

Standard State Thermodynamic Properties of Completely Ionized Aqueous Sodium Sulfate Using High Dilution Calorimetry up to 598.15 K

Essmaïl Djamali,^{*,†,‡} Keith Chen,[‡] and James W. Cobble^{*,‡}

Center for Hydrothermal Research and the Department of Chemistry, San Diego State University, San Diego, California 92182

Received: May 26, 2009; Revised Manuscript Received: July 8, 2009

Pabalan and Pitzer (*Geochim. Cosmochim. Acta* **1988**, 52, 2393–2404) reported a comprehensive set of thermodynamic properties of aqueous solutions of sodium sulfate without using ion association or hydrolysis. However, there is now ample evidence available indicating that the ion association cannot be ignored at temperatures $T \geq 373$ K. For example, even at the lowest concentration of their studies ($m \geq 0.05$) and at 573.15 K, less than 20% of $\text{SO}_4^{2-}(\text{aq})$ is available as free ions. In the present study, the integral heats of solution of sodium sulfate were measured to very low concentrations (10^{-4} m) up to 573.16 K. The data were analyzed correcting for the hydrolysis of $\text{SO}_4^{2-}(\text{aq})$ and the association of $\text{Na}^+(\text{aq})$ with $\text{SO}_4^{2-}(\text{aq})$ and $\text{NaSO}_4^-(\text{aq})$ in order to obtain the final standard state thermodynamic properties of completely ionized aqueous sodium sulfate, $\text{Na}_2\text{SO}_4(\text{aq})$. From these and the available solubility data, the stoichiometric activity coefficients of saturated aqueous solutions of sodium sulfate were calculated up to 573.15 K and compared with literature data. The stoichiometric activity coefficients of aqueous solutions of sodium sulfate, as a function of temperature at all concentrations ($0 \leq m \leq m_{\text{sat}}$), were also calculated up to 573.15 K.

1. Introduction

Thermodynamic properties of aqueous sodium sulfate are important in a variety of geochemical and industrial processes. Sulfates represent an important component of the mineral economy and of pollution problems in air and water. There is considerable scientific interest in the mineralogy and geochemistry of sulfate minerals in both high temperature (igneous and hydrothermal) and low temperature weathering environments. The thermodynamic properties of sodium sulfate in aqueous solutions at elevated temperatures are also of great importance in many industrial processes; for instance, material transport, solid deposition, and corrosion in electric power plants. Sulfates are also common products of hydrothermal waste destruction by supercritical water oxidation.

However, because of equipment limitations¹ most of the data on sodium sulfate reported in literature are from calorimetric measurements at concentrations greater than 0.05 m. Further evidence in the literature² now indicates that at the concentrations $m \geq 0.05$ the ion association/hydrolysis of $\text{SO}_4^{2-}(\text{aq})$ cannot be ignored in this system at temperatures $T \geq 373$ K. Therefore, the extrapolation of experimental thermodynamic values to standard state conditions becomes even more uncertain at higher temperatures.

The purpose of the present study is to properly combine thermal measurements of aqueous solutions of sodium sulfate at very low concentrations (10^{-4} m) with the most recent conductance measurements^{2a} to provide a reliable thermodynamic characterization of this important electrolyte to high temperatures and pressures.

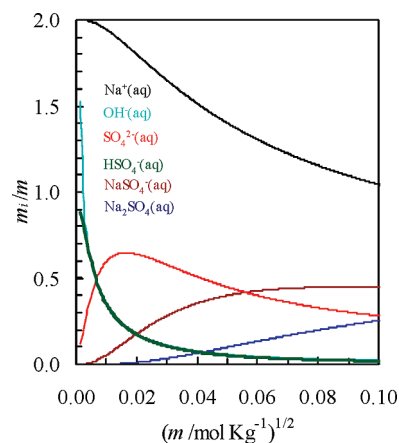


Figure 1. Distribution of species in aqueous solutions of sodium sulfate at 573.16 K and p_{sat} , calculated from conductance data.^{2a}

In aqueous sodium sulfate solutions at higher temperatures, as the concentration of $\text{SO}_4^{2-}(\text{aq})$ ion approaches zero, hydrolysis of $\text{SO}_4^{2-}(\text{aq})$ becomes the dominating factor and the concentration of free $\text{SO}_4^{2-}(\text{aq})$ ion decreases dramatically, as determined by conductance measurements^{2a} (cf. Figure 1). Therefore, an optimum range, at which the concentrations of the free $\text{SO}_4^{2-}(\text{aq})$ ion are dominating, becomes important when extrapolating the thermal data to infinite dilution. For example, at 573.15 K, in a previous study of sodium sulfate solutions,³ even at the lowest concentration ($m \geq 0.05$), less than 20% of $\text{SO}_4^{2-}(\text{aq})$ is available as free ions.

