3.2. Direct Vapor Pressure Measurements

Table V contains a summary of available thermodynamic measurements, excluding the isopiestic studies, that yield osmotic coefficients of Na₂SO₄(aq).^(50–67) The molality range, temperature(s), number of observations, and the experimental method used for each study are given in this

Table V. Summary in Chronological Order of Available Non-isopiestic Results Yielding Osmotic Coefficients of Na₂SO₄(aq) at Various Temperatures

<i>m</i> Range	<i>t</i> (°C)	No. of points	Exp. method ^a	Rel. wt. ^b	Ref.
0.05–2.00 ^c	bt ^d	7	btd	0	Jones and Getman (64)
1.4–3.3 ^e	20.8–50.6	7	svp	0	Leopold and Johnston (50)
0.0009–0.1	ft ^d	9	ftd	0.4(3)	Randall and Scott (61)
Sat. ^e	7–25	^g	dsvp	0	Foote <i>et al.</i> (51)
0.96–2.2	27.50	6	dvp	1	Gibson and Adams (52)
0.33–1.4	20.00	8	dsvp	0	Perreu (53)
0.0008–0.3	bt ^d	9	btd	0	Plake (63)
0.1–1.96	25.00	8 ^g	dvp?	0	Pearce and Eckstrom (54)
0.0067–0.22	ft ^d	20	ftd	0.4(4)	Indelli (62)
0.5–3.0	20, 25	12 ^g	dsvp	0	Kangro and Groeneveld (55)
0.01–0.4	37.0	7 ^g	vpo	0	Burge(56)
0.1–1.2	75–150	20	svp	0	Fabuss and Korosi (57)
2.0, Sat. ^e	35–90	^g	dsvp	0	Jakli <i>et al.</i> (58)
0.47–1.85	50–150	25	svp	0	Bhatnagar and Campbell (59)
0.29–3.2	150–250	30	svp	0	Bhatnagar and Campbell (60)
3.6–13.2	20.0	21	edb/hyg	NA	Cohen <i>et al.</i> (65)
2.4–14.4	25.0	101	edb	NA	Tang and Munkelwitz (66)
3.5–14.4	25.0	28	edb/dpd	NA	Chan <i>et al.</i> (67)

^a Abbreviations used for the experimental methods: btd, boiling temperature determination; dsvp, differential static vapor pressure; dpd, dew point determination; dvp, dynamic vapor pressure; edb, electrodynamic balance; ftd, freezing temperature determination; hyg, hygrometry; svp, static vapor pressure; and vpo, vapor-pressure osmometry. For the electrodynamic balance results, the method of determining the water vapor pressure is also listed. Static vapor pressure measurements may involve a direct measurement of the vapor pressure of a solution (svp) or a differential measurement (dsvp) of the difference between the vapor pressures of the pure solvent and the solution of interest.

^b A few data points from otherwise reliable data sets were given zero weights in the least-squares fits. The number of these rejected points is given in parentheses and their molalities are: 0.000875, 0.060975, and 0.10338 from the study of Randall and Scott (Ref. 61) 0.006678, 0.019288, 0.037395, and 0.22209 from the study of Indelli (Ref. 62). NA denotes that these edb results were not analyzed nor were they included in the final thermodynamic models.

^c The concentration scale for this study was described as being “molecular concentration.”

^d The abbreviation ft denotes that the measurements yield ϕ at the freezing temperature of each solution in equilibrium with pure ice. For the measurements of Indelli (Ref. 62) these ftd vary from -0.03420 to -0.8810°C and for the measurements of Randall and Scott (Ref. 61) from -0.00480 to -0.4510°C . Rard and Miller (Ref. 6) calculated and tabulated ϕ values at the reported molalities and freezing temperatures of these two studies. The abbreviation bt denotes that the measurements yield ϕ at the boiling temperatures, which range from 100.00123 to 100.344°C for the study of Plake (Ref. 63) and 100.050 to 102.085°C for the study of Jones and Getman. (Ref. 64).

^e These measurements yield ϕ at the molality of the saturated solution. Leopold and Johnston (Ref. 50) obtained their molalities by an analysis of published solubility data, but Foote *et al.* (Ref. 51) and Jakli *et al.* (Ref. 58) did not report the saturation molalities at their experimental temperatures.

^f No actual results were tabulated. The results were only presented graphically and as an equation for the variation of vapor pressure with temperature.

^g The actual number of experimental measurements in these studies is unknown since only smoothed results were reported.

table. Most of these studies involved direct measurement of the water vapor pressure of the solution or the difference between the vapor pressure of the solution and pure solvent at the same temperature, but Burge⁽⁵⁶⁾ used vapor-pressure osmometry. Rard and Platford⁽²⁸⁾ have described most of these experimental methods.

Osmotic coefficients were calculated from the reported vapor pressures using Eq. (26) of Rard and Platford,⁽²⁸⁾ in which non-ideal vapor pressure corrections are made using the second virial coefficient of $\text{H}_2\text{O}(\text{g})$. This treatment of non-ideal behavior is accurate below $\sim 100^\circ\text{C}$, but the use of the third virial coefficient or a more complete equation-of-state for $\text{H}_2\text{O}(\text{g})$ may be necessary for calculations involving measurements at much higher temperatures. However, none of the three vapor pressure investigations of $\text{Na}_2\text{SO}_4(\text{aq})$ above 100°C ^(57,59,60) is precise or accurate enough to warrant this additional refinement. Auxiliary data required for these calculations are the same as described by Rard and Clegg.⁽⁴⁹⁾

Rard and Miller⁽⁶⁾ examined several of these sets of vapor pressures measured at 25.00 or 27.50°C . They rejected those of Pearce and Eckstrom⁽⁵⁴⁾ and of Kangro and Groeneveld⁽⁵⁵⁾ as yielding erroneous values of ϕ at 25°C . A detailed comparison by us indicates that the Pearce and Eckstrom results are too high by $\Delta\phi \approx 0.006$ to 0.012 , whereas those of Kangro and Groeneveld are too low by 0.004 to 0.006 . These two studies were consequently rejected. In contrast, the vapor pressures of Gibson and Adams⁽⁵²⁾ yield ϕ at 27.50°C that are both precise and highly consistent with the better quality isopiestic data. This was also the only set of direct vapor pressures accepted by Holmes and Mesmer⁽¹⁰⁾ in their evaluation of the thermodynamic properties of $\text{Na}_2\text{SO}_4(\text{aq})$.

Holmes and Mesmer⁽⁹⁾ discussed the two high-temperature vapor pressure studies of Bhatnagar and Campbell,^(59,60) and compared the derived values of ϕ to isopiestic results at $1.0m$ as a function of temperature. Their plot indicates that the ϕ values from Bhatnagar and Campbell are too high by ~ 0.02 at the lower temperatures, but are low by $|\Delta\phi| > 0.1$ or more at the higher temperatures. Goldberg⁽⁷⁾ derived two values of ϕ at 25.00°C from the vapor pressure equations of Jakli *et al.*,⁽⁵⁸⁾ one was too low by $\Delta\phi \approx 0.05$ and the other too high by ≈ 0.07 . The vapor pressures from these three studies^(58–60) were consequently not included in our thermodynamic models.

Water vapor pressures were reported for saturated $\text{Na}_2\text{SO}_4(\text{aq})$ solutions by Leopold and Johnston⁽⁵⁰⁾ from 20.83 to 50.55°C , and yield values of ϕ that are too large by about a factor of 2 at the lower temperatures, but which become slightly low at the higher temperatures. It is difficult to imagine any type of experimental error that would produce such a large temperature-dependent skewing. Similar measurements by Foote *et al.*⁽⁵¹⁾ were reported only as a least-squares equation. However, their Fig. 2 indicates that this

equation does not reliably reproduce the experimental measurements, but rather cycles about them. Consequently, their vapor pressures were not reanalyzed. Vapor pressures reported by Perreu⁽⁵³⁾ at 20.00°C yield ϕ values that are scattered by $\Delta\phi \approx 0.01$ at higher molalities and by $\approx 0.02\text{--}0.03$ at the lower molalities. Values of ϕ derived from the vapor pressures of Fabuss and Korosi⁽⁵⁷⁾ are also scattered, especially at lower molalities where $|\Delta\phi| > 0.1$. Our examination indicates that the vapor pressures from these four studies are too imprecise and/or too inaccurate to be included in our thermodynamic models.

We note that failure to completely remove air from the solution and its vapor phase prior to a “static” vapor pressure measurement will yield a calculated ϕ that is erroneously low.

The most accurate of the vapor pressures are those of Gibson and Adams⁽⁵²⁾ at 27.50°C. Our derived results from that study are: (0.9600₄, 0.6505), (1.338₀, 0.6335), (1.544₄, 0.6270), (1.759₀, 0.6262), (1.984₆, 0.6281), and (2.222₀, 0.6353), where the first number of each pair is the molality and the second the corresponding value of ϕ . These molalities were recalculated to a molar mass of 142.044 g·mol⁻¹ for Na_2SO_4 .

3.3. Freezing Temperature Depressions and Boiling Temperature Elevations

Table V lists two reasonably consistent studies of the freezing temperature depressions of $\text{Na}_2\text{SO}_4(\text{aq})$ in equilibrium with ice.^(61,62) Rard and Miller⁽⁶⁾ derived values of ϕ at the freezing temperatures and list them in their Table III; we accepted their values. Goldberg⁽⁷⁾ listed values of ϕ (corrected to 25.00°C) for several other published freezing temperature depression studies. Based on Goldberg’s comparisons, these other studies were judged to be too inaccurate to warrant reexamination.

Plake⁽⁶³⁾ reported boiling temperature elevations for 0.00081 to 0.308*m* $\text{Na}_2\text{SO}_4(\text{aq})$. The molalities of each of their solutions were recalculated from their reported mass ratios using 142.044 g·mol⁻¹ for the molar mass of Na_2SO_4 . Values of ϕ were calculated from the vapor pressures of water at the boiling temperatures, using Eq. (26) of Rard and Platford.⁽²⁸⁾ Our derived results from that study are: (0.00081₀, 0.9855, 100.00123°C), (0.00161₉, 0.9783, 100.00244°C), (0.00323₈, 0.9496, 100.00473°C), (0.00647₀, 0.9297, 100.00925°C), (0.0158₄, 0.8870, 100.0216°C), (0.0325₃, 0.8498, 100.0425°C), (0.0646₃, 0.8111, 100.0806°C), (0.158₄, 0.7635, 100.186°C), and (0.308₄, 0.7250, 100.344°C), where the first number of each set is the molality, the second the value of ϕ , and the third the temperature of measurement. The mass ratios were only reported by Plake⁽⁶³⁾ to three significant figures, which

implies that derived values of ϕ , which depend inversely on the molality, are uncertain by at least 0.2–0.9%.

Jones and Getman⁽⁶⁴⁾ also reported boiling temperature elevations for $\text{Na}_2\text{SO}_4(\text{aq})$. Their measurements were made at eight concentrations from 0.05 to 2.00 on the “molecular concentration scale,” which was taken to be the same as molarity. However, the precision of ϕ at the three highest concentrations is only about ± 0.05 , values of ϕ at the two intermediate concentrations are low, and at the lowest two concentrations are considerably in error.

3.4. Electrodynamic Balance Measurements

Three electrodynamic balance (edb) studies have been reported for the vapor pressures of $\text{Na}_2\text{SO}_4(\text{aq})$.^(65–67) In brief, an edb measurement consists of placing a charged particle of some electrolyte or mixture between two electrodes, and then varying the D.C. electric field until the particle is suspended. Under this condition, the electrical and gravitation forces on the particle exactly balance and thus the mass-to-charge-ratio of the particle is determined. Water vapor is then admitted to the electrodynamic balance from some external source until the particle deliquesces and the potential difference is continually changed to keep the particle in gravitational balance. By monitoring the relative humidity of the external source, the vapor pressure of water is known, and by determining the mass of the particle, the molality of the particle can be calculated. The vapor pressure of water can be varied to give a series of measurements for the same particle.

In practice, however, the degree of hydration of the original particle is generally not known and thus the mass of anhydrous electrolyte(s) is unknown. In this case, the molality of the suspended solution particle is determined by matching the water activities at the lower concentrations to those from some other measurement (such as isopiestic data). Very high degrees of supersaturation can be achieved, which allows measurements at molalities not accessible by other methods. These edb data were not included in the data base used to evaluate the parameters of our thermodynamic models, because of their considerably lower precision.

3.5. Electromotive Force (emf) Measurements

Several studies report emfs as a function of molality of reversible electrochemical cells containing $\text{Na}_2\text{SO}_4(\text{aq})$. These are summarized in Table VI, which lists their molality ranges, temperature ranges, and the cells used.

Seven different kinds of electrochemical cells were utilized. Shibata and Murata⁽⁶⁸⁾ and Rondinini *et al.*⁽¹⁶⁾ investigated the cell

Table VI. Summary in Chronological Order of Available emf Studies Involving $\text{Na}_2\text{SO}_4(\text{aq})$ at Various Temperatures

<i>m</i> Range	<i>t</i> (°C)	No. of points	Cell type	Rel. wt. ^a	Ref.
Sat. ^b	18–30	30	B	—	Henderson and Stegeman (69)
Sat., unsat. ^b	25.00	11	B	—	Mellon and Henderson (70)
0.025–2.0 ^c	25.00	7	D	0	Åkerlöf (73)
0.05–2.0	22–31	28	A	1(5)	Shibata and Murata (68)
0.005–0.6 ^d	25.0	6	G	0	Hass and Jellinek (75)
0.075–1.3	0–40	≤144 ^e	E	1(9)	Harned and Hecker (74)
Sat. ^b	0.0–60	13	B	—	Harned and Hamer (71)
0.03–0.27	10–70	60	A	0	Rondinini <i>et al.</i> (16)
<0.5 ^f	25.00	? ^f	C	0	Luts <i>et al.</i> (72)
0.33–3.3	25.00	7	B	—	Fusi and Mussini (17)
0.10–3.3	25.00	44	F	0	Fusi and Mussini (17)

^a A few data points from otherwise reliable data sets were given zero weights in the least-squares fits. The number of these rejected points is given in parentheses and their molalities are: 0.049 mol·kg⁻¹ at all temperatures and 1.975*m* at 25°C from the study of Shibata and Murata (Ref. 68); 0.075*m* at all temperatures from the study of Harned and Hecker (Ref. 74).

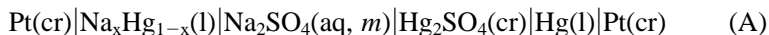
^b Henderson and Stegeman (Ref. 69), Mellon and Henderson (Ref. 70), and Harned and Hamer (Ref. 71) studied a saturated solution of unspecified molality and Mellon and Henderson also studied one unsaturated solution. The emf of cell (B) is independent of the $\text{Na}_2\text{SO}_4(\text{aq})$ molality. Thus, these emfs do not yield the activities of $\text{Na}_2\text{SO}_4(\text{aq})$.

^c The ratio of molality divided by molarity is > 1 for nearly all aqueous electrolyte solutions. However, for the concentrations of $\text{Li}_2\text{SO}_4(\text{aq})$, $\text{Na}_2\text{SO}_4(\text{aq})$, and $\text{K}_2\text{SO}_4(\text{aq})$ reported in Table I of that study, this ratio is < 1 which cannot be correct. As discussed in the text, their molality and molarity values appear to have been reversed. However, the emfs of this study are highly discrepant from other studies, which suggests that one or more of their electrodes was not functioning properly.

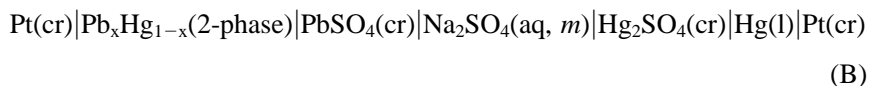
^d The reported concentration units for this study are mol·dm⁻³.

^e Harned and Hecker (Ref. 74) did not report their experimental emfs, but instead gave the parameters of equations representing the temperature dependences of emfs at rounded molalities. The listed number of ≤144 is based on statements made in their paper. At all temperatures the calculated emfs at 0.075*m* were given zero weight in our model fits because they are inconsistent with the emfs at other molalities. Either their original measurements or one or more of their temperature coefficients at this molality are in error.