In the present study, the integral heats of solution of sodium sulfate were measured up to 573.16 K and down to very low concentrations (10^{-4} m). In this range of solution concentrations, it will be shown that the concentration of the free $\text{SO}_4^{2-}(\text{aq})$ ion is dominating (Figure 1) and a more reliable extrapolation to standard state is possible.

* To whom correspondence should be addressed. E-mail: hydrothermal@projects.sdsu.edu. Tel.: (619)-594-7395. Fax: (619)-594-7311. E-mail: djamali@sciences.sdsu.edu, jcobble@sbcglobal.net. Tel.: (858)-454-4767.

[†] Center for Hydrothermal Research.

[‡] Department of Chemistry.

TABLE 1: Equilibrium Concentrations (mol kg⁻¹) of Species in Sodium Sulfate Solutions at p_{sat} ^a

m_{initial}	H ⁺ (aq)	OH ⁻ (aq)	NaSO ₄ ⁻ (aq)	Na ⁺ (aq)	SO ₄ ²⁻ (aq)	Na ₂ SO ₄ (aq)	HSO ₄ ⁻ (aq)	NaHSO ₄ (aq)
$T = 444.76 \text{ K}$								
1.3417×10^{-03}	4.9749×10^{-07}	8.3736×10^{-06}	8.0886×10^{-05}	2.5966×10^{-03}	1.2500×10^{-03}	2.9184×10^{-06}	7.7913×10^{-06}	8.4874×10^{-08}
1.9371×10^{-03}	4.4424×10^{-07}	9.7278×10^{-06}	1.5182×10^{-04}	3.7072×10^{-03}	1.7685×10^{-03}	7.5387×10^{-06}	9.1464×10^{-06}	1.3713×10^{-07}
3.2262×10^{-03}	3.8538×10^{-07}	1.1915×10^{-05}	3.5173×10^{-04}	6.0468×10^{-03}	2.8361×10^{-03}	2.6811×10^{-05}	1.1270×10^{-05}	2.5938×10^{-07}
3.8635×10^{-03}	3.6831×10^{-07}	1.2776×10^{-05}	4.6833×10^{-04}	7.1757×10^{-03}	3.3414×10^{-03}	4.1341×10^{-05}	1.2085×10^{-05}	3.2209×10^{-07}
4.2295×10^{-03}	3.6040×10^{-07}	1.3225×10^{-05}	5.3952×10^{-04}	7.8167×10^{-03}	3.6259×10^{-03}	5.1216×10^{-05}	1.2506×10^{-05}	3.5844×10^{-07}
5.5812×10^{-03}	3.3879×10^{-07}	1.4675×10^{-05}	8.2433×10^{-04}	1.0143×10^{-02}	4.6452×10^{-03}	9.7347×10^{-05}	1.3843×10^{-05}	4.9356×10^{-07}
$T = 486.65 \text{ K}$								
9.9720×10^{-04}	3.4755×10^{-07}	2.0533×10^{-05}	6.7906×10^{-05}	1.9204×10^{-03}	9.0620×10^{-04}	2.9119×10^{-06}	1.9945×10^{-05}	2.4085×10^{-07}
1.0433×10^{-03}	3.4233×10^{-07}	2.0934×10^{-05}	7.3437×10^{-05}	2.0064×10^{-03}	9.4599×10^{-04}	3.2762×10^{-06}	2.0336×10^{-05}	2.5548×10^{-07}
2.2887×10^{-03}	2.7008×10^{-07}	2.8948×10^{-05}	2.7191×10^{-04}	4.2576×10^{-03}	1.9645×10^{-03}	2.3595×10^{-05}	2.7994×10^{-05}	6.8407×10^{-07}
2.9812×10^{-03}	2.5242×10^{-07}	3.2100×10^{-05}	4.1207×10^{-04}	5.4609×10^{-03}	2.4930×10^{-03}	4.4254×10^{-05}	3.0913×10^{-05}	9.3489×10^{-07}
3.4930×10^{-03}	2.4317×10^{-07}	3.4100×10^{-05}	5.2519×10^{-04}	6.3319×10^{-03}	2.8701×10^{-03}	6.3903×10^{-05}	3.2735×10^{-05}	1.1217×10^{-06}