^f The exact molality range and number of data points are unknown since no experimental results were reported. Insufficient information was presented in this report to allow a reanalysis.



from 22 to 31°C and from 10 to 70°C, respectively, where *x* denotes the mole fraction of the other metal in a liquid amalgam. Single-phase unsaturated liquid amalgams were used. Fusi and Mussini⁽¹⁷⁾ investigated the cell

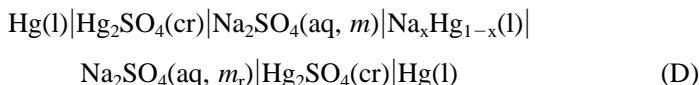


from 0.3333 to 3.333 mol·kg⁻¹ at 25°C. Henderson and Stegeman,⁽⁶⁹⁾ Mellon and Henderson,⁽⁷⁰⁾ and Harned and Hamer⁽⁷¹⁾ also investigated cell (B) using a saturated solution of Na₂SO₄(aq) in contact with Na₂SO₄·10H₂O(cr), and Mellon and Henderson also studied one unsaturated solution composition. Luts *et al.*⁽⁷²⁾ investigated the cell

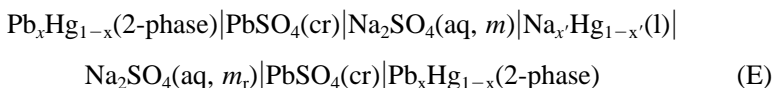


at 25°C where SSGE denotes a sodium-sensitive glass electrode.

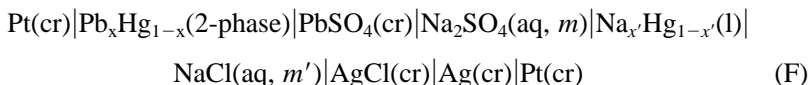
Several emf studies were performed with double cells. Åkerlöf⁽⁷³⁾ investigated the cell



where m_r denotes a constant reference molality. Åkerlöf did not report the temperature of these experiments, but according to Harned and Hecker⁽⁷⁴⁾ it was 25°C. Harned and Hecker used a related double cell of the type



from 0 to 40°C. Fusi and Mussini⁽¹⁷⁾ used a more complicated double cell arrangement at 25°C which contained both Na₂SO₄(aq) and NaCl(aq) solutions.



The experimental emfs were not reported in two of these studies.^(72,74) However, Harned and Hecker⁽⁷⁴⁾ presented quadratic equations for the temperature dependences of the emfs of cell (E) at twelve different molalities, based on experimental measurements at sixteen molalities, which were then smoothed graphically to the twelve rounded molalities. Their equations were used to calculate emfs at each experimental temperature with little loss in accuracy. In contrast, Luts *et al.*⁽⁷²⁾ only reported their derived value of E° for cell (C) and the slope of the emf against the logarithm of the activity of Na₂SO₄(aq). Their reported slope of 0.08682 ± 0.00009 V at 25.00°C is similar to, but not quite equal to, the reversible Nernstian slope of $(vRT \ln 10 / 2F) = (3/2)(0.059160) = 0.088740$ V, where R is the gas constant and F Faraday's constant. Luts *et al.* did not give sufficient information to allow their emfs to be reanalyzed, so that study is not considered further.

Hass and Jellinek⁽⁷⁵⁾ reported emfs for the double cell

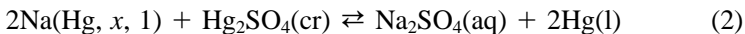


at 25.0°C, where KCl SB denotes a salt bridge containing KCl. The concentration of the KCl(aq) reference solution c_r was held constant at 0.1 mol-dm⁻³. Since it is not possible to correct the emfs accurately for the effect of this salt bridge, they are not analyzed here.

The molalities listed by Åkerlöf⁽⁷³⁾ for Na₂SO₄(aq) are smaller than the corresponding listed molarities at higher concentrations, whereas they should be larger. The highest concentration was assumed to be 1.882 mol-dm⁻³ rather than 1.882 mol-kg⁻¹ as reported. The density equation of Rard *et al.*⁽⁷⁶⁾ yields $d = 1.21099 \text{ g-cm}^{-3}$ at 1.882 mol-dm⁻³ and 25°C, from which we calculate a molality of 1.994 mol-kg⁻¹. This is numerically close to Åkerlöf's reported "molarity" of 2.0. It thus appears that the two column headings "c" and "m" in Åkerlöf's Table I should be reversed.

We now describe the reactions occurring in these various electrochemical cells and the composition dependences of the emfs. Cells (C) and (G) are not considered here since the available studies^(72,75) do not yield any usable thermodynamic information.

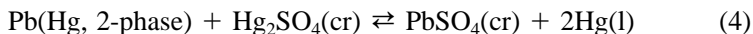
The chemical reaction occurring in cell (A) is



for which the emf for this cell is given by

$$\begin{aligned} E(\text{cell A}) &= E^\circ(\text{cell A}) + (RT/F) \ln a(\text{Na}, x, \text{Hg}) - (RT/2F) \ln a(\text{Na}_2\text{SO}_4) \\ &= E^\circ'(\text{cell A}) - (RT/2F) \ln a(\text{Na}_2\text{SO}_4) \end{aligned} \quad (3)$$

where $a(\text{Na}, x, \text{Hg})$ is the activity of Na in the liquid amalgam, $a(\text{Na}_2\text{SO}_4)$ is the activity of Na₂SO₄(aq), $E^\circ'(\text{cell A}) = E^\circ(\text{cell A}) + (RT/F) \ln a(\text{Na}, x, \text{Hg})$, $E^\circ(\text{cell A}) = -E^\circ\{\text{Na}^+(\text{aq})|\text{Na}(\text{Hg})\} + E^\circ\{\text{Hg}_2\text{SO}_4(\text{cr})|2\text{Hg}(\text{l}) + \text{SO}_4^{2-}(\text{aq})\}$, and where $E^\circ\{\text{Na}^+(\text{aq})|\text{Na}(\text{Hg})\}$ and $E^\circ\{\text{Hg}_2\text{SO}_4(\text{cr})|2\text{Hg}(\text{l}) + \text{SO}_4^{2-}(\text{aq})\}$ are the corresponding standard electrode (reduction) potentials. In both studies with cell (A),^(16,68) emf measurements were made at several different mole fractions x of sodium in the amalgam. The chemical reaction occurring in cell (B) is



and thus the emf of this cell is independent of the Na₂SO₄(aq) molality. Consequently, the emfs reported for this cell^(17,69-71) do not yield any thermodynamic data for Na₂SO₄(aq). However, they do provide a useful consistency check for the standard potentials derived for the other cells since

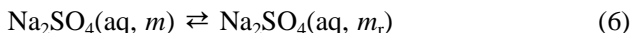
$$\begin{aligned}
E(\text{cell B}) &= E^\circ(\text{cell B}) = -E^\circ\{\text{PbSO}_4(\text{cr})|\text{Pb}(\text{Hg}) + \text{SO}_4^{2-}(\text{aq})\} \\
&\quad - (RT/2F)\ln a(\text{Pb}, x, \text{Hg}) \\
&\quad + E^\circ\{\text{Hg}_2\text{SO}_4(\text{cr})|2\text{Hg}(\text{l}) + \text{SO}_4^{2-}(\text{aq})\} \\
&= -E^\circ\{\text{PbSO}_4(\text{cr})|\text{Pb}(\text{Hg}) + \text{SO}_4^{2-}(\text{aq})\} \\
&\quad + E^\circ\{\text{Hg}_2\text{SO}_4(\text{cr})|2\text{Hg}(\text{l}) + \text{SO}_4^{2-}(\text{aq})\}
\end{aligned} \tag{5}$$

where $E^\circ\{\text{PbSO}_4(\text{cr})|\text{Pb}(\text{Hg}) + \text{SO}_4^{2-}(\text{aq})\}$ is the corresponding standard reduction potential of the lead amalgam–lead sulfate electrode, $E^\circ\{\text{PbSO}_4(\text{cr})|\text{Pb}(\text{Hg}) + \text{SO}_4^{2-}(\text{aq})\} = E^\circ\{\text{PbSO}_4(\text{cr})|\text{Pb}(\text{Hg}) + \text{SO}_4^{2-}(\text{aq})\} + (RT/2F)\ln a(\text{Pb}, x, \text{Hg})$, and $a(\text{Pb}, x, \text{Hg})$ is the activity of lead in the two-phase amalgam.

Early emf measurements of Henderson and Stegeman⁽⁶⁹⁾ give $E^\circ(\text{cell B}) = (0.96463 \pm 0.00004)(1.00033) = 0.96495 \pm 0.00004$ V, those of Harned and Hamer⁽⁷¹⁾ give $E^\circ(\text{cell B}) = (0.96462)(1.00033) = 0.96494$ V with an uncertainty of about 0.02 mV, and those of Mellon and Henderson⁽⁷⁰⁾ yield $E^\circ(\text{cell B}) = (0.96466 \pm 0.00002)(1.00033) = 0.96498 \pm 0.00002$ V, all at 25.00°C. These three studies reported precise and highly consistent results, and their average of 0.96496 ± 0.00002 V was selected. In contrast, the recent measurements of Fusi and Mussini⁽¹⁷⁾ yield $E^\circ(\text{cell B}) = 0.96631 \pm 0.00092$ V, which is significantly less precise and is discrepant by 1.35 mV from the other three values. This later study is not considered further.

Clegg *et al.*⁽²⁵⁾ derived a self-consistent pair of $E^\circ\{\text{PbSO}_4(\text{cr})|\text{Pb}(\text{Hg}) + \text{SO}_4^{2-}(\text{aq})\}$ and $E^\circ\{\text{Hg}_2\text{SO}_4(\text{cr})|2\text{Hg}(\text{l}) + \text{SO}_4^{2-}(\text{aq})\}$ values from analysis of the emfs for reversible electrochemical cells containing $\text{H}_2\text{SO}_4(\text{aq})$. At 25.00°C, their standard potentials yield $E^\circ(\text{cell B}) = -(-0.35277 \pm 0.00003) + (0.61236 \pm 0.00006) = 0.96513 \pm 0.00007$ V, which agrees to 0.17 mV with the selected value of 0.96496 ± 0.00003 V.

Cells (D) and (E) are concentration cells without transport.^(73,74) The overall reaction for cells (D) and (E) is thus simply



The corresponding equations for the emf are

$$E(\text{cell D}) \text{ or } E(\text{cell E}) = (RT/2F)\ln\{a(\text{Na}_2\text{SO}_4)/a_r(\text{Na}_2\text{SO}_4)\} \tag{7}$$

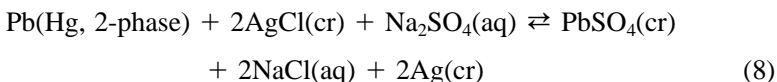
where $a_r(\text{Na}_2\text{SO}_4)$ is the activity of $\text{Na}_2\text{SO}_4(\text{aq})$ at the reference solution molality. Since both Åkerlöf⁽⁷³⁾ and Harned and Hecker⁽⁷⁴⁾ used the same reference molality of 0.05, in principle their emfs at 25.00°C should be the same at any given molality. However, at high molalities there were actually differences of up to 3 mV. Comparisons of these emfs to isopiestic and other vapor pressure data indicate that those of Åkerlöf are erroneous, probably

due to some kind of electrode failure, whereas those of Harned and Hecker are fairly accurate.

Both Shibata and Murata⁽⁶⁸⁾ and Rondinini *et al.*⁽¹⁶⁾ studied cell (A), but performed series of experiments with slightly different concentrations of sodium metal in the amalgam. Thus the emfs of each series are displaced slightly from the others because of the $(RT/F)\ln a(\text{Na}, x, \text{Hg})$ term in Eq. (3). A preliminary comparison was made of the quality and consistency of each set by taking the difference in emf for each experiment of a particular series relative to the emf at some fixed experimental molality. This effectively transforms the emfs to those for an equivalent concentration cell without transference. These comparisons indicate that the emfs of Shibata and Murata, except for the experiments at 0.049*m*, are generally internally consistent to 0.2 mV and agree about as well with the emfs of Harned and Hecker.⁽⁷⁴⁾ However the highest molality point of Shibata and Murata⁽⁶⁸⁾ at 1.975*m* at 25.00°C could not be analyzed since it was their only experiment with that particular sodium amalgam concentration. These comparisons also indicate that the various series of experiments of Rondinini *et al.*⁽¹⁶⁾ are mostly consistent to about 0.4–0.5 mV with a few experiments having significantly larger deviations. Because of this larger scatter, their emfs were not included in subsequent calculations.

A similar comparison of the measurements of Fusi and Mussini⁽¹⁷⁾ for cell (F) indicates that their emfs for any given Na₂SO₄(aq) molality with different NaCl(aq) solutions in the reference solution compartment are completely consistent relative to the emf of the 0.1000*m* Na₂SO₄(aq) solution with the same NaCl(aq) reference molality. However, their emfs sometimes have large discrepancies when the Na₂SO₄(aq) solution was changed. For example, the emfs for the two series of experiments with 0.6667*m* Na₂SO₄(aq) differ by 0.86 mV, emfs for the two series with 1.3333–1.3334*m* Na₂SO₄(aq) differ by 0.4 mV, and the emfs for the experiments with 2.0000 and 2.6665*m* are about 1 to 1.5 mV lower than expected from isopiestic and other emf data. The emfs of Åkerlöf⁽⁷³⁾ show even larger deviations, of opposite sign.

The overall reaction for cell (F) is



Emfs of cell (F) used by Fusi and Mussini⁽¹⁷⁾ depend on the ratios of the thermodynamic activities of NaCl(aq) and Na₂SO₄(aq)

$$E(\text{cell F}) = E^\circ(\text{cell F}) + (RT/2F)\ln\{a(\text{Na}_2\text{SO}_4)/a(\text{NaCl})^2\} \quad (9)$$

where $a(\text{NaCl})$ is the activity of NaCl(aq) and $E^\circ(\text{cell F}) = -E^\circ\{\text{PbSO}_4(\text{cr})|\text{Pb(Hg)} + \text{SO}_4^{2-}(\text{aq})\} + E^\circ\{\text{AgCl(cr)}|\text{Ag(cr)} + \text{Cl}^-(\text{aq})\}$. The

required activity coefficients of NaCl(aq) were calculated from the equation of Archer.⁽²³⁾

Solutions of Na₂SO₄(aq) used in the emf measurements were saturated with PbSO₄, with Hg₂SO₄, or with both. Corrections to the emfs for dissolution of electrode material are negligible at the molalities of Na₂SO₄(aq) used in these studies.

3.5. Enthalpies of Dilution and Heat Capacities

The molar enthalpies of dilution, $\Delta_{\text{dil}}H_{\text{m}}$, of Na₂SO₄(aq) have been reported in 14 studies^(18,19,77–88) which, in combination, cover wide ranges of molality at temperatures mainly between about 15 and 150.50°C, with some results by Plake⁽⁷⁹⁾ and Gritsus *et al.*⁽⁸⁴⁾ below 15°C. Above 100.2°C, however, the only enthalpy of dilution measurements are those of Mayrath and Wood⁽⁸⁸⁾ at 150.50°C. (See Table VII for a summary of these studies.)

The enthalpy of dilution is related to the difference between the relative apparent molar enthalpies of the solutions at the final and initial molalities

$$\Delta_{\text{dil}}H_{\text{m}} = L_{\phi}(m_{\text{f}}) - L_{\phi}(m_{\text{i}}) \quad (10)$$

In all but one of these studies there was sufficient information provided to analyze the dilution enthalpies using this equation. Snipes *et al.*⁽⁸⁷⁾ only reported $L_{\phi}(m_{\text{i}})$, based on their own extrapolations to obtain $L_{\phi}(m_{\text{f}})$ and there was insufficient information to allow a rigorous recalculation. Also, comparisons of the results of Snipes *et al.* with other sources of thermodynamic data and with the dependence of their own $L_{\phi}(m_{\text{i}})$ values on molality, indicates that the sign of $L_{\phi}(m_{\text{i}})$ at 40°C at the two highest molalities of 1.208 and 1.504 should be negative rather than positive.

Table VII also summarizes the published studies of heat capacities of Na₂SO₄(aq),^(8,11,18,20,89–95) which mainly cover the temperature range of 25.00 to 299.59°C, with a few measurements at lower temperatures. The earlier determinations^(89–93) were performed with traditional calorimetry while the others were done mainly with flow microcalorimetry.^(8,11,18,94,95) The latter method generally yields significantly more precise values of the apparent molar heat capacity $C_{\text{p},\phi}$, especially at lower molalities. Conti *et al.*⁽²⁰⁾ reported heat capacities from 60.00 to 220.00°C obtained from drop calorimetry (relative enthalpy) measurements.