5.3405×10^{-03}	2.2281×10^{-07}	3.9864×10^{-05}	9.8062×10^{-04}	9.3689×10^{-03}	4.1554×10^{-03}	1.6482×10^{-04}	3.7850×10^{-05}	1.7915×10^{-06}
6.3377×10^{-03}	2.1624×10^{-07}	4.2354×10^{-05}	1.2478×10^{-03}	1.0950×10^{-02}	4.8101×10^{-03}	2.3771×10^{-04}	3.9992×10^{-05}	2.1455×10^{-06}
$T = 573.16 \text{ K}$								
4.8030×10^{-04}	6.2678×10^{-08}	7.5883×10^{-05}	9.4913×10^{-05}	8.5072×10^{-04}	3.0273×10^{-04}	6.8405×10^{-06}	7.4532×10^{-05}	1.2887×10^{-06}
9.9900×10^{-04}	5.0609×10^{-08}	1.0082×10^{-04}	2.9450×10^{-04}	1.6249×10^{-03}	5.6594×10^{-04}	3.7790×10^{-05}	9.7760×10^{-05}	3.0095×10^{-06}
1.0341×10^{-03}	5.0178×10^{-08}	1.0207×10^{-04}	3.0955×10^{-04}	1.6740×10^{-03}	5.8177×10^{-04}	4.0768×10^{-05}	9.8893×10^{-05}	3.1247×10^{-06}
1.6617×10^{-03}	4.5228×10^{-08}	1.1976×10^{-04}	5.9480×10^{-04}	2.5021×10^{-03}	8.3648×10^{-04}	1.1071×10^{-04}	1.1459×10^{-04}	5.1173×10^{-06}
1.7021×10^{-03}	4.5020×10^{-08}	1.2068×10^{-04}	6.1387×10^{-04}	2.5527×10^{-03}	8.5139×10^{-04}	1.1622×10^{-04}	1.1539×10^{-04}	5.2410×10^{-06}
1.7082×10^{-03}	4.4990×10^{-08}	1.2081×10^{-04}	6.1675×10^{-04}	2.5603×10^{-03}	8.5362×10^{-04}	1.1706×10^{-04}	1.1551×10^{-04}	5.2596×10^{-06}
2.1169×10^{-03}	4.3305×10^{-08}	1.2914×10^{-04}	8.1223×10^{-04}	3.0573×10^{-03}	9.9666×10^{-04}	1.7891×10^{-04}	1.2262×10^{-04}	6.4799×10^{-06}
2.4893×10^{-03}	4.2212×10^{-08}	1.3556×10^{-04}	9.9276×10^{-04}	3.4903×10^{-03}	1.1170×10^{-03}	2.4400×10^{-04}	1.2797×10^{-04}	7.5456×10^{-06}
2.8549×10^{-03}	4.1398×10^{-08}	1.4106×10^{-04}	1.1709×10^{-03}	3.9001×10^{-03}	1.2279×10^{-03}	3.1511×10^{-04}	1.3246×10^{-04}	8.5523×10^{-06}
3.0211×10^{-03}	4.1090×10^{-08}	1.4335×10^{-04}	1.2519×10^{-03}	4.0821×10^{-03}	1.2763×10^{-03}	3.4959×10^{-04}	1.3431×10^{-04}	8.9979×10^{-06}
3.8110×10^{-03}	3.9988×10^{-08}	1.5291×10^{-04}	1.6359×10^{-03}	4.9153×10^{-03}	1.4924×10^{-03}	5.2989×10^{-04}	1.4184×10^{-04}	1.1023×10^{-05}
4.8815×10^{-03}	3.9081×10^{-08}	1.6336×10^{-04}	2.1494×10^{-03}	5.9781×10^{-03}	1.7578×10^{-03}	8.1098×10^{-04}	1.4976×10^{-04}	1.3556×10^{-05}
4.9368×10^{-03}	3.9046×10^{-08}	1.6384×10^{-04}	2.1757×10^{-03}	6.0312×10^{-03}	1.7708×10^{-03}	8.2649×10^{-04}	1.5012×10^{-04}	1.3681×10^{-05}
6.4773×10^{-03}	3.8358×10^{-08}	1.7571×10^{-04}	2.8955×10^{-03}	7.4595×10^{-03}	2.1148×10^{-03}	1.2913×10^{-03}	1.5869×10^{-04}	1.6979×10^{-05}
7.6692×10^{-03}	3.8078×10^{-08}	1.8332×10^{-04}	3.4369×10^{-03}	8.5068×10^{-03}	2.3613×10^{-03}	1.6877×10^{-03}	1.6397×10^{-04}	1.9316×10^{-05}
9.9251×10^{-03}	3.7865×10^{-08}	1.9537×10^{-04}	4.4273×10^{-03}	1.0389×10^{-02}	2.7972×10^{-03}	2.5053×10^{-03}	1.7198×10^{-04}	2.3348×10^{-05}