Gardner *et al.*⁽⁹⁶⁾ obtained values of the solute heat capacity at infinite dilution by use of the “integral heat” method. This method involves determination of the enthalpy of solution of a solid, in this case Na₂SO₄(cr), to form an extremely dilute solution, which is then extrapolated to infinite dilution to obtain the standard enthalpy of solution $\Delta_{\text{sol}}H_{\text{m}}^{\circ}$. These measurements are performed as a function of temperature, and the temperature dependence of

Table VII. Summary in Chronological Order of Available Calorimetric Data (Enthalpies and Heat Capacities) for Na₂SO₄(aq) at Various Temperatures

<i>m</i> Range	<i>t</i> (°C)	No. of points	Property ^a	Rel. Wt. ^b	Ref.
0.00028–0.002 ^c	25?	1	$\Delta_{\text{dil}}H$	1	Lange and Meßner (77)
0.00016–0.1 ^c	25	18	$\Delta_{\text{dil}}H$	1	Lange and Streeck (78)
0.00025–0.5 ^c	0.26–20.3	20	$\Delta_{\text{dil}}H$	0.5(11)	Plake (79)
0.000086–0.4	15, 20, 25	28	$\Delta_{\text{dil}}H$	1(2)	Wallace and Robinson (80)
0.03–2.1	≈25	4	$\Delta_{\text{dil}}H$	0	Brodale and Giauque (81)
0.001–0.02	0.8–95 ^d	7/40 ^d	$\Delta_{\text{sol}}H/\Delta_{\text{sol}}C_p^o$	1(1)	Gardner <i>et al.</i> (96)
0.061–4.55	25.00	30	$\Delta_{\text{dil}}H$	0	Gritsus <i>et al.</i> (82)
0.0135–1.25	25	2	$\Delta_{\text{dil}}H$	0	Greyson and Snell (83)
0.014–3.63	11, 50	43	$\Delta_{\text{dil}}H$	0	Gritsus <i>et al.</i> (84)
0.25–3.0	25	14	$\Delta_{\text{dil}}H$	1(4)	Thompson <i>et al.</i> (85)
0.18–0.99	30	6	$\Delta_{\text{dil}}H$	0.2	Leung and Millero (86)
0.003?–1.5	40.00	9	$\Delta_{\text{dil}}H$	0.1(1)	Snipes <i>et al.</i> (87)
0.003?–1.6	60, 80	11	$\Delta_{\text{dil}}H$	0	Snipes <i>et al.</i> (87)
0.0026–2.1	100, 150.5	25	$\Delta_{\text{dil}}H$	Var.(7)	Mayrath and Wood (88)
0.025–1.4	100	6(0?) ^e	$\Delta_{\text{dil}}H$	0.1(1)	Conti <i>et al.</i> (18)
0.50–1.50	40.0–100.2	28	$\Delta_{\text{dil}}H$	0.1(7)	Rumpf <i>et al.</i> (19)
0.28–1.1	~21.5	3 ^f	C_p	0	Marignac (89)
0.04–1.6	25.0	13 ^g	C_p	1(3)	Randall and Rossini (90)
Sat. ^h	35–95	6	C_p	NA ⁱ	Kobe and Anderson (91)
1.5–2.9	~24, ~43, ~86	6	C_p	0	D'Ans and Tollert (92)
0.14–0.77	80–180	30(20) ^e	C_p	1(1)	Likke and Bromley (93)
0.022–0.33	25.00	7 ^j	C_p	1	Perron <i>et al.</i> (94)
0.038–0.29	25.00	15 ^j	C_p	1	Olofsson <i>et al.</i> (95)
0.05–2.6	31–202	63(34) ^e	C_p	1(7) ⁱ	Rogers and Pitzer (8)
0.05–1.5	140–300	67(0) ^e	C_p	NA ⁱ	Pabalan and Pitzer (11)
0.05–1.0	50–200	13(0) ^e	C_p	NA ⁱ	Conti <i>et al.</i> (18)
1.0–3.0	60–220	45(25) ^e	$\Delta H(T)/C_p$	1(4)	Conti <i>et al.</i> (20)

^a Abbreviations used for the experimental methods: $\Delta_{\text{dil}}H$ denotes enthalpy of dilution; $\Delta_{\text{sol}}H$ enthalpy of solution; $\Delta H(T)$ relative enthalpy (drop calorimetry); and C_p heat capacity. The $\Delta_{\text{sol}}H$ solution measurements were used by Gardner *et al.* (Ref. 96) to derive the enthalpies of solution to form an infinitely dilute solution and those values were then used by them to derive the heat-capacity change for dissolution to form an infinitely dilute solution. The $\Delta_{\text{sol}}H(T)$ measurements yield $\Delta_{\text{sol}}C_p$ values from differentiation of their dependence on temperature.

^b A few data points from otherwise reliable data sets were given zero weights in the least-squares fits. The number of these rejected points is given in parentheses. For the enthalpy of dilution studies the rejected points are: the solution with the initial molality of 0.0501 (experiment with final molality of 0.00100) at 20.08°C and the last ten tabulated values from the study of Plake (Ref. 79); the two solutions with initial molalities of 0.4014 at 15°C from the study of Wallace and Robinson (Ref. 80); solutions with initial molalities of 0.02112 at 100.00°C, and 0.01040, 0.01467, 0.02122, 0.03135, 0.04320, and 1.579 at 150.50°C from the study of Mayrath and Wood (Ref. 88); solutions with initial molalities of 0.7121, 1.016, 1.648, and 3.000 (experiment with final molality of 0.9566) at 25°C from the study of Thompson *et al.* (Ref. 85); the solution with an initial molality of 1.504 at 40.00°C from the study of

Table VII. Continued.

Snipes *et al.* (Ref. 87); the solution with the initial molality of 0.0502 from the study of Conti *et al.* (Ref. 18); solution with an initial molality of 1.001 (experiment with final molality of 0.3644) at 40.0°C and all results at 100.2°C from the study of Rumpf *et al.* (Ref. 19). For the heat-capacity studies the rejected points are: 0.1435*m* at 80.00°C from the study of Likke and Bromley (Ref. 93); 0.995*m* at 60.00°C, 1.496 and 2.526*m* at 120.00°C, and 1.496*m* at 140.00°C from the study of Conti *et al.* (Ref. 20); 0.0418, 0.0834, and 0.7090*m* from the study of Rossini (Ref. 90); 1.9406*m* at 31.47°C, 0.0500*m* at 50.85°C, 0.0500, 0.1092, and 2.0393*m* at 76.03°C, and 0.0528 and 0.0995*m* at 140.75°C from the study of Rogers and Pitzer (Ref. 8); and the $C_{p,\phi}^o$ value at 90.08°C from the study of from Gardner *et al.* (Ref. 96). Variable weights were assigned to the data of Mayrath and Wood, (Ref. 88), based on the reported uncertainties of their enthalpies of dilution.

^cThe reported concentration units for these three studies are mol-dm⁻³. Lange and Meßner (Ref. 77) did 4 replicate experiments with the same initial and final molalities, and Lange and Streeck (Ref. 78) did 51 experiments with 18 different combinations of initial and final concentrations.

^dGardner *et al.* (Ref. 96) measured 69 $\Delta_{\text{sol}}H$ values for Na₂SO₄(cr) into water at various temperatures from 0.81 to 95.00°C and report the 40 average values. These results were used by them to derive values of $\Delta_{\text{sol}}C_p^o$ at seven temperatures from 2.67 to 90.08°C.

^eThe first number is the number of reported data points. When a number in parentheses is also given, that number is the number of points that falls within the temperature and pressure range of the present model.

^fMarignac (Ref. 89) did three experiments with a temperature rise of 5°C and four with a temperature rise of 32°C, but only reported the resulting average heat capacities. The temperature rise during the latter four experiments was so large that no meaningful results could be derived from the reported heat capacities.

^gOnly smoothed results were given in the published report. The experimental heat capacities were obtained from Rossini's thesis (Ref. 90).

^hKobe and Anderson (Ref. 91) measured heat capacities of saturated solutions. These results were not reanalyzed since each reported heat capacity is the average of experimental measurements for saturated solutions over a 10°C temperature range, where the solubilities vary considerably. In addition, the original measurements involved mixtures of liquid and solid phases and insufficient information was provided to assess the corrections made for the changing amounts of solid phase(s).

ⁱNA denotes that the data from these studies were not reanalyzed since they were measured at higher pressures of up to 20 MPa (Refs. 11 and 18). Similarly, the higher-pressure heat capacities of Rogers and Pitzer (Ref. 8) also were not reanalyzed. In addition, the measurements of Kobe and Anderson (Ref. 91) were not reanalyzed since they did not report sufficient information.

^jThe experimental results are not given in these reports but are available as deposited data.

$\Delta_{\text{sol}}H_m^o$ is used to derive the corresponding standard heat capacity change during dissolution.

We examined the enthalpies of solution of Gardner *et al.*⁽⁹⁶⁾ as follows. They performed from three to seven solution experiments at each of eight different temperatures from 0.81 to 95.00°C. Differences between these enthalpies of solution to form solutions with different final molalities, at any particular fixed temperature, were used to construct the equivalent of 40

enthalpies of dilution relative to infinite dilution. However, these derived values of $\Delta_{\text{dil}}H$ showed molality-dependent skewing compared to other available enthalpy of dilution data. At least part of this discrepancy results because these calculations involve the relatively small differences of two large solution enthalpies. In contrast, their derived values of $C_{p,\phi}^\circ$ from 2.67 to 72.72°C are compatible with results from other heat-capacity studies and are included in our subsequent model calculations.

Vichutinskii and Golikov⁽⁹⁷⁾ made enthalpy of dilution measurements at 10 and 18°C for low concentrations of $\text{Na}_2\text{SO}_4(\text{aq})$. However, since no experimental data were presented, no useful information could be derived from that study.

Most of the calorimetric measurements at or below 100°C were made at an ambient laboratory pressure of ≈ 0.1 MPa. Some of the higher temperature measurements were made at or slightly above the saturation vapor pressure of the solution,^(8,20,88,93) whereas others were made at some fixed pressure ranging up to 20 MPa.^(11,18) These enthalpies of dilution and heat capacities at higher pressures could be converted to values at 1 bar (below 100°C) or at the saturation vapor pressure of the solution (above 100°C) using available volumetric data.⁽⁹⁸⁾ However, since there are sufficient calorimetric data at ambient pressures to constrain our model, most of the higher-pressure results were not reanalyzed.

The one exception was the dilution enthalpy results of Conti *et al.*⁽¹⁸⁾ They performed six enthalpy of dilution experiments for $\text{Na}_2\text{SO}_4(\text{aq})$ at 100°C at some pressure above ambient, but they did not report the actual pressure used. However, their measurements for $\text{NaOH}(\text{aq})$ were described as being measured at 1 MPa. If the measurements for $\text{Na}_2\text{SO}_4(\text{aq})$ were also performed at 1 MPa, the calculated corrections to convert the enthalpies of dilution from 1 to 0.1 MPa vary from 4 to 30 J·mol⁻¹. Inasmuch as we are not certain that the measurements were made at 1 MPa, and because these corrections are smaller than the precision of the measurements, these pressure corrections were neglected and the data were taken as being equal to those at a pressure of 0.1 MPa.

Thompson *et al.*⁽⁸⁵⁾ rejected the 25°C dilution enthalpy measurements of Gritsus *et al.*⁽⁸²⁾ as being in error by up to 1.6 kJ·mol⁻¹ at high molalities and both Rogers and Pitzer⁽⁸⁾ and Holmes and Mesmer⁽¹⁰⁾ similarly rejected the Gritsus *et al.*⁽⁸⁴⁾ measurements at 50°C as being incompatible with other thermodynamic data. The 11°C measurements of Gritsus *et al.*⁽⁸⁴⁾ were not discussed,^(8,10,85) but were found in this study to also be inconsistent with dilution enthalpies from other laboratories.

Kobe and Anderson⁽⁹¹⁾ measured heat capacities of saturated solutions containing variable amounts of solid phase(s). Since the reported heat capacities were averages of measurements involving 10°C temperature changes,

over which the solubility changes considerably, no reliable results could be derived from this study.

The very early heat-capacity measurements of Marignac⁽⁸⁹⁾ involved temperature rises of 5°C or more during the measurement. In addition, there are uncertainties concerning calibration factors, energy unit conversions, molar masses, etc., which make it impossible to properly correct their data to modern values of these quantities. D'Ans and Tollert⁽⁹²⁾ only reported their temperature rises to the nearest 0.1°C, which suggests that the heat-capacity measurements were not very precise. The results from these two studies were consequently rejected.

Published values of the heat capacities were converted to apparent molar heat capacities using the heat capacities of H₂O(l) calculated from the equation of state of Hill,⁽⁹⁹⁾ whose equation was chosen to maintain consistency with the Debye–Hückel limiting slopes of Archer and Wang.⁽¹⁰⁰⁾

3.6. Relative Weights and Least-Squares Fitting

Relative weights w_r were assigned to each data set, which reflect our assessment of their accuracy and precision relative to other measurements of the same property. The available thermodynamic data were reanalyzed to yield one of four different properties: ϕ , emf, $\Delta_{\text{dil}}H_m \{= L_\phi(m_f) - L_\phi(m_i)\}$, or $C_{p,\phi}$. Unit relative weights were assigned to the higher quality data and zero weights to inaccurate and discrepant data. A few data points and sets of intermediate quality were assigned reduced weights. In addition, isopiestic data sets involving two or three reference standards were given fractional weights for each reference standard such that the total weight at each Na₂SO₄(aq) molality was appropriate for the overall quality of that data set. The precision of the enthalpies of dilution of Mayrath and Wood⁽⁸⁸⁾ varied significantly for different molality regions and the values of w_r were adjusted to reflect this.

Some trial fits of the models described below gave an accurate representation of the osmotic coefficients at 25.00°C, but exhibited increasing systematic deviations at higher temperatures. Isothermal fits of the models to the same data base gave better agreement between model and experiment. This difficulty arises in part from the disproportionate amount of isopiestic data at 25.00°C compared to other temperatures. For example, there are 161 values of ϕ given nonzero weight at 25.00°C, 49 values at 50.00°C, 28 values at 109.99°C, and 18 values at 140.08°C. To partially compensate for the lesser amount of isopiestic data at higher temperatures, higher weights were assigned to the isopiestic results of Table III and to those of Holmes and Mesmer.⁽⁹⁾

The different properties vary in the precision of their determination and in their contribution to the model parameters. For example, ϕ for higher-

quality isopiestic measurements are typically uncertain by 0.1–0.2%, whereas emfs may be precise to 1×10^{-4} V and this difference should be reflected in the weights given to the individual data sets in the model fits. Consequently, each property was assigned a property weight w_p and the actual weights given to the individual data points in the least-squares models were $w_r \cdot w_p$. The assigned values are $w_p = 2 \times 10^3$ for ϕ , $w_p = 5 \times 10^4$ for emfs, $w_p = 2 \times 10^{-5}$ for $\Delta_{\text{dil}}H_m$, and $w_p = 2.5 \times 10^{-4}$ for $C_{p,\phi}$. These values of w_p were obtained as described by Clegg *et al.*⁽²⁵⁾ They were determined from the inverse of the sum of the squares of the deviations for each property from a preliminary model fit, using Eq. (22) of Clegg *et al.*,⁽²⁵⁾ and some minor adjustments of the w_p were made subsequently, to reflect the overall consistency of each property type relative to the entire thermodynamic data base for $\text{Na}_2\text{SO}_4(\text{aq})$.

All of the least-squares model parameter evaluations were performed using the generalized nonlinear least-squares computer fitting routine “E04FDF” as described in ref. 111 of Clegg *et al.*⁽²⁵⁾

4. CONSIDERATION OF ION PAIRING AND HYDROLYSIS

Solutions of $\text{Na}_2\text{SO}_4(\text{aq})$ undergo some association to form $\text{NaSO}_4^-(\text{aq})$ ion pairs.⁽¹⁰¹⁾ The extent of ionic association for $\text{Na}_2\text{SO}_4(\text{aq})$ is significantly less than for solutions of $\text{H}_2\text{SO}_4(\text{aq})$ ⁽²⁵⁾ at comparable temperatures and molalities, and the formation constant for $\text{NaSO}_4^-(\text{aq})$ is far less well characterized than the formation constant for $\text{HSO}_4^-(\text{aq})$. For example, the thermodynamic association constants listed by Oscarson *et al.*⁽¹⁰¹⁾ at 25°C yield $K_a(\text{NaSO}_4^-) = 6.6 \pm 3.7$ (56% uncertainty), whereas the information summarized by Clegg *et al.*⁽²⁵⁾ yields $K_a(\text{HSO}_4^-) = 95.2 \pm 2.7$ (2.8% uncertainty). Because of this very large uncertainty in $K_a(\text{NaSO}_4^-)$, the dissociation enthalpy for this ion pair is poorly known and the corresponding heat-capacity change entirely unknown. This makes it nearly impossible to properly constrain any thermodynamic model that includes the $\text{NaSO}_4^-(\text{aq})$ ion-pair. Figure 4 of Oscarson *et al.*,⁽¹⁰¹⁾ which compares their results for the temperature dependence of $\log_{10}K_a(\text{NaSO}_4^-)$ to those reported in two other studies, illustrates this difficulty quite clearly. However, the previous reviews^(6,7,10–12) of $\text{Na}_2\text{SO}_4(\text{aq})$ have established that it is still possible to model its thermodynamic properties by neglecting the presence of $\text{NaSO}_4^-(\text{aq})$ and thus by formally treating $\text{Na}_2\text{SO}_4(\text{aq})$ as a fully dissociated electrolyte, which we do here.

Bisulfate ion formation is extensive enough that it must be considered explicitly when modeling the thermodynamic properties of $\text{H}_2\text{SO}_4(\text{aq})$.⁽²⁵⁾ Some hydrolysis also occurs in solutions of $\text{Na}_2\text{SO}_4(\text{aq})$ to yield small amounts of $\text{HSO}_4^-(\text{aq})$ ions. At “room temperature,” the pHs of air-saturated

$\text{Na}_2\text{SO}_4(\text{aq})$ solutions⁽¹⁰²⁾ are ≤ 8.2 , which implies that the amount of hydrolysis is quite small. Although the extent of formation of $\text{HSO}_4^-(\text{aq})$ increases with increasing temperature, at the temperatures under consideration in this review its concentrations are fairly low and thus hydrolysis can be neglected in the analysis of thermodynamic data.

5. ANALYSIS USING EXTENDED ION-INTERACTION (PITZER) MODEL AT 25.00 AND 50.00°C

We represent the available thermodynamic data for $\text{Na}_2\text{SO}_4(\text{aq})$ using Pitzer's model, as revised by Archer^(22,23) to include an ionic-strength dependent third virial coefficient. The following equations use the notation introduced by Clegg *et al.*⁽²⁵⁾

Pitzer's equation and Archer's extension of Pitzer's equation may be written in the general form for the osmotic coefficient of $\text{Na}_2\text{SO}_4(\text{aq})$

$$\phi - 1 = -2A_\phi I^{1/2}/(1 + bI^{1/2}) + (4/3)mB_{\text{M},\text{X}}^\phi + (16/3)m^2C_{\text{M},\text{X}}^{\text{T}\phi} \quad (11)$$

where M denotes Na^+ , X denotes SO_4^{2-} , and m is the stoichiometric molality. Here $b = 1.2 \text{ kg}^{1/2}\text{-mol}^{-1/2}$, A_ϕ is the Debye–Hückel limiting slope for osmotic coefficients, and the ionic strength is the stoichiometric value $I = 3m$. The quantities $B_{\text{M},\text{X}}^\phi$ and $C_{\text{M},\text{X}}^{\text{T}\phi}$ are defined by

$$B_{\text{M},\text{X}}^\phi = \beta_{\text{M},\text{X}}^{(0)} + \beta_{\text{M},\text{X}}^{(1)} \exp(-\alpha_{\text{M},\text{X}} I^{1/2}) \quad (12)$$

and

$$C_{\text{M},\text{X}}^{\text{T}\phi} = C_{\text{M},\text{X}}^{(0)} + C_{\text{M},\text{X}}^{(1)} \exp(-\omega_{\text{M},\text{X}} I^{1/2}) \quad (13)$$

where $\alpha_{\text{M},\text{X}}$ is usually assigned a value of $2.0 \text{ kg}^{1/2}\text{-mol}^{-1/2}$ except for the divalent metal sulfates.⁽²¹⁾ Mean activity coefficients γ_\pm of $\text{Na}_2\text{SO}_4(\text{aq})$ are given by

$$\begin{aligned} \ln \gamma_\pm = & -2A_\phi \{I^{1/2}/(1 + bI^{1/2}) + (2/b) \ln(1 + bI^{1/2})\} + (4/3)m[2\beta_{\text{M},\text{X}}^{(0)} \\ & + 2(\beta_{\text{M},\text{X}}^{(1)}/\alpha_{\text{M},\text{X}}^2 I) \{1 - (1 + \alpha_{\text{M},\text{X}} I^{1/2} - \alpha_{\text{M},\text{X}}^2 I/2) \exp(-\alpha_{\text{M},\text{X}} I^{1/2})\}] \\ & + (8/3)m^2[3C_{\text{M},\text{X}}^{(0)} + 4C_{\text{M},\text{X}}^{(1)} \{6 - (6 + 6\omega_{\text{M},\text{X}} I^{1/2} + 3\omega_{\text{M},\text{X}}^2 I + \omega_{\text{M},\text{X}}^3 I^{3/2} \\ & - \omega_{\text{M},\text{X}}^4 I^2/2) \exp(-\omega_{\text{M},\text{X}} I^{1/2})\}/(\omega_{\text{M},\text{X}}^4 I^2)] \end{aligned} \quad (14)$$

The corresponding expressions for the relative apparent molar enthalpy L_ϕ and apparent molar heat capacity $C_{\text{p},\phi}$ at constant pressure are

$$L_\phi = 6A_\text{H} \ln(1 + bI^{1/2})/2b - 4RT^2(mB_{\text{M},\text{X}}^{\text{L}} + 2m^2C_{\text{M},\text{X}}^{\text{L}}) \quad (15)$$

$$C_{\text{p},\phi} = C_{\text{p},\phi}^\circ + 6A_\text{C} \ln(1 + bI^{1/2})/2b - 4RT^2(mB_{\text{M},\text{X}}^{\text{C}} + 2m^2C_{\text{M},\text{X}}^{\text{C}}) \quad (16)$$

where A_H and A_C are the Debye–Hückel limiting slopes for enthalpy and heat capacity, respectively. The Pitzer parameters in these expressions are defined by

$$B_{M,X}^L = (\partial\beta_{M,X}^{(0)}/\partial T)_p + 2(\partial\beta_{M,X}^{(1)}/\partial T)_p \{1 - (1 + \alpha_{M,X}I^{1/2}) \times \exp(-\alpha_{M,X}I^{1/2})\}/\alpha_{M,X}^2I \quad (17)$$

$$C_{M,X}^L = (\partial C_{M,X}^{(0)}/\partial T)_p + 4(\partial C_{M,X}^{(1)}/\partial T)_p \{6 - (6 + 6\omega_{M,X}I^{1/2} + 3\omega_{M,X}^2I + \omega_{M,X}^3I^{3/2}) \times \exp(-\omega_{M,X}I^{1/2})\}/(\omega_{M,X}^4I^2) \quad (18)$$

$$B_{M,X}^C = (\partial^2\beta_{M,X}^{(0)}/\partial T^2)_p + (2/T)(\partial\beta_{M,X}^{(0)}/\partial T)_p + 2\{(\partial^2\beta_{M,X}^{(1)}/\partial T^2)_p + (2/T) \times (\partial\beta_{M,X}^{(1)}/\partial T)_p\} \{1 - (1 + \alpha_{M,X}I^{1/2}) \exp(-\alpha_{M,X}I^{1/2})\}/\alpha_{M,X}^2I \quad (19)$$

$$C_{M,X}^C = (\partial^2C_{M,X}^{(0)}/\partial T^2)_p + (2/T)(\partial C_{M,X}^{(0)}/\partial T)_p + 4\{(\partial^2C_{M,X}^{(1)}/\partial T^2)_p + (2/T)(\partial C_{M,X}^{(1)}/\partial T)_p\} \{6 - (6 + 6\omega_{M,X}I^{1/2} + 3\omega_{M,X}^2I + \omega_{M,X}^3I^{3/2}) \times \exp(-\omega_{M,X}I^{1/2})\}/(\omega_{M,X}^4I^2) \quad (20)$$

Values of the Debye–Hückel limiting slope A_ϕ and its derivatives A_H and A_C were calculated up to 100°C using the Chebychev (Chebyshev) series of Clegg *et al.*,⁽²⁵⁾ which is based on the critical evaluation of the relative permittivity (dielectric constant) of water by Archer and Wang.⁽¹⁰⁰⁾ Above 100°C, the Debye–Hückel limiting slopes (A_ϕ , A_H/RT , A_C/R) were evaluated at the vapor pressure of pure water using the equation of Archer and Wang and those values from 100 to 157°C were then represented as power series in the absolute temperature.

A considerable effort was made to represent the more accurate thermodynamic data for Na₂SO₄(aq) with Eqs. (11–20) for temperatures ranging from the freezing temperatures to 150°C. Eq. (11–20) gave an excellent nearly quantitative representation of the available 25.00°C data using the traditional value of $\alpha_{M,X} = 2.0 \text{ kg}^{1/2}\cdot\text{mol}^{-1/2}$.⁽²¹⁾ Good fits were also obtained at lower temperatures, but the available data are far less complete and usually restricted to smaller molality regions. Reasonable quality fits were obtained at temperatures of 50°C and higher, but there were significant systematic differences between experimental thermodynamic values and those calculated from the optimized model parameters.

The authors of previous Pitzer models for Na₂SO₄(aq) also reported difficulties in representing the higher temperature thermodynamic data for this system. Holmes and Mesmer^(9,10) and Hovey *et al.*⁽¹²⁾ found that assigning the smaller value of 1.4 or 1.7 $\text{kg}^{1/2}\cdot\text{mol}^{-1/2}$ to $\alpha_{M,X}$ gave a significant improvement of the model fits to the usual form of Pitzer's equation without an ionic-strength dependence for $C_{M,X}$. However, Holmes and Mesmer⁽⁹⁾

found that while $\alpha_{M,X} = 1.4 \text{ kg}^{1/2}\cdot\text{mol}^{-1/2}$ gave an improved representation for isothermal fits to the higher temperature osmotic coefficients, the value $\alpha_{M,X} = 2.0 \text{ kg}^{1/2}\cdot\text{mol}^{-1/2}$ gave slightly better results at 25.00°C. Our calculations using the Archer-type extension^(22,23) of Pitzer's equation with the ionic-strength dependent $C_{M,X}^{T\phi}$ term gave similar results.

A number of different variations of Pitzer's model with an ionic-strength dependent $C_{M,X}^{T\phi}$ term were used to represent the available thermodynamic data base for $\text{Na}_2\text{SO}_4(\text{aq})$. These variations included allowing $\alpha_{M,X}$ to have values smaller than $\alpha_{M,X} = 2.0 \text{ kg}^{1/2}\cdot\text{mol}^{-1/2}$, allowing $\alpha_{M,X}$ to vary with temperature, and inclusion of a $\beta_{M,X}^{(2)}$ term which is normally used only for higher valence electrolytes (2 - 2 and higher charge types). Harvie *et al.*⁽¹⁰³⁾ have clearly demonstrated that if the dissociation constant of a complex exceeds ≈ 0.05 , then the available thermodynamic data can be represented about equally well with Pitzer's model either by recognizing the presence of this complex implicitly by use of the $\beta_{M,X}^{(2)}$ term or by neglecting it, which is the situation for $\text{Na}_2\text{SO}_4(\text{aq})$. Although all of these approaches led to some improvement in the model representation of the data base, they were incapable of representing these data to their full experimental accuracy at all molalities and temperatures.

At least some of the above difficulty arises because of the complicated molality and temperature dependences of the thermodynamic properties of $\text{Na}_2\text{SO}_4(\text{aq})$. For example, the osmotic coefficients of many electrolytes at a fixed molality have a regular increase with increasing temperature at lower temperatures, go through maxima, but then decrease monotonically with temperature above about 25 to 60°C.^(22-24,48,104) In contrast, for ϕ of $\text{Na}_2\text{SO}_4(\text{aq})$, these maxima occur at higher temperatures.⁽¹⁰⁾ Figures 1 through 3 illustrate the temperature dependences of ϕ , L_ϕ , and $C_{p,\phi}$, respectively.

It is likely that the extended Pitzer models will be able to represent the available thermodynamic data for $\text{Na}_2\text{SO}_4(\text{aq})$ to essentially full experimental accuracy provided that one or more fourth virial terms are added to the equations. However, each of the fourth virial coefficients would require several parameters to represent its dependence on temperature, which would then result in a large number of additional parameters for the extended Pitzer models.

We found that an accurate representation of the thermodynamic properties of $\text{Na}_2\text{SO}_4(\text{aq})$ could be obtained for wide ranges of both molality and temperature without introducing speciation or higher-order terms, based on use of the mole fraction composition scale rather than the molalities. That model is described in the next section.

Table VIII contains the evaluated parameters for Eq. (11-14) for temperatures of 25 and 50°C, along with related information. At 25°C, the extended Pitzer model with an ionic-strength dependent third virial coefficient gives

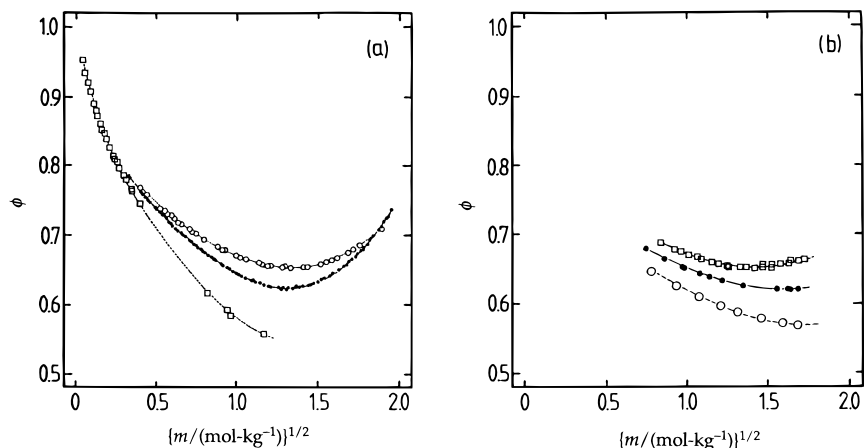


Fig. 1. Osmotic coefficients of $\text{Na}_2\text{SO}_4(\text{aq})$ as a function of the square root of molality at various selected temperatures: (a) \square , 0°C and at the freezing temperatures; \bullet , 25°C ; \circ , 50°C . (b) \square , 80.22°C ; \bullet , 109.99°C ; \circ , 140.08°C .

an excellent representation of the experimental osmotic coefficients and emfs, which, for osmotic coefficients, extend about $1.85m$ above the saturation limit for $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}(\text{cr})$. We set $\omega_{\text{M},\text{X}} = 2.5 \text{ kg}^{1/2}\cdot\text{mol}^{-1/2}$ for this fit, which was the value used in our previous extended Pitzer models for $\text{H}_2\text{SO}_4(\text{aq})$ and $\text{CaCl}_2(\text{aq})$.^(25,49) However, the resulting extended Pitzer model fit at 50°C showed some small systematic deviations from the experimental osmotic coefficients for this choice of $\omega_{\text{M},\text{X}}$. These systematic deviations were eliminated by optimizing the value of $\omega_{\text{M},\text{X}}$, but, of course, $\omega_{\text{M},\text{X}}$ is now treated as an additional adjustable parameter

5. MOLE FRACTION-BASED THERMODYNAMIC MODEL

Pitzer and Simonson⁽¹⁰⁵⁾ introduced a system of thermodynamic equations for electrolyte solutions, based on the mole fraction composition scale, which is applicable to highly soluble electrolytes, including those with complete miscibility with the solvent, and to mixtures of electrolytes with nonelectrolytes. These equations contain an extended Debye–Hückel expression, along with terms resulting from a Margules expansion in the mole fractions of the individual components. Their original equations were restricted to binary and pseudobinary solutions, but several years later this approach was extended to include arbitrary mixtures of symmetrical⁽¹⁰⁶⁾ and unsymmetrical⁽¹⁰⁷⁾ electrolytes. The general equations for arbitrary mixtures are complicated at the four suffix or higher levels, and contain numerous expansion terms.^(106,107) However, for a