^a Concentrations corresponding to the experimental condition of the present calorimetric measurements, Table 2.

The heat of solution of sodium sulfate refers to the following reaction:



Since the thermodynamic functions of the solid salt have already been characterized,⁴ the enthalpies of solution in effect provide the thermodynamic properties of the dissolved solute, Na₂SO₄(aq). The advantage of the present calorimeter is that measurements to extremely dilute solutions of the electrolyte are possible; 10^{-2} – 10^{-4} m is the normal operating range and even concentrations down to 10^{-5} m are feasible. These concentrations make it possible to obtain standard state enthalpy of solution values which are less sensitive to the theoretical model used for the extrapolation to infinite dilution or to the exact value of Debye–Hückel limiting law slopes.

Up to 373.15 K the integral heats of solution of sodium sulfate have been measured at concentrations sufficiently low to obtain standard state properties.⁵ But above 373.15 K, where the nonideality of ionic solution becomes more pronounced, measurements applicable to accurately defining standard state values are scarce. Most of the data in the literature are from calorimetric measurements at concentrations greater than 0.05 m.^{3,6} At these higher concentrations, ion association greatly increases the uncertainties. Apparent molar heat capacity, $C_{p,\varphi}$, measurements were reported by Rogers and Pitzer⁶ up to 473.15 K at p_{sat} and 20 MPa using flow calorimetry, at $m \geq 0.05$. Pabalan and Pitzer³ also measured $C_{p,\varphi}$ of aqueous sodium sulfate solutions from 413.15 to 573.15 K at 20 MPa using a flow calorimeter over the range of 0.05–1.5 m. Isopiestic studies of concentrated solutions ($m > 0.5$) of aqueous sodium sulfate up to 498.15 K

have also been reported by Holmes and Mesmer.⁷ The standard state partial molal volumes, \bar{V}_2° , of Na₂SO₄(aq) at 10 MPa have been reported up to 573.15 K.⁸ The values for \bar{V}_2° from 298.15 to 473.15 K and at p_{sat} , are also available in literature.⁹

In this communication, reliable standard state thermodynamic data for Na₂SO₄(aq) are reported up to 598.15 K.

2. Experimental Section

2.1. Materials. Distilled water used in the measurements and in the calorimeter was passed through a Milli-Q reagent grade mixed bed ion exchange column/activated charcoal system (resistivity $\geq 18 \text{ M}\Omega \text{ cm}$). Anhydrous sodium sulfate salt (99.99%), from Alfa-Aesar, was recrystallized twice and dried at 573.15 K. Quartz bulbs containing the dried material were sealed under vacuum.

2.2. Apparatus. The integral heats of solution of sodium sulfate were measured from 444.76 to 573.16 K in the high temperature calorimeter previously described.¹⁰ The main calorimeter reaction vessel is a cylindrical pressure vessel about 17 cm in length and 13 cm in diameter, machined out of a titanium-0.2% palladium alloy ingot and has available volume of approximately 865 mL. The calorimeter vessel has a lid that is pressure sealed with a gold O-ring and positioned inside a stainless steel vacuum jacket, and is placed inside a large air thermostat. The calorimeter is stirred magnetically, and an electromagnetic trip assembly causes the bulb containing a chemical sample to break under the solvent. A thermistor (VECO 0.100 glass probes series) serves as the temperature-sensing element. The calorimeter has a maximum thermal drift of 1×10^{-4} K/min at a temperature of 573 K and a sensitivity of 10^{-5} K. All the electrical connections inside the calorimeter