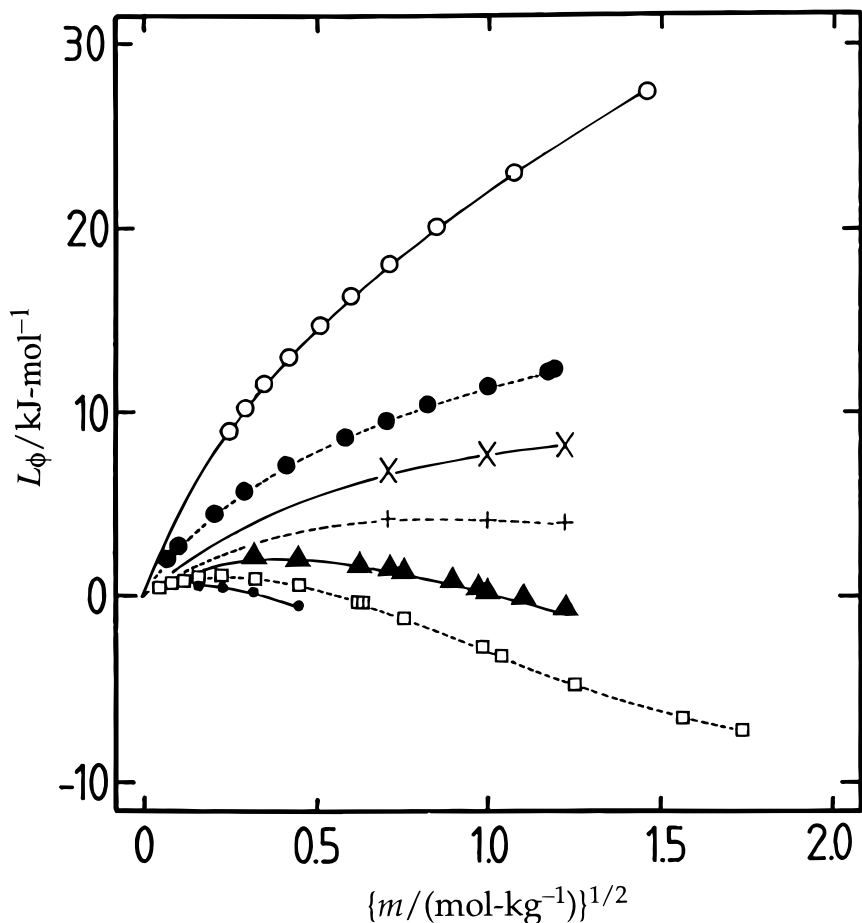


Fig. 2. Relative apparent molar enthalpies of $\text{Na}_2\text{SO}_4(\text{aq})$ as a function of the square root of molality at various temperatures: \bullet , 15°C; \square , 25°C; \blacktriangle , 40°C; $+$, 60°C; \times , 80°C; \bullet , 100°C; \circ , 150.5°C.

single binary electrolyte in a single solvent,^(106,108) the mole fraction composition model equations are greatly simplified.⁽²¹⁾

Mole fractions are defined for solutions containing one or more dissociating solutes as:

$$x_k = n_k / \sum_j n_j = m_k / \sum_j m_j \quad (21)$$

where the summation index j covers all component ionic species, undissociated solutes, and the solvent(s); n_j denotes the number of moles of each one

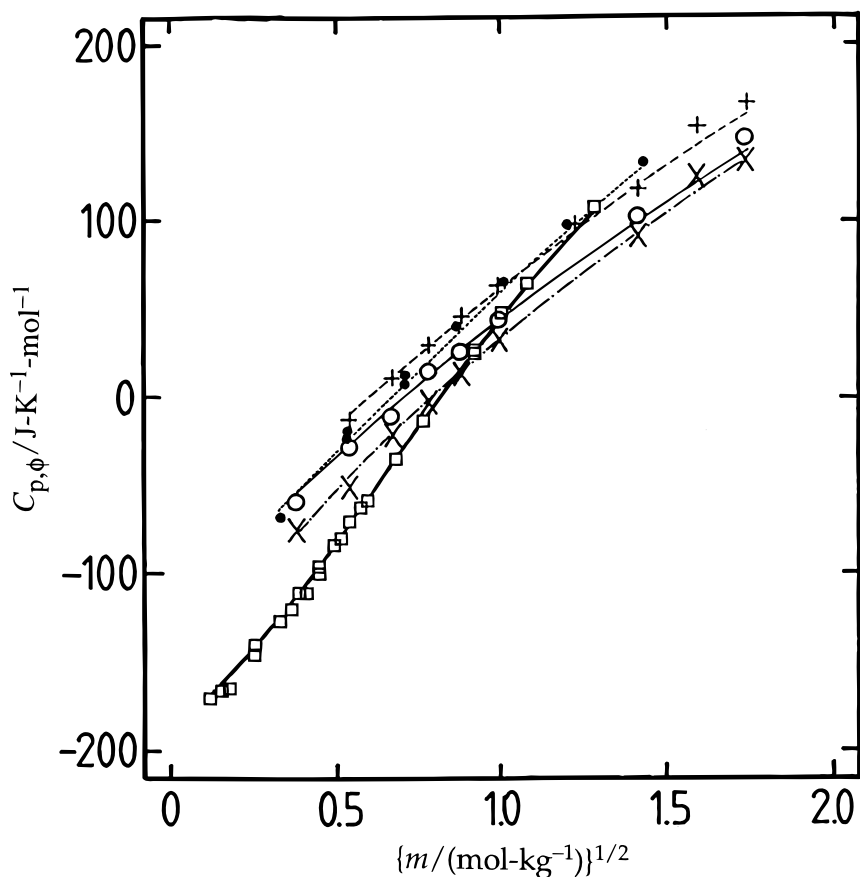


Fig. 3. Apparent molar heat capacities of $\text{Na}_2\text{SO}_4(\text{aq})$ as a function of the square root of molality at various temperatures: \square , 25°C; \bullet , 50.85°C; $+$, 80°C; \circ , 120°C; \times , 140°C.

of these components, and m_j is the corresponding molality of that component. The molality of a solvent m_S is a constant and is equal to

$$m_S = 1/M_S \quad (22)$$

where M_S is the molar mass of the solvent in units of $\text{kg}\cdot\text{mol}^{-1}$. For water $m_S = (1/0.0180153) = 55.5084 \text{ mol}\cdot\text{kg}^{-1}$. The total ionic strength of a solution on the mole fraction composition scale is given by

$$I_x = (1/2) \sum_i x_i z_i^2 \quad (23)$$

where the summation index i includes only ionic species. Also of interest is the mole fraction due to all ionic species x_I , where

Table VIII. Parameters for the $\text{Na}_2\text{SO}_4(\text{aq})$ Pitzer's Model, Standard Potentials, and Debye–Hückel Limiting Slope at 25.00°C and 50.00°C

25.00°C		50.00°C	
Parameter	Value ^a	Parameter	Value ^a
$\beta_{\text{M},\text{X}}^{(0)}$	0.011976 (0.0028)	$\beta_{\text{M},\text{X}}^{(0)}$	0.034461 (0.0041)
$\beta_{\text{M},\text{X}}^{(1)}$	0.951276 (0.00078)	$\beta_{\text{M},\text{X}}^{(1)}$	1.15412 (0.0013)
$C_{\text{M},\text{X}}^{(0)}$	0.0024359 (0.0010)	$C_{\text{M},\text{X}}^{(0)}$	0.0009888 (0.0074)
$C_{\text{M},\text{X}}^{(1)}$	0.236044 (0.0040)	$C_{\text{M},\text{X}}^{(1)}$	0.248702 (0.0079)
$\alpha_{\text{M},\text{X}}$	2.0	$\alpha_{\text{M},\text{X}}$	2.0
$\omega_{\text{M},\text{X}}$	2.5	$\omega_{\text{M},\text{X}}$	2.13808 (0.0027)
E' (cell A)	2.48381 ± 0.00024^b	A_ϕ	0.410277
E' (cell A)	2.48190 ± 0.00006^b		
A_ϕ	0.391475		

^aUnits: $\text{kg}\cdot\text{mol}^{-1}$ for $\beta_{\text{M},\text{X}}^{(0)}$ and $\beta_{\text{M},\text{X}}^{(1)}$; $\text{kg}^2\cdot\text{mol}^{-2}$ for $C_{\text{M},\text{X}}^{(0)}$ and $C_{\text{M},\text{X}}^{(1)}$; $\text{kg}^{1/2}\cdot\text{mol}^{-1/2}$ for $\alpha_{\text{M},\text{X}}$ and $\omega_{\text{M},\text{X}}$; V for E ; and $\text{kg}^{1/2}\cdot\text{mol}^{-1/2}$ for A_ϕ . The number in parentheses following a coefficient value is the standard error of that coefficient divided by the value of that coefficient. The standard deviations (weighted) of the model for each property are $\sigma(\phi) = 0.00091$ (161) and $\sigma(\text{emf}) = 0.133$ mV (17) for the fit at 25.00°C, and $\sigma(\phi) = 0.00077$ (49) for the fit at 50.00°C, where the numbers in parentheses are the number of values of that property given nonzero weight in the least-squares calculations. The maximum molalities to which these equations apply are 3.8140 at 25.00°C and 3.5686 at 50.00°C.

^b E' (cell A) = 2.48381 V when $x(\text{Na}) = 0.01818$ and E' (cell A) = 2.48190 V when $x(\text{Na}) = 0.01765$ at 25.00°C. These uncertainty limits are unweighted standard deviations.

$$x_1 = \sum_i x_i \quad (24)$$

For a single solvent system such as $\text{Na}_2\text{SO}_4(\text{aq})$, $x_1 = 1 - x_s$, where x_s is the solvent mole fraction. All subsequent equations are restricted to single solvent systems.

Activities of solvents in solutions of electrolytes or non-electrolytes are almost universally defined in terms of Raoult's law. That is, the pure solvent serves as both reference state and standard state, with solvent activity coefficients defined on the mole fraction composition scale. The activity of the solvent is given by

$$a_s = f_s x_s \quad (25)$$

where f_s is the solvent activity coefficient on this basis. The “rational” or mole fraction-based osmotic coefficient ϕ_x (sometimes denoted by g) is then defined by

$$\ln a_s = \phi_x \ln x_s = -M_s \phi (\sum_i m_i) \quad (26)$$

where the last equality allows ϕ_x to be related to the more commonly reported molality-based osmotic coefficient ϕ .

There are two commonly used reference states and several standard states for a solute, either molecular or ionic. When the solutes and solvents are completely miscible with each other, it is possible to define solute activities relative to the pure unionized solute, which then becomes both reference and standard state. However, for electrolyte mixtures made by mixing n noncommon ion electrolytes, n^2 binary electrolytes can be constructed from these ions, and different combinations of binary electrolytes can be used to define the reference state.

For most systems where the solubilities of the solute or solutes are limited, it is more convenient to define solute activities using infinite dilution as the reference state, treating the electrolyte as fully dissociated. The activity of an electrolyte of the charge type $M_{\nu_M}X_{\nu_X}$ on the mole fraction composition scale is given by

$$a(M_{\nu_M}X_{\nu_X}) = (f_M^*)^{\nu_M}(f_X^*)^{\nu_X}(x_M)^{\nu_M}(x_X)^{\nu_X} \quad (27)$$

where M denotes a cation and ν_M its stoichiometric ionization number, X denotes an anion and ν_X its stoichiometric ionization number, x_M and x_X are the mole fractions of these cations and anions, respectively, f_M and f_X are the corresponding "rational" activity coefficients on the mole fraction composition scale, and the asterisk is used to emphasize that the activity coefficients are defined by an infinite dilution reference state rather than a pure solute reference state. In the case of a single electrolyte in a single solvent, the mean mole fraction activity coefficient f_{\pm} is defined by

$$(f_{\pm}^*)^{\nu} = (f_M^*)^{\nu_M}(f_X^*)^{\nu_X} \quad (28)$$

and $\nu = \nu_M + \nu_X$ is the stoichiometric ionization number for this electrolyte.

The relationship between the activity coefficient of an ion of type k on the molality and on the mole fraction concentration scales is usually given⁽¹⁰⁶⁾ as

$$f_k^* = \gamma_k(1 + M_S \sum_i m_i) \quad (29)$$

However, it is quite easy to show that $(1 + M_S \sum_i m_i) = 1/x_S$ and thus that $f_k^* = \gamma_k/x_S$.

The equations for the activity coefficient of the solvent and for the mean activity coefficient of a single ionic solute in a single nonionized solvent on the mole fraction composition scale are taken from those given by Clegg *et al.*^(107, 108) with very minor changes in notation. These equations are:

$$\ln f_S = \ln(a_S/x_S) = 2A_X\{I_x^{3/2}/(1 + \rho I_x^{1/2})\} - x_M x_X B_{MX} \exp(-\alpha_{MX} I_x^{1/2}) + x_1^2\{W_{1,MX} + (x_1 - x_S)U_{1,MX}\} + 4x_S x_M x_X (2 - 3x_S) V_{1,MX} \quad (30)$$

$$\ln(f_{\pm}^*) = -z_M z_X A_X\{(2/\rho)\ln(1 + \rho I_x^{1/2}) + I_x^{1/2}(1 - 2I_x/z_M z_X)/(1 + \rho I_x^{1/2})\}$$

$$\begin{aligned}
& + 2z_M z_X x_I \{B_{MX} g(\alpha_{MX} I_x^{1/2}) / (z_M + z_X)^2\} - x_M x_X B_{MX} \{ (z_M z_X / 2I_x) g(\alpha_{MX} I_x^{1/2}) \\
& + (1 - z_M z_X / 2I_x) \exp(-\alpha_{MX} I_x^{1/2}) \} + (x_S - x_S x_I - 1) W_{1,MX} + 2x_S^2 x_I U_{1,MX} \\
& + 4x_S^2 x_I (2 - 3x_I) \{z_M z_X / (z_M + z_X)^2\} V_{1,MX}
\end{aligned} \quad (31)$$

The corresponding equations for the relative apparent molar enthalpy and the apparent molar heat capacity are:

$$\begin{aligned}
L_\phi &= \nu z_M z_X (A_{HX} / 2\rho) \ln(1 + \rho I_x^{1/2}) - \nu RT^2 x_I \{z_M z_X / (z_M + z_X)^2\} B_{MX}^L g(\alpha_{MX} I_x^{1/2}) \\
&+ \nu RT^2 x_I [W_{1,MX}^L - x_S U_{1,MX}^L - 4x_S^2 \{z_M z_X / (z_M + z_X)^2\} V_{1,MX}^L]
\end{aligned} \quad (32)$$

$$\begin{aligned}
C_{p,\phi} &= C_{p,\phi}^0 + \nu z_M z_X (A_{CX} / 2\rho) \ln(1 + \rho I_x^{1/2}) - \nu RT^2 x_I \{z_M z_X / (z_M + z_X)^2\} \\
&\times B_{MX}^J g(\alpha_{MX} I_x^{1/2}) + \nu RT^2 x_I [W_{1,MX}^J - x_S U_{1,MX}^J - 4x_S^2 \{z_M z_X / (z_M + z_X)^2\} \\
&\times V_{1,MX}^J]
\end{aligned} \quad (33)$$

In these equations the various “ W ”, “ U ”, and “ V ” parameters are obtained from the Margules suffix expansion, the “ B ” parameters arise from the extended Debye–Hückel terms, z_M and z_X are the absolute values of the valences of the cation and anion, respectively, and A_{HX} and A_{CX} are the Debye–Hückel limiting slopes for enthalpy and heat capacity, respectively, for the mole fraction composition scale. The B_{MX}^L parameter and its temperature derivatives, which were included in the earlier mole fraction-based models,^(107,108) are not necessary for an accurate representation of the thermodynamic properties of $\text{Na}_2\text{SO}_4(\text{aq})$. The function $g(x)$ is defined by

$$g(x) = 2\{1 - (1 + x) \exp(-x)\} / x^2 \quad (34)$$

The Debye–Hückel constant on the mole fraction composition scale A_X can be related to A_ϕ using Eqs. (44) and (I.33) from Pitzer⁽²¹⁾

$$A_X / A_\phi = (1/M_S)^{1/2} = 7.45039 \text{ mol}^{1/2} \cdot \text{kg}^{-1/2} \quad (35)$$

The same relation also occurs for A_{HX}/A_H and A_{CX}/A_C .

The temperature dependences of the parameters of the mole fraction-based model were represented by the following functions of the absolute temperature T . For the parameters $P(G)$ of the excess Gibbs energy functions (osmotic and activity coefficients), the chosen temperature dependences have the form

$$\begin{aligned}
P(G) &= (p_1/6)T^2 + (p_2/2)T - (p_4 T / 2T_{r1}^2)(T_{r1} - T)^{-1} \\
&- p_6 T^{-1} + p_7 + (p_9/3)T^3
\end{aligned} \quad (36)$$

where the reference temperature $T_{r1} = 240.00 \text{ K}$ and $P(G)$ denotes B_{MX} ,

Table IX. Parameters for the Na₂SO₄(aq) Mole Fraction-Based Model, Standard Cell Potentials, and Debye–Hückel Limiting Slopes at 25.00°C

Parameter	Value ^a	Parameter	Value ^a
B_{MX}	34.5286 (0.0016)	B_{MX}^I	-0.0106872 (0.0049)
$W_{1,MX}$	-9.07930 (0.0036)	$W_{1,MX}^I$	0.00228076 (0.0117)
$U_{1,MX}$	-15.3454 (0.0052)	$U_{1,MX}^I$	0.00654259 (0.0048)
$V_{1,MX}$	5.36653 (0.0104)	$V_{1,MX}^I$	-0.006 ^b
α_{MX}	11.0 ^b	$C_{p,\phi}^o$	-193.7 ^b
ρ	13.0 ^b	$E^{o'd}$	2.48410 ± 0.00063 ^c
B_{MX}^L	0.445963 (0.0012)	$E^{o'd}$	2.48218 ± 0.00076 ^c
$W_{1,MX}^L$	0.124631 (0.0141)	A_X	2.91664
$U_{1,MX}^L$	0.218285 (0.0183)	A_{HX}/RT	5.97405
$V_{1,MX}^L$	-0.0470256 (0.0546)	A_{CX}/R	28.5798

^aUnits for $C_{p,\phi}^o$ are J-K⁻¹-mol⁻¹; V for E ; K⁻¹ for B_{MX}^L , $W_{1,MX}^L$, $U_{1,MX}^L$, and $V_{1,MX}^L$; and K⁻² for B_{MX}^I , $W_{1,MX}^I$, $U_{1,MX}^I$, and $V_{1,MX}^I$. All other quantities are dimensionless. The Debye–Hückel constants are given in dimensionless form. The number in parentheses following the coefficient value is the standard error of that coefficient divided by the value of that coefficient. The standard deviations (weighted) of the model for each property are $\sigma(\phi) = 0.00108$ (399), $\sigma(\text{emf}) = 0.168$ mV (102), $\sigma(\Delta_{\text{dil}}H) = 16.05$ J·mol⁻¹ (122), and $\sigma(C_{p,\phi}) = 3.89$ J-K⁻¹-mol⁻¹ (99), where the numbers given in parentheses are the number of values of that property given nonzero weight in the least-squares calculations.

^bThese quantities were set at these values and are not least-squares parameters. The value of $C_{p,\phi}^o$ was fixed at -193.7 J-K⁻¹-mol⁻¹ as discussed in the text.

^c $E^{o'}$ (cell A) = 2.48410 V when $x(\text{Na}) = 0.01818$ and $E^{o'}$ (cell A) = 2.48218 V when $x(\text{Na}) = 0.01765$.

^dCell A, 25°C.

$W_{1,MX}$, $U_{1,MX}$, or $V_{1,MX}$. The temperature dependences of the parameters for relative apparent molar enthalpy $P(L)$ are obtained by partial differentiation of $P(G)$ with regard to temperature⁽¹⁰⁸⁾

$$\begin{aligned}
 P(L) &= [\partial\{P(G)\}/\partial T]_{p,nj} \\
 &= (p_1/3)T + (p_2/2) - (p_4/2T_{r1})(T_{r1} - T)^{-2} + p_6T^{-2} + p_9T^2 \quad (37)
 \end{aligned}$$

where $P(L)$ denotes B_{MX}^L , $W_{1,MX}^L$, $U_{1,MX}^L$, or $V_{1,MX}^L$. Similarly, the parameters for relative apparent molar capacity $J = C_{p,\phi}^o - C_{p,\phi}^o$ are given by⁽¹⁰⁸⁾

$$\begin{aligned}
 P(J) &= 2T^{-1}[\partial\{P(G)\}/\partial T]_{p,nj} + [\partial^2\{P(G)\}/\partial T^2]_{p,nj} \\
 &= p_1 + p_2T^{-1} + p_4(T^{-1})(T - T_{r1})^{-3} + 4p_9T \quad (38)
 \end{aligned}$$

where $P(J)$ denotes B_{MX}^J , $W_{1,MX}^J$, $U_{1,MX}^J$, or $V_{1,MX}^J$. For $C_{p,\phi}^o$ the following temperature dependent function was used:

Table X. Coefficients for the Temperature Dependences of the Parameters of the Mole Fraction-Based Model for Na₂SO₄(aq) and Standard Cell Potentials at $t \neq 25.00^\circ\text{C}$

Parameter	Value ^a	Parameter	Value ^a
$p_1(B_{\text{MX}})$	-0.65647536^b	$p_7(W_{1,\text{MX}})$	$-5.0116432 \times 10^{3b}$
$p_1(W_{1,\text{MX}})$	-0.24274253^b	$p_7(U_{1,\text{MX}})$	$-1.2261152 \times 10^{4b}$
$p_1(U_{1,\text{MX}})$	-0.59525356^b	$p_7(V_{1,\text{MX}})$	9.2063595×10^{3b}
$p_1(V_{1,\text{MX}})$	0.44014897^b	$p_9(B_{\text{MX}})$	$2.2633705 \times 10^{-4} (0.0130)$
$p_2(B_{\text{MX}})$	$118.14904 (0.0143)$	$p_9(W_{1,\text{MX}})$	$8.2717974 \times 10^{-5} (0.0121)$
$p_2(W_{1,\text{MX}})$	$43.315916 (0.0124)$	$p_9(U_{1,\text{MX}})$	$2.0324882 \times 10^{-4} (0.0059)$
$p_2(U_{1,\text{MX}})$	$106.04071 (0.0086)$	$p_9(V_{1,\text{MX}})$	-1.5×10^{-4c}
$p_2(V_{1,\text{MX}})$	$-78.822814 (0.0079)$	u_2	$3.89175 (0.0149)$
$p_4(B_{\text{MX}})$	$-1.1968438 \times 10^6 (0.0138)$	u_3	$-7.15785 \times 10^{-3} (0.0119)$
$p_4(W_{1,\text{MX}})$	$6.3991744 \times 10^4 (0.2029)$	u_4	$6.7156 \times 10^3 (0.0009)$
$p_4(U_{1,\text{MX}})$	$2.1921913 \times 10^5 (0.1420)$	$E^{\circ'}(\text{cell A}, 22^\circ\text{C})$	2.48422 ± 0.00044^d
$p_4(V_{1,\text{MX}})$	$-1.6918968 \times 10^5 (0.1305)$	$E^{\circ'}(\text{cell A}, 22^\circ\text{C})$	2.48239 ± 0.00036^d
$p_6(B_{\text{MX}})$	$-1.2661191 \times 10^{6b}$	$E^{\circ'}(\text{cell A}, 28^\circ\text{C})$	2.48393 ± 0.00034^e
$p_6(W_{1,\text{MX}})$	$-4.1979239 \times 10^{5b}$	$E^{\circ'}(\text{cell A}, 28^\circ\text{C})$	2.48199 ± 0.00007^e
$p_6(U_{1,\text{MX}})$	$-1.0290484 \times 10^{6b}$	$E^{\circ'}(\text{cell A}, 31^\circ\text{C})$	2.48371 ± 0.00025^f
$p_6(V_{1,\text{MX}})$	7.8676752×10^{5b}	$E^{\circ'}(\text{cell A}, 31^\circ\text{C})$	2.48176 ± 0.00008^f
$p_7(B_{\text{MX}})$	$-1.4045379 \times 10^{4b}$		

^aUnits for E are V. The units of “ p ” and “ u ” coefficients may be deduced from Eqs. (36–39), where the units for each individual term are those given in footnote a of Table IX. Quantities given in parentheses are the standard error of the coefficient divided by the value of that coefficient. Table IX gives the value of $C_{\text{p},\phi}^\circ$ at 25.00°C .

^bThe reported values of the twelve p_1 , p_6 , and p_7 coefficients were not obtained as least-squares parameters, but were calculated using Eqs. (36–38) and the other parameter values given in Tables IX and X.

^cThe quantity $p_9(V_{1,\text{MX}})$ was fixed at this value and was not a least-squares parameter.

^d $E^{\circ'}(\text{cell A}) = 2.48422$ V when $x(\text{Na}) = 0.01818$ and $E^{\circ'}(\text{cell A}) = 2.48239$ V when $x(\text{Na}) = 0.01765$.

^e $E^{\circ'}(\text{cell A}) = 2.48393$ V when $x(\text{Na}) = 0.01818$ and $E^{\circ'}(\text{cell A}) = 2.48199$ V when $x(\text{Na}) = 0.01765$.

^f $E^{\circ'}(\text{cell A}) = 2.48371$ V when $x(\text{Na}) = 0.01818$ and $E^{\circ'}(\text{cell A}) = 2.48176$ V when $x(\text{Na}) = 0.01765$.

$$C_{\text{p},\phi}^\circ(T) = C_{\text{p},\phi}^\circ(298.15 \text{ K}) + u_2(T - T_{r2}) + u_3\{T^2 - T_{r2}^2\} + u_4(T_{r2} - T)/(T_{r2} - T_{r3})(T - T_{r3}) \quad (39)$$

where the reference temperatures are $T_{r2} = 298.15$ K and $T_{r3} = 263.00$ K.

The enthalpies of dilution of Mayrath and Wood⁽⁸⁸⁾ at 150.50°C with the five lowest initial molalities, 0.01040 to 0.4320, exhibited significant systematic deviations from the mole fraction-based model, whereas most of their higher-molality results agreed with this model. As a comparison, an isothermal fit was done with Eq. (32) using only this data set, and very similar deviations were observed. It thus appears probable that these deviations were

Table XI. Smoothed Values of ϕ , γ_{\pm} , L_{ϕ} and $C_{p,\phi}$ for Na₂SO₄(aq) at Selected Molalities and Temperatures, Using the Mole Fraction-Based Model and the Parameters of Tables IX and X^a

<i>m</i>	ϕ	γ_{\pm}	L_{ϕ}	$C_{p,\phi}$
0.00°C ^b				
0.05	0.8214	0.5337 ₅	−0.431	−564.4
0.1	0.7785	0.4453	−1.378	−499.4 ₅
0.2	0.7282	0.3571	−3.111	−400.9
0.5	0.6460	0.2473	−7.166	−217.5
1.0	0.5781	0.1765	−11.751	−66.1
1.5	0.5534	0.1443	−14.788	0.7
2.0	0.5587	0.1276	−16.813	23.7
2.5	0.5866	0.1192	−18.098	20.9
3.0	0.6323	0.1161	−18.816	2.4
25.00°C				
0.05	0.8260 ₅	0.5337	1.046	−149.3
0.1	0.7902	0.4508	0.975	−127.6
0.2	0.7516	0.3702	0.574	−95.2
0.5	0.6931	0.2709	−0.874 ₅	−28.8
1.0	0.6451	0.2053	−2.990	42.8
1.5	0.6259	0.1736	−4.633	91.1
2.0	0.6264	0.1559	−5.860	125.5
2.5	0.6421	0.1459	−6.722	150.5
3.0	0.6700	0.1409	−7.263	168.5
50.00°C				
0.05	0.8226	0.5233	2.127	−84.1
0.1	0.7889	0.4422	2.528	−66.3
0.2	0.7549	0.3649	2.813	−41.4
0.5	0.7076	0.2722	2.752	7.3
1.0	0.6707	0.2114	2.164	60.7
1.5	0.6557	0.1816	1.606	99.9
2.0	0.6548	0.1643	1.201	130.6
2.5	0.6643	0.1537	0.973	155.4
3.0	0.6818	0.1473	0.923	175.2
75.00°C				
0.05	0.8148	0.5069	3.303	−67.8
0.1	0.7810	0.4260	4.154	−49.3
0.2	0.7481	0.3501	5.050	−24.8
0.5	0.7050	0.2611	6.137	19.2
1.0	0.6725	0.2036	6.770	64.4
1.5	0.6582	0.1752	7.107	97.3
2.0	0.6547	0.1581 ₅	7.416	123.9
2.5	0.6588	0.1471	7.771	145.8
3.0	0.6686 ₅	0.1397	8.193 ₅	163.6
100.00°C				
0.05	0.8036	0.4862	4.665	−73.3
0.1	0.7682	0.4045	5.996	−53.4

Table XI. Continued.

m	ϕ	γ_{\pm}	L_{ϕ}	$C_{p,\phi}$
0.2	0.7344	0.3292	7.512	-28.2
0.5	0.6917	0.2425	9.682	14.8
1.0	0.6595	0.1875	11.394	56.6
1.5	0.6432	0.1601	12.508	86.4
2.0	0.6359	0.1433	13.445	110.5
2.5	0.6349	0.1319	14.319	130.4
3.0	0.6387	0.1239 ₅	15.165	146.6
125.00°C				
0.05	0.7896	0.4623	6.253	-92.8
0.1	0.7515	0.3795 ₅	8.097	-71.6
0.2	0.7156	0.3044	10.255	-45.6
0.5	0.6710	0.2198	13.503	-1.8
1.0	0.6365	0.1670	16.264	41.2
1.5	0.6166	0.1407	18.128	72.1
2.0	0.6046	0.1243	19.666	96.8
2.5	0.5987	0.1130	21.034	116.9
3.0	0.5979	0.1050	22.278	133.0

^aUnits for m are mol·kg⁻¹, of L_{ϕ} are kJ·mol⁻¹, and of $C_{p,\phi}$ are J·K⁻¹·mol⁻¹.

^bFew experimental heat capacities are available below 25°C, and thus $C_{p,\phi}$ calculated from the mole fraction-based model at 0°C are not realistic, especially at higher molalities.

due to experimental error as stated by the authors, rather that a limitation of our model and, consequently, those five points were given zero weight in subsequent fits.

The thermodynamic models of Rogers and Pitzer,⁽⁸⁾ Holmes and Mesmer,⁽¹⁰⁾ and Pabalan and Pitzer⁽¹¹⁾ predict values of $C_{p,\phi}^{\circ}$ (298.15 K) varying between -187.5 and -199 J·K⁻¹·mol⁻¹, with an average of -194 ± 6 J·K⁻¹·mol⁻¹. The enthalpy of solution measurements of Gardner *et al.*⁽⁹⁶⁾ yield -195.4 J·K⁻¹·mol⁻¹ for this quantity, and the more recent flow microcalorimetry experiments^(94,95) yield -191.7 and -190.1 J·K⁻¹·mol⁻¹, respectively. However, based on heat-capacity measurements for a variety of aqueous electrolytes and using additivity relations, Desnoyers *et al.*⁽⁹⁴⁾ derived a set of ionic values that yield $C_{p,\phi}^{\circ}$ (298.15 K) = -193 J·K⁻¹·mol⁻¹ for Na₂SO₄(aq). We selected $C_{p,\phi}^{\circ}$ (298.15 K) = -193.7 J·K⁻¹·mol⁻¹ as a reasonable compromise, and fixed this term in Eq. (39) at this value, thereby reducing the number of model parameters. However, we recognize that given the limitations of the published heat-capacity studies, this value of $C_{p,\phi}^{\circ}$ (298.15 K) is uncertain by ~ 2 J·K⁻¹·mol⁻¹.