TABLE 2: Experimental Integral Heats of Solution of Sodium Sulfate^a

$n_{\text{Na}_2\text{SO}_4(\text{cr})}$ ($\times 10^4$)	$m_{\text{Na}_2\text{SO}_4(\text{cr})}$ ($\times 10^4$)	I_f^b ($\times 10^3$)	q_{obs}^c (Joules)	q_b^d (Joules)	q_{vp}^e (Joules)	$q_{\text{HSO}_4^-}^f$ (Joules)	$q_{\text{NaSO}_4^-}^g$ (Joules)	$q_{\text{Na}_2\text{SO}_4}^h$ (Joules)	q_{sol}^i (Joules)	$\Delta_{\text{sol}}\bar{H}^j$ (kJ mol ⁻¹)	ρ (kJ mol ⁻¹)
$T = 444.76 \text{ K}$											
6.5010	13.4170	3.8486	-30.285	5.837	0.079	0.286	0.593	0.022	-36.943	-56.827	-58.894
8.8900	19.3710	5.4798	-44.404	4.812	0.201	0.318	1.053	0.053	-50.439	-56.737	-59.154
15.3970	32.2620	8.8967	-75.424	5.908	0.192	0.408	2.538	0.197	-84.282	-54.739	-57.707
15.7830	38.6350	10.5381	-84.065	5.197	0.356	0.374	2.893	0.260	-92.433	-58.565	-61.745
20.5040	42.2950	11.4686	-94.168	7.238	0.218	0.459	3.955	0.382	-105.985	-51.690	-54.980
25.7030	55.8120	14.8371	-129.432	4.774	0.368	0.483	5.740	0.691	-140.752	-54.761	-58.401
$T = 486.56 \text{ K}$											
4.6130	9.9720	2.8284	-28.372	13.941	0.222	0.685	0.921	0.031	-43.728	-94.793	-97.590
5.3340	10.4330	2.9543	-42.012	13.368	0.180	0.771	1.101	0.038	-57.111	-107.069	-109.921
11.2070	22.8870	6.2342	-97.316	10.146	0.452	1.017	3.905	0.264	-112.197	-100.113	-104.044
14.7350	29.8120	7.9763	-97.512	9.293	0.544	1.134	5.974	0.500	-113.869	-77.278	-81.620
17.0430	34.9300	9.2341	-108.880	13.150	0.653	1.185	7.516	0.713	-130.792	-76.742	-81.342
26.3860	53.4050	13.6070	-189.866	11.255	0.937	1.388	14.210	1.863	-217.645	-82.485	-87.806
31.5420	63.3770	15.8792	-212.380	10.163	1.079	1.477	18.214	2.707	-243.861	-77.313	-82.938
$T = 573.16 \text{ K}$											
2.0670	4.8030	1.1569	-21.665	31.326	0.321	1.572	5.072	0.153	-59.466	-287.693	-293.052
4.4500	10.3410	2.2762	-73.124	32.154	0.669	2.085	16.541	0.912	-124.146	-278.981	-285.795
7.1510	16.6170	3.3939	-116.934	42.957	1.046	2.416	31.785	2.476	-195.523	-273.420	-281.094
7.3250	17.0210	3.4622	-126.315	38.058	1.071	2.433	32.805	2.599	-201.138	-274.592	-282.308
7.3510	17.0820	3.4725	-90.128	67.643	1.074	2.436	32.958	2.618	-194.707	-264.872	-272.595
9.1100	21.1690	4.1434	-166.640	37.120	1.310	2.586	43.404	4.001	-252.442	-277.104	-285.202
12.2860	28.5490	5.2856	-196.560	66.333	1.728	2.793	62.572	7.046	-333.576	-271.509	-280.120
13.0010	30.2110	5.5333	-240.329	40.468	1.824	2.832	66.899	7.817	-356.521	-274.226	-282.933
16.4003	38.1100	6.6726	-248.040	68.705	2.251	2.991	87.419	11.849	-416.753	-254.114	-263.218
21.0050	48.8150	8.1414	-329.875	81.847	2.816	3.158	114.848	18.132	-545.045	-259.483	-269.018
21.2450	49.3680	8.2153	-377.158	41.476	2.845	3.166	116.265	18.481	-553.700	-260.626	-270.180
27.8070	64.7730	10.2200	-414.132	85.341	3.628	3.338	154.355	28.805	-682.344	-245.386	-255.431
33.0040	76.6920	11.7120	-561.338	79.981	4.209	3.458	183.663	37.739	-861.969	-261.171	-271.540
42.7120	99.2510	14.4388	-705.711	83.977	5.247	3.627	236.587	56.021	-1080.68	-253.015	-263.911