Least-squares fits were performed initially for this mole-fraction based model using the apparent molar heat capacities. After values of B_{MX}^J , $W_{1,MX}^J$, $U_{1,MX}^J$, and $V_{1,MX}^J$ were obtained along with their temperature dependences, the model

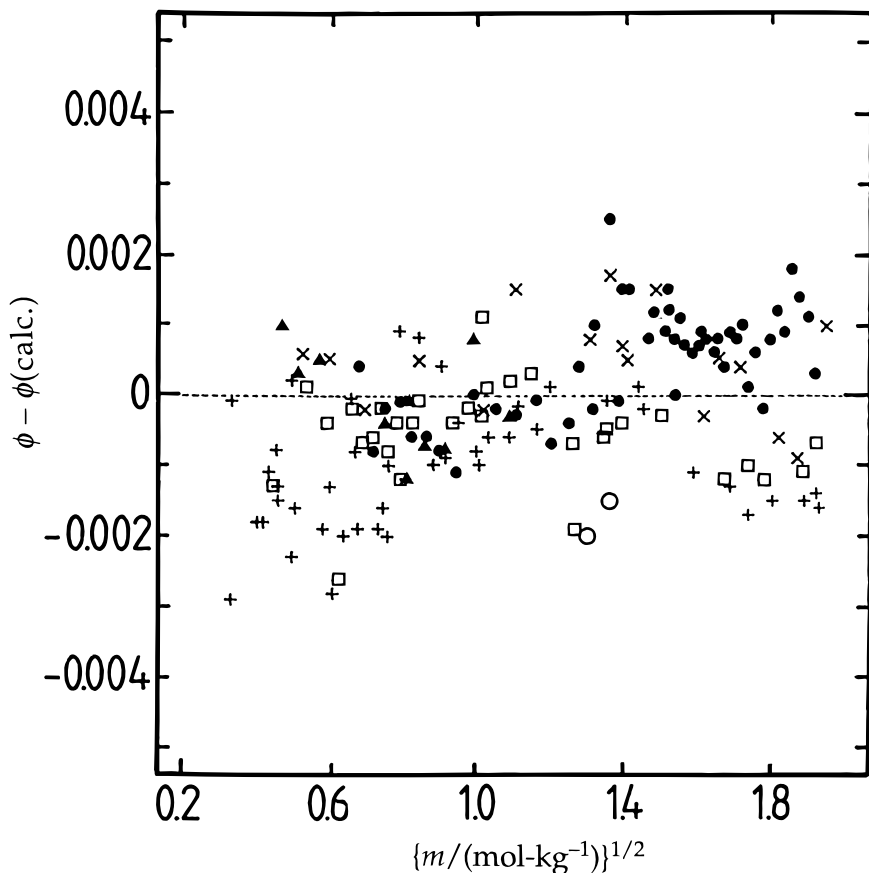


Fig. 4. Deviations of the critically assessed experimental osmotic coefficients at 25.00°C, as a function of the square root of molality, from the mole fraction-based model using the parameters of Table IX: +, Table II older combined series; □, Table II numbered series; ●, Rard and Miller (Ref. 6); ▲, Downes and Pitzer (Ref. 42); ×, Platford (Ref. 37); ○, Filippov *et al.* (Ref. 43).

was extended to include the enthalpy parameters B_{MX}^{L} , $W_{1,\text{MX}}^{\text{L}}$, $U_{1,\text{MX}}^{\text{L}}$, and $V_{1,\text{MX}}^{\text{L}}$ and their temperature dependences, and, finally, the osmotic and activity coefficient parameters B_{MX} , $W_{1,\text{MX}}$, $U_{1,\text{MX}}$, and $V_{1,\text{MX}}$ and their temperature dependences. These sequential calculations, together with the more direct graphical comparisons described in Section 3, allowed us to assign the relative weights for each data set as listed in Tables IV through VII.

Table IX contains the values of the parameters of Eqs. (30–33), the standard potentials of cell (A), and the Debye–Hückel constants on the mole

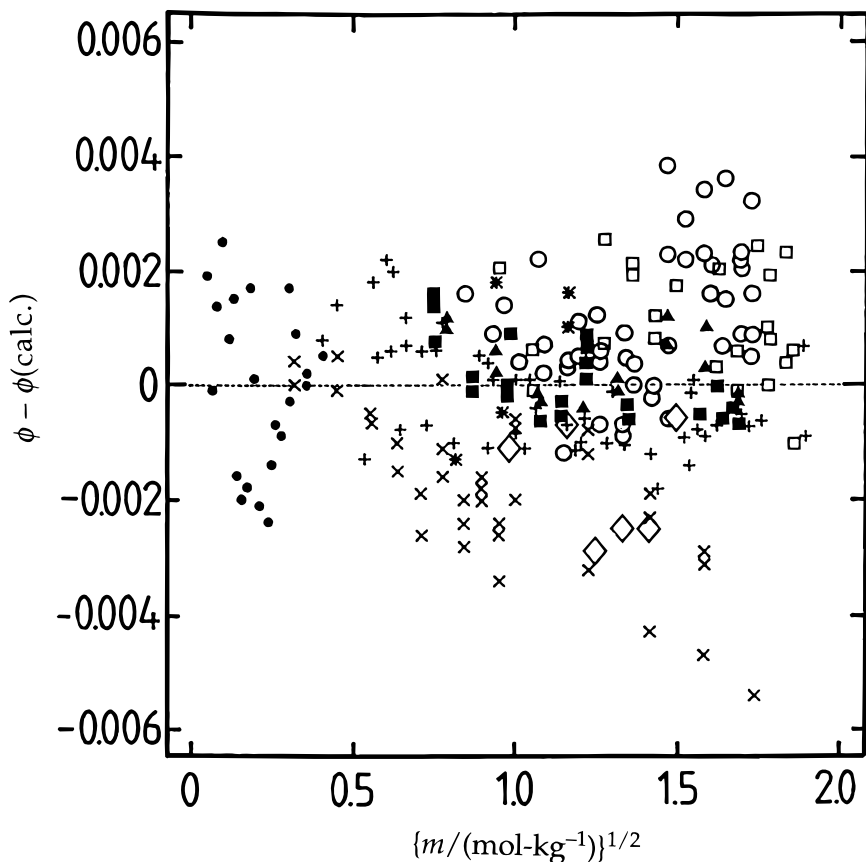


Fig. 5. Deviations of the critically assessed experimental osmotic coefficients at all temperatures excluding 25.00°C, as a function of the square root of molality, from the mole fraction-based model using the parameters of Tables IX and X: ●, at freezing temperatures (Refs. 61 and 62); *, 0.00°C (Ref. 41); ×, 15.00°C (Ref. 47); ◇, 27.50°C (Ref. 52); +, Table III 50.00°C; □, 59.98°C (Ref. 36); ○, 80.22°C (Ref. 40); ■, 109.99°C (Ref. 9); ▲, 140.08°C (Ref. 9).

fraction composition scale, all evaluated at 25.00°C. Table X contains values of the coefficients p_1 , p_2 , p_4 , p_6 , p_7 , p_9 , u_2 , u_3 , and u_4 for Eqs. (36–39).

Table XI contains values of ϕ , γ_{\pm} , L_{ϕ} , and $C_{p,\phi}$ calculated from the mole fraction-based model at selected molalities and at 25°C intervals. The mole fraction-based quantities ϕ_x and f_{\pm}^* generated by the model were transformed into ϕ and γ_{\pm} in order to facilitate comparisons with other evaluations. The evaluated ϕ values at 25.00°C are about 0.1–0.2% larger than those of Rard and Miller⁽⁶⁾ for $m \leq 2$, but the difference increases to nearly 0.4% by $3m$. Most of these changes result from Archer's revisions^(23,48) of the isopiestic reference standards, rather than from changes in the data base for $\text{Na}_2\text{SO}_4(\text{aq})$.

Figure 4 illustrates the deviations between the experimental values of ϕ and the mole fraction-based model at 25.00°C, and Fig. 5 illustrates these deviations at all other temperatures. At 25.00°C and for $m > 0.5$, the deviations between the experimental and model values are nearly completely random, and for $m < 0.5$ the minor systematic differences of 0.1 to 0.2% result from the inclusion of other data in the model, especially the emfs. Figure 5 indicates that this model represents the values of ϕ at temperatures $\neq 25.00^\circ\text{C}$ nearly as well, with all of the larger negative deviations occurring for the less precise freezing temperature depression data and for isopiestic data at 15°C.

Figure 6 illustrates the deviations between experiment and model for emf data. The cell (A) measurements of Shibata and Murata⁽⁶⁸⁾ at all temperatures are highly consistent with the model as are those of Harned and Hecker⁽⁷⁴⁾ for cell (E) at 15–40°C, with systematic differences being ≤ 0.1 and ≤ 0.2 mV, respectively. Deviations of the Harned and Hecker emfs from the model can be as large as 0.4–0.5 mV at 0–15°C, where the available thermodynamic data are not numerous enough to constrain the model as well.

Figure 7 indicates that our model represents the values of L_ϕ quite well over the entire molality and temperature regions, without any significant systematic deviations. However, Fig. 8 indicates that the values of $C_{p,\phi}$ predicted by our model are low by 5–10 $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ for molalities above 1.

It should be possible to eliminate the minor systematic deviations for $C_{p,\phi}$ at high molalities by including another parameter in the mole fraction model expression for $C_{p,\phi}$. However, if this were done, then additional param-

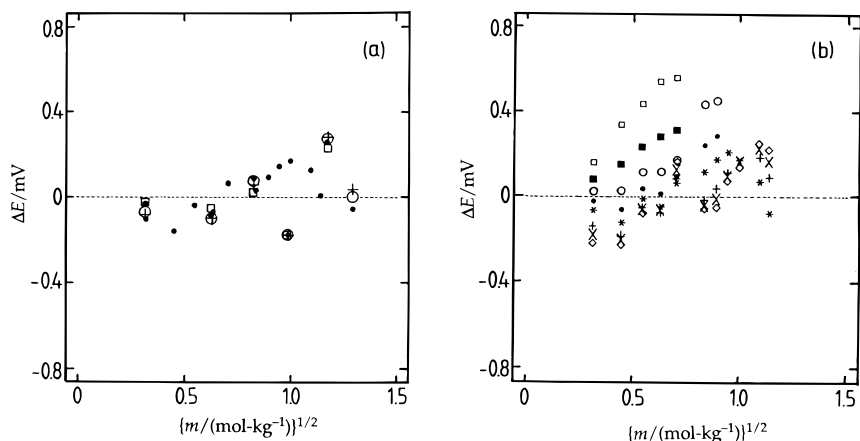


Fig. 6. Deviations of the critically assessed experimental emfs at all temperatures, as a function of the square root of molality, from the mole fraction-based model using the parameters of Tables IX and X. (a) Data of Shibata and Murata (Ref. 68) for cell (A): □, 22.00°C; ●, 25.00°C; ○, 28.00°C; +, 31.00°C. (b) Data of Harned and Hecker (Ref. 74) for cell (E): □, 0.00°C; ■, 5.00°C; ○, 10.00°C; ●, 15.00°C; *, 20.00°C; +, 30.00°C; ×, 35.00°C; ◇, 40.00°C.

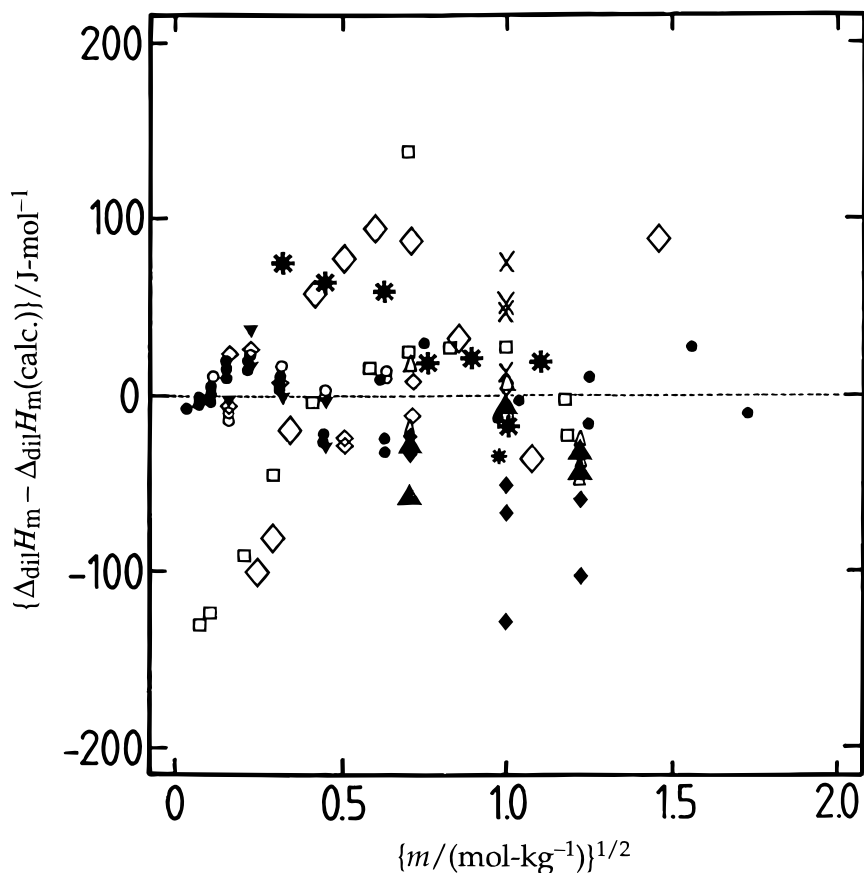


Fig. 7. Deviations of the critically assessed experimental enthalpies of dilution at all temperatures, as a function of the square root of molality, from the mole fraction-based model using the parameters of Tables IX and X; ▼, 15.00°C (Ref. 80); ◇, ~20°C (Ref. 79); ○, 20.00°C (Ref. 80); ●, 25.00°C (Refs. 77, 78, 80 and 85); ×, 30.00°C (Ref. 86); *, 40.00°C (Ref. 87); Δ, 40.0°C (Ref. 19); ▲, 60.0°C (Ref. 19); ◆, 80.0°C (Ref. 19); □, 100.0–100.2°C (Refs. 18, 19, and 88); ◇, 150.50°C (Ref. 88).

ters would also be added to the expressions for ϕ and L_ϕ , and they clearly are not needed for these properties. The mole fraction-based model in its present form is quite able to represent the experimental values of both ϕ and L_ϕ to within their experimental precision and accuracy.

We end this paper by noting that although the thermodynamic data base for $\text{Na}_2\text{SO}_4(\text{aq})$ is extensive and fairly accurate, there are some temperature regions which are less well characterized. In particular, there is a need for enthalpy of

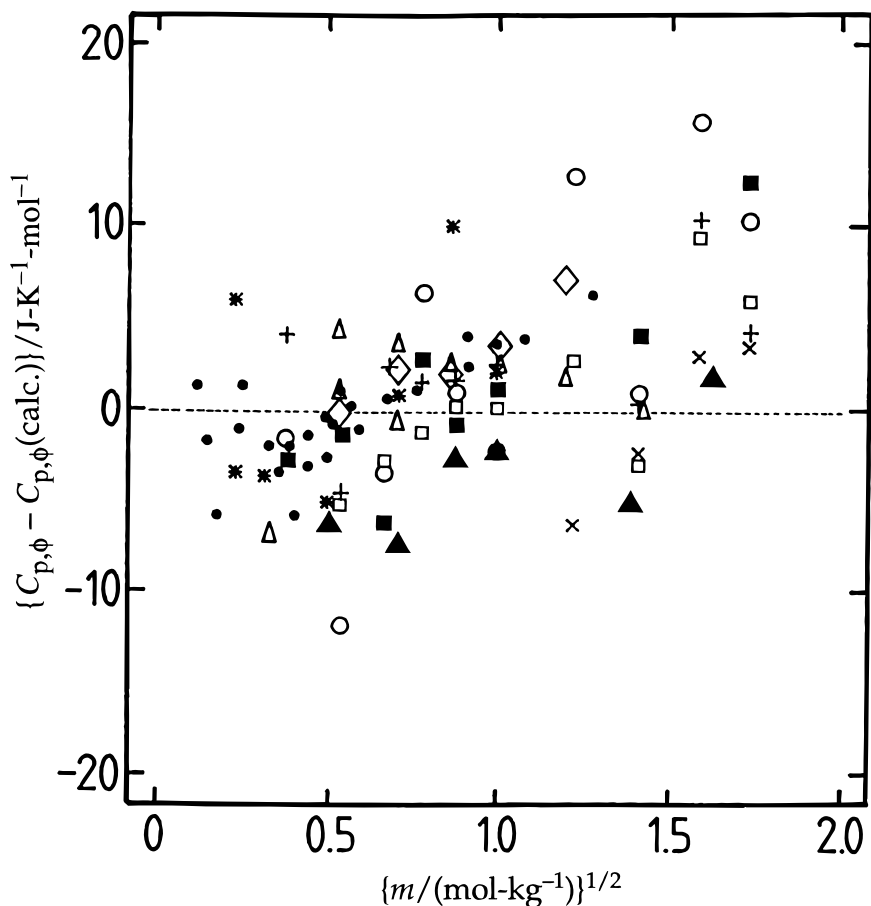


Fig. 8. Deviations of the critically assessed experimental apparent molar heat capacities at all temperatures, as a function of the square root of molality, from the mole fraction-based model using the parameters of Tables IX and X: ●, 25.00°C (Refs. 90, 94, and 95); *, 31.47°C (Ref. 8); Δ, 50.85°C (Ref. 8); ×, 60.00°C (Ref. 20); ◇, 76.03°C (Ref. 8); □, 80.00°C (Refs. 20 and 93); ○, 100.00°C (Refs. 20 and 93); ■, 120.00°C (Refs. 20 and 93); +, 140.00°C (Refs. 20 and 93); ▲, 140.75°C (Ref. 8).

dilution measurements between 100 and 150°C and for additional isopiestic, enthalpy of dilution, and heat-capacity measurements from 0 to 15°C. We make our critically assessed data base available to assist future workers making such measurements and copies can be obtained from any of the authors. Copies of a FORTRAN computer code containing our mole fraction-based thermodynamic model for $\text{Na}_2\text{SO}_4(\text{aq})$ can be obtained from S. L. Clegg.