^a $\text{Na}_2\text{SO}_4(\text{cr}) = \text{Na}_2\text{SO}_4(\text{aq})$. ^b Final ionic strength. ^c Observed heat. ^d Calculated bulb-breaking heat from the steam tables.¹² ^e Heat due to vapor pressure correction. ^f Heat contribution due to hydrolysis of $\text{SO}_4^{2-}(\text{aq})$ (eq 10). ^g Heat contribution due to association of $\text{SO}_4^{2-}(\text{aq})$ with $\text{Na}^+(\text{aq})$ (eq 4). ^h Heat contribution due to association of $\text{NaSO}_4^-(\text{aq})$ with $\text{Na}^+(\text{aq})$ (eq 5). ⁱ Heat of solution (eq 1). ^j $\Delta_{\text{sol}}\bar{H} = q_{\text{sol}}/n_{\text{Na}_2\text{SO}_4}$.

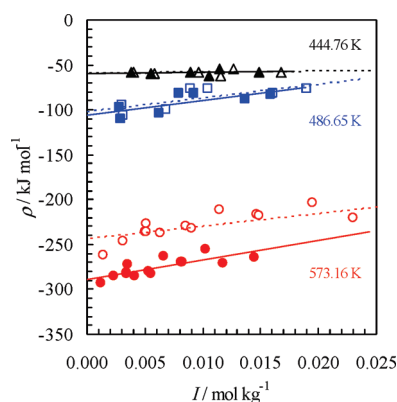


Figure 2. Rho plot (weighted values) of the heats of solution of sodium sulfate at 573.16 K: open symbols, experimental values not corrected for hydrolysis or ion associations; solid symbols, experimental values corrected for hydrolysis and ion associations; solid and dashed lines, least-squares fits.

system use gold wire and connections are made either by fusing the gold wires or by silver soldering.

2.3. Procedures. Experimental procedures used have been described previously.¹¹ The calorimeter was calibrated electrically for each experimental run, and calibration was confirmed by also measuring the molar energy of vaporization of water, $\Delta_{\text{vap}}\bar{E}(T, p_{\text{sat}})$, by breaking empty bulbs of known volumes. The overall accuracy of the calorimetric measurements by this separate test is on average approximately $\pm 0.5\%$, when compared to values given in the steam tables.¹²

TABLE 3: The Experimental Enthalpies (kJ mol⁻¹) of Solution of Sodium Sulfate at p_{sat}

T (K)	ρ^a	σ_p^b	δH_V^c	σ_V^d	$\Delta_{\text{sol}}\bar{H}^e$ (T, p_{sat})	$\sigma_{\rho,V}^f$
273.96	8.347	0.105	0.000	0.000	8.347	0.105
277.68	5.937	0.042	-0.001	0.000	5.937	0.042
285.69	2.121	0.013	-0.001	0.000	2.121	0.013
298.15	-2.435	0.021	-0.002	0.000	-2.436	0.021
313.24	-6.841	0.021	-0.004	0.000	-6.852	0.021
333.43	-12.088	0.025	-0.011	0.000	-12.088	0.025
358.32	-18.389	0.021	-0.033	0.001	-18.422	0.021
368.15	-21.188	0.025	-0.049	0.002	-21.237	0.025
444.76	-59.440	6.566	-0.690	0.034	-60.130	6.566
486.56	-106.163	8.199	-2.361	0.118	-108.524	8.200
573.16	-288.983	2.913	-37.613	1.881	-326.596	3.372

^a Extrapolated heat of solution to infinite dilution. Values below 373 K are recalculated from data of Gardner et al.⁵ ^b Estimated uncertainty in ρ . ^c Heat contribution due to volume change on introduction of solute (eq 11). ^d Estimated uncertainty for δH_V . ^e Enthalpy of solution at p_{sat} . ^f Propagated error for enthalpy of solution at p_{sat} .