ACKNOWLEDGMENT

The experimental part of this work was performed at Oak Ridge National Laboratory with support by the Office of Basic Energy Sciences, Division of Chemical Sciences, of the U.S. Department of Energy under contract No. DE-AC-05-96OR22464 with Lockheed Martin Energy Research Corporation. The work of J.A.R. was performed under the auspices of the Office of Basic Energy Sciences, Division of Geosciences, of the U.S. Department of Energy by the Lawrence Livermore National Laboratory under contract No. W-7405-ENG-48, and that of S.L.C. was supported by an Advanced Research Fellowship from the Natural Environment Research Council of the U. K.

REFERENCES

1. E. A. Burton, T. Hahn, and H. G. Machel, in *Proceedings of the 7th International Symposium on Water-Rock Interaction*, Y. K. Kharaka and A. S. Maest, eds. (Balkema, Rotterdam, 1992), pp. 617–620.
2. G. Matthes, *The Properties of Groundwater* [Wiley (Interscience) New York, 1982].
3. A. R. Felmy and J. H. Weare, *Geochim. Cosmochim. Acta* **50**, 2771 (1986).
4. D. C. Gosselin, S. Sibray, and J. Ayers, *Geochim. Cosmochim. Acta* **58**, 1403 (1994).
5. K. U. G. Raju and G. Atkinson, *J. Chem. Eng. Data* **34**, 361 (1989).
6. J. A. Rard and D. G. Miller, *J. Chem. Eng. Data* **26**, 33 (1981).
7. R. N. Goldberg, *J. Phys. Chem. Ref. Data* **10**, 671 (1981).
8. P. S. Z. Rogers and K. S. Pitzer, *J. Phys. Chem.* **85**, 2886 (1981).
9. H. F. Holmes and R. E. Mesmer, *J. Chem. Thermodyn.* **18**, 263 (1986).
10. H. F. Holmes and R. E. Mesmer, *J. Solution Chem.* **15**, 495 (1986).
11. R. T. Pabalan and K. S. Pitzer, *Geochim. Cosmochim. Acta* **52**, 2393 (1988).
12. J. K. Hovey, K. S. Pitzer, and J. A. Rard, *J. Chem. Thermodyn.* **25**, 173 (1993).
13. J. Baabor, M. A. Gilchrist, and E. J. Delgado, *Bol. Soc. Chil. Quím.* **39**, 329 (1994).
14. J. Baabor, M. A. Gilchrist, and E. J. Delgado, *Bol. Soc. Chil. Quím.* **41**, 397 (1996).
15. J. Baabor, M. A. Gilchrist, and E. J. Delgado, *J. Solution Chem.* **27**, 67 (1998).
16. S. Rondinini, A. Cavadore, P. Longhi, and T. Mussini, *J. Chem. Thermodyn.* **20**, 711 (1988).
17. P. Fusi and P. R. Mussini, *J. Solution Chem.* **26**, 337 (1997).
18. G. Conti, P. Gianni, A. Papini, and E. Matteoli, *J. Solution Chem.* **17**, 481 (1988).
19. B. Rumpf, F. Weyrich, and G. Maurer, *Thermochim. Acta* **303**, 77 (1997).
20. G. Conti, P. Gianni, and M. R. Tiné, *Thermochim. Acta* **145**, 61 (1989).
21. K. S. Pitzer, in *Activity Coefficients in Electrolyte Solutions*, 2nd edn. K. S. Pitzer, ed. (CRC Press, Boca Raton, 1991), Chap. 3.
22. D. G. Archer, *J. Phys. Chem. Ref. Data* **20**, 509 (1991).
23. D. G. Archer, *J. Phys. Chem. Ref. Data* **21**, 793 (1992).
24. D. G. Archer and J. A. Rard, *J. Chem. Eng. Data* **43**, 791 (1998).
25. S. L. Clegg, J. A. Rard, and K. S. Pitzer, *J. Chem. Soc. Faraday Trans.* **90**, 1875 (1994).
26. R. M. Rush and J. S. Johnson, *J. Chem. Eng. Data* **11**, 590 (1966).
27. S. L. Clegg, S. Milioto, and D. A. Palmer, *J. Chem. Eng. Data* **41**, 455 (1996).
28. J. A. Rard and R. F. Platford, in *Activity Coefficients in Electrolyte Solutions*, 2nd edn. K. S. Pitzer, ed. (CRC Press, Boca Raton, 1991), Chap. 5.
29. J. A. Rard, *J. Chem. Thermodyn.* **28**, 83 (1996).
30. R. A. Robinson, J. M. Wilson, and R. H. Stokes, *J. Amer. Chem. Soc.* **63**, 1011 (1941).

31. C. S. Patterson, L. O. Gilpatrick, and B. A. Soldano, *J. Chem. Soc.*, p. 2730 (1960).
32. B. A. Soldano and C. S. Patterson, *J. Chem. Soc.*, p. 937 (1962).
33. B. A. Soldano and M. Meek, *J. Chem. Soc.*, p. 4424 (1963).
34. K. L. Hellams, C. S. Patterson, B. H. Prentice, III, and M. J. Taylor, *J. Chem. Eng. Data* **10**, 323 (1965).
35. B. A. Soldano and P. B. Bien, *J. Chem. Soc.* p. 1825 (1966)
36. W. T. Humphries, C. F. Kohrt, and C. S. Patterson, *J. Chem. Eng. Data* **13**, 327 (1968).
37. R. F. Platford, *J. Chem. Eng. Data* **13**, 46 (1968).
38. Y. C. Wu, R. M. Rush, and G. Scatchard, *J. Phys. Chem.* **72**, 4048 (1968); correction, *J. Phys. Chem.* **73**, 4433 (1969).
39. Y. C. Wu, R. M. Rush, and G. Scatchard, *J. Phys. Chem.* **73**, 2047 (1969); correction, *J. Phys. Chem.* **73**, 4434 (1969).
40. J. T. Moore, W. T. Humphries, and C. S. Patterson, *J. Chem. Eng. Data* **17**, 180 (1972).
41. R. F. Platford, *J. Chem. Eng. Data* **18**, 215 (1973).
42. C. J. Downes and K. S. Pitzer, *J. Solution Chem.* **5**, 389 (1976).
43. V. K. Filippov, V. I. Nokhrin, and A. P. Muzalevskaya, *Russ. J. Inorg. Chem.* **30**, 1372 (1985).
44. V. K. Filippov, A. M. Kalinkin, and S. K. Vasin, *J. Chem. Thermodyn.* **21**, 935 (1989).
45. V. K. Filippov and A. M. Kalinkin, *Russ. J. Inorg. Chem.* **32**, 120 (1987).
46. T. Michimoto, Y. Awakura, and H. Majima, *Denki Kagaku* **51**, 373 (1983); H. Majima, Y. Awakura, and Y. Kawasaki, *Activities of Water and Solutes in the Aqueous Solution Systems $\text{H}_2\text{SO}_4\text{-M}_x(\text{SO}_4)_y$ and HCl-MCl_x* (Agne Shofu, Tokyo, 1988).
47. C. W. Childs and R. F. Platford, *Aust. J. Chem.* **24**, 2487 (1971).
48. D. G. Archer, *J. Phys. Chem. Ref. Data* **28**, 1 (1999).
49. J. A. Rard and S. L. Clegg, *J. Chem. Eng. Data* **42**, 819 (1997).
50. H. G. Leopold and J. Johnston, *J. Amer. Chem. Soc.* **49**, 1974 (1927).
51. H. W. Foote, B. Saxton, and J. K. Dixon, *J. Amer. Chem. Soc.* **54**, 563 (1932).
52. R. E. Gibson and L. H. Adams, *J. Amer. Chem. Soc.* **55**, 2679 (1933).
53. J. Perreu, *C. R. Acad. Sci.* **200**, 1030 (1935).
54. J. N. Pearce and H. C. Eckstrom, *J. Amer. Chem. Soc.* **59**, 2689 (1937).
55. W. Kangro and A. Groeneveld, *Z. Phys. Chem. N. F.* **32**, 110 (1962).
56. D. E. Burge, *J. Phys. Chem.* **67**, 2590 (1963).
57. B. M. Fabuss and A. Korosi, *Desalination* **1**, 139 (1966).
58. G. Jakli, T. C. Chan, and W. A. Van Hook, *J. Solution Chem.* **4**, 71 (1975).
59. O. N. Bhatnagar and A. N. Campbell, *Can. J. Chem.* **59**, 123 (1981).
60. O. N. Bhatnagar and A. N. Campbell, *Can. J. Chem.* **60**, 1754 (1982).
61. M. Randall and G. N. Scott, *J. Amer. Chem. Soc.* **49**, 647 (1927).
62. A. Indelli, *Ricer. Sci.* **23**, 2258 (1953).
63. E. Plake, *Z. Phys. Chem.* **A172**, 113 (1935).
64. H. C. Jones and F. H. Getman, *Z. Phys. Chem.* **46**, 244 (1903).
65. M. D. Cohen, R. C. Flagan, and J. H. Seinfeld, *J. Phys. Chem.* **91**, 4563 (1987).
66. I. N. Tang and H. R. Munkelwitz, *J. Geophys. Res.* **99**, 18801 (1994).
67. C. K. Chan, Z. Liang, J. Zheng, S. L. Clegg, and P. Brimblecombe, *Aerosol Sci. Technol.* **27**, 324 (1997).
68. E. Shibata and F. Murata, *Nippon Kagaku Kaishi* **51**, 639 (1931).
69. W. E. Henderson and G. Stegeman, *J. Amer. Chem. Soc.* **40**, 84 (1918).
70. M. G. Mellon and W. E. Henderson, *J. Amer. Chem. Soc.* **42**, 676 (1920).
71. H. S. Harned and W. J. Hamer, *J. Amer. Chem. Soc.* **57**, 33 (1935); H. S. Harned and W. J. Hamer, *Researches on the Physical Chemistry of the Lead-Acid Storage Cell* U. S.

- Naval Research Laboratory Rep. No. P-1071 (U.S. Naval Research Laboratory, Washington, D.C., 1934).
72. P. Luts, J. L. C. Vanhees, J. H. E. Yperman, J. M. A. Mullens, and L. C. Van Poucke, *Talanta* **37**, 455 (1990).
73. G. Åkerlöf, *J. Amer. Chem. Soc.* **48**, 1160 (1926).
74. H. S. Harned and J. C. Hecker, *J. Amer. Chem. Soc.* **56**, 650 (1934).
75. K. Hass and K. Jellinek, *Z. Phys. Chem. (Leipzig)* **162A**, 153 (1932).
76. J. A. Rard, J. G. Albright, D. G. Miller, and M. E. Zeidler, *J. Chem. Soc., Faraday Trans.* **92**, 4187 (1996).
77. E. W. Lange and G. Meßner, *Z. Elektrochem.* **33**, 431 (1927).
78. E. Lange and H. Streeck, *Z. Phys. Chem.* **A157**, 1 (1931).
79. E. Plake, *Z. Phys. Chem.* **A162**, 257 (1932).
80. W. E. Wallace and A. L. Robinson, *J. Amer. Chem. Soc.* **63**, 958 (1941).
81. G. Brodale and W. F. Giauque, *J. Amer. Chem. Soc.* **80**, 2042 (1958).
82. B. V. Gritsus, E. I. Akhumov, and L. P. Zhilina, *J. Appl. Chem. USSR* **42**, 183 (1969).
83. J. Greyson and H. Snell, *J. Chem. Eng. Data* **16**, 73 (1971).
84. B. V. Gritsus, E. I. Akhumov, and L. P. Zhilina, *J. Appl. Chem. USSR* **44**, 179 (1971).
85. P. T. Thompson, D. E. Smith, and R. H. Wood, *J. Chem. Eng. Data* **19**, 386 (1974).
86. W. H. Leung and F. J. Millero, *J. Solution Chem.* **4**, 145 (1975).
87. H. P. Snipes, C. Manly, and D. D. Ensor, *J. Chem. Eng. Data* **20**, 287 (1975).
88. J. E. Mayrath and R. H. Wood, *J. Chem. Eng. Data* **28**, 56 (1983).
89. C. Marignac, *Ann. Chim. Phys.* **8**, 410 (1878).
90. M. Randall and F. D. Rossini, *J. Amer. Chem. Soc.* **51**, 323 (1929); F. D. Rossini, *Heat Capacities in Aqueous Salt Solutions*, Ph.D. thesis, University of California, Berkeley, 1928.
91. K. A. Kobe and C. H. Anderson, *J. Phys. Chem.* **40**, 429 (1936).
92. J. D'Ans and H. Tollert, *Z. Elektrochem.* **43**, 81 (1937).
93. S. Likke and L. A. Bromley, *J. Chem. Eng. Data* **18**, 189 (1973); S. Likke, *Heat Capacity and Some Thermodynamic Properties of Several Aqueous Salt Solutions to 200°C*, Ph.D. thesis, University of California, Berkeley, 1972.
94. G. Perron, J. E. Desnoyers, and F. J. Millero, *Can. J. Chem.* **53**, 1134 (1975); J. E. Desnoyers, C. de Visser, G. Perron, and P. Picker, *J. Solution Chem.* **5**, 605 (1976).
95. I. V. Olofsson, J. J. Spitzer, and L. G. Hepler, *Can. J. Chem.* **56**, 1871 (1978); Depository of Unpublished Data, National Research Council of Canada, Ottawa, Ontario, Canada, file number 2410, deposit number 811, July 21, 1978.
96. W. L. Gardner, E. C. Jekel, and J. W. Cobble, *J. Phys. Chem.* **73**, 2017 (1969).
97. A. A. Vichutinskii and A. G. Golikov, *Proc. Acad. Sci. USSR, Phys. Chem. Sect.* **238**, 9 (1978).
98. M. Obšil, V. Majer, J.-P. E. Grolier, and G. T. Hefter, *J. Chem. Soc., Faraday Trans.* **92**, 4445 (1996); M. Obšil, V. Majer, G. T. Hefter, and V. Hynek, *J. Chem. Eng. Data* **42**, 137 (1997).
99. P. G. Hill, *J. Phys. Chem. Ref. Data* **19**, 1233 (1990).
100. D. G. Archer and P. Wang, *J. Phys. Chem. Ref. Data* **19**, 371 (1990).
101. J. L. Oscarson, R. M. Izatt, P. R. Brown, Z. Pawlak, S.E. Gillespie, and J. J. Christensen, *J. Solution Chem.* **17**, 841 (1988).
102. J. A. Rard and D. G. Miller, *J. Solution Chem.* **8**, 755 (1979).
103. C. E. Harvie, N. Møller, and J. H. Weare, *Geochim. Cosmochim. Acta* **48**, 723 (1984).
104. H. F. Holmes and R. E. Mesmer, *J. Chem. Thermodyn.* **28**, 1325 (1996).
105. K. S. Pitzer and J. M. Simonson, *J. Phys. Chem.* **90**, 3005 (1986).

106. S. L. Clegg and K. S. Pitzer, *J. Phys. Chem.* **96**, 3513 (1992); correction, *J. Phys. Chem.* **98**, 1368 (1994).
107. S. L. Clegg, K. S. Pitzer, and P. Brimblecombe, *J. Phys. Chem.* **96**, 9470 (1992); correction, *J. Phys. Chem.* **98**, 1368 (1994).
108. S. L. Clegg, S. S. Ho, C. K. Chan, and P. Brimblecombe, *J. Chem. Eng. Data* **40**, 1079 (1995).