3. Calculations and Results

The molal enthalpies of the solution, $\Delta_{\text{sol}}\bar{H}$, are calculated from the experimentally observed heats, q_{obs} , in the present calorimeter as follows. The heats observed in the solution process contain contributions from several sources:¹³

$$q_{\text{obs}} = q_{\text{sol}} + q_{\text{bulb}} + q_{\text{vp}} + q \quad (2)$$

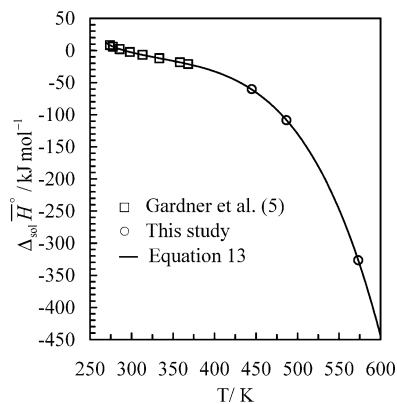


Figure 3. Standard state enthalpies of solutions of sodium sulfate at p_{sat} .

TABLE 4: Empirical Parameters for Calculating Standard State Enthalpies of Solution of Sodium Sulfate from eq 13

a_1	4.17513×10^{02}
a_2	-3.07510×10^{00}
a_3	9.25978×10^{-03}
a_4	-5.39942×10^{03}
a_5	1.50939×10^{03}
a_6	2.07929×10^{-02}
a_7	2.53632×10^{02}

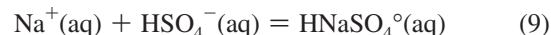
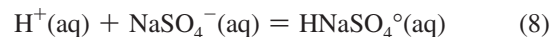
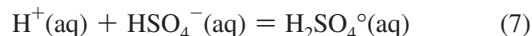
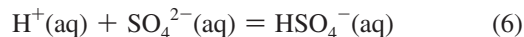
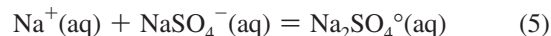
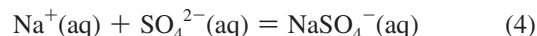
TABLE 5: Standard State Partial Molal Heat Capacities ($\text{J mol}^{-1} \text{K}^{-1}$) of Completely Ionized Aqueous Sodium Sulfate at p_{sat}

T (K)	$\bar{C}_{p,2}^{oa}$	$\bar{C}_{p,2}^{ob}$	$\bar{C}_{p,2}^{oc}$	$\bar{C}_{p,2}^{od}$
298.15	-195.7	-196.0	-187.5	-196.5
323.15	-123.5	-122.8	-118.3	-132.5
348.15	-119.0	-119.5	-105.9	-128.4
373.15	-172.3	-173.4	-130.7	-153.5
398.15	-288.1	-284.2	-174.1	-199.7
423.15	-474.4	-453.7	-228.0	-264.1
448.15	-741.6	-685.4	-296.2	-345.3
473.15	-1104.4	-985.0	-396.4	-442.5
498.15	-1585.1	-1364.6	-565.9	
523.15	-2217.7	-1845.9	-879.6	
548.15	-3136.0	-2547.9	-1505.5	
573.15	-4742.6	-3855.5	-2896.5	

^a This study, corrected explicitly for hydrolysis and ion associations. ^b This study, not corrected for hydrolysis or ion associations. ^c Pabalan and Pitzer,³ not corrected for hydrolysis or ion associations. ^d Rogers and Pitzer,⁶ not corrected for hydrolysis or ion associations.

where q_{sol} is the integral heats of solution of the salt, q_{bulb} is the heat involved when liquid water is evaporated in the calorimeter due to the breaking and collapse of the evacuated bulb containing the salt, and q_{vp} is the heat due to condensation of some vapor because of the small lowering of the vapor pressure of water when the solute is introduced. The values for q are calculated depending on what corrections are included in the present model as follows.

To correct the observed heats for contribution from side reactions, the nonlinear system of mass balance equations and mass action law equations corresponding to the following chemical reactions in aqueous solution of sodium sulfate was solved by a modified Newton method.¹⁴



The equilibrium constant for dissociation of water, reaction 3, is from Marshall and Franck¹⁵ and those for reactions 4–9 are from the conductance measurements of Hnedkovsky et al.^{2a} However, in the present study since the concentration of $\text{H}^+(\text{aq})$ is low (approximately 10^{-8}), contributions from reactions 7–8 are negligible and therefore will be ignored. The equilibrium constants for hydrolysis of $\text{SO}_4^{2-}(\text{aq})$ ion

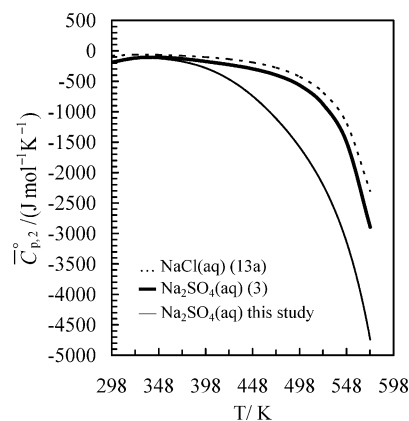


Figure 4. Standard state partial molal heat capacities of fully ionized aqueous sodium sulfate at p_{sat} .

TABLE 6: Stoichiometric Activity Coefficients for Saturated Solution of Sodium Sulfate at p_{sat}

T (K)	m_{sat}^a (mol kg ⁻¹)	γ_{sat}^b	γ_{sat}^c	γ_{sat}^d
323.15	3.23	0.1433	0.1433	0.1430
348.15	3.08	0.1346	0.1346	0.1360
373.15	2.99	0.1195	0.1195	0.1220
398.15	2.95	0.1013	0.1013	0.1040
423.15	2.96	0.0807	0.0807	0.0850
448.15	3.04	0.0593	0.0596	0.0680
473.15	3.16	0.0401	0.0407	0.0510
498.15	3.22	0.0252	0.0261	0.0370
523.15	3.09	0.0151	0.0163	0.0280
548.15	2.60	0.0091	0.0105	0.0220
573.15	1.69	0.0062	0.0081	0.0210

^a Solubilities from Linke and Seidell.²¹ ^b This study, corrected for hydrolysis of $\text{SO}_4^{2-}(\text{aq})$ and association of $\text{Na}^+(\text{aq})$ with $\text{SO}_4^{2-}(\text{aq})$ and $\text{NaSO}_4^-(\text{aq})$. ^c This study, with no explicit corrections for hydrolysis of $\text{SO}_4^{2-}(\text{aq})$ or association of $\text{Na}^+(\text{aq})$ with $\text{SO}_4^{2-}(\text{aq})$ and $\text{NaSO}_4^-(\text{aq})$. ^d Pabalan and Pitzer,³ with no explicit corrections for hydrolysis of $\text{SO}_4^{2-}(\text{aq})$ or association of $\text{Na}^+(\text{aq})$ with $\text{SO}_4^{2-}(\text{aq})$.



were obtained from addition of reactions 3 and 6. The values for activity coefficients of mixed electrolytes at the final ionic strength were estimated from a Pitzer model,¹⁶ and the solution of the nonlinear chemical system was repeated until the desirable convergence was achieved. The equilibrium concentrations of the principal species in aqueous solutions of sodium sulfate from this study were then calculated and are summarized in Table 1.

There is an additional correction due to the resulting change in the volume of the solution upon introduction of a solute sample. This correction, $\delta\bar{H}_V$, is added as a molal correction to the resulting molal enthalpies and is calculated as follows:

$$\delta\bar{H}_V = \Delta_{\text{sol}}\bar{V}^\circ\Delta_{\text{vap}}\bar{E}/\Delta_{\text{vap}}\bar{V} \quad (11)$$

$$\Delta_{\text{sol}}\bar{V}^\circ = \bar{V}_2^\circ - V^\circ(\text{cr}) \quad (12)$$

where $\Delta_{\text{sol}}\bar{V}^\circ$ is the standard molal volume change for the process of solution of the sample, \bar{V}_2° is the standard state partial molal volume of the electrolyte, $V^\circ(\text{cr})$ is the molar volume of solid solute; $\Delta_{\text{vap}}\bar{E}$ and $\Delta_{\text{vap}}\bar{V}$ are the molar energy and molar volume of vaporization of water calculated from the steam tables.¹² The values of $\bar{V}_2^\circ(\text{Na}_2\text{SO}_4, \text{aq})$ at p_{sat} are calculated from the unified theory of electrolytes¹⁷ and $V^\circ(\text{Na}_2\text{SO}_4, \text{cr})$ is calculated from its density.¹⁸ The uncertainties in the values of $\bar{V}_2^\circ(\text{Na}_2\text{SO}_4, \text{aq})$ are directly proportional to the uncertainties in dielectric constant and its temperature and pressure derivatives.

The heats of solution (reaction 1) of sodium sulfate measured from 444.76 to 573.16 K are summarized in Table 2. The values of ρ , ρ° ,^{11,13} were obtained by subtracting the extended Debye–Hückel heat of dilution at a given temperature and concentration from the measured heat of solution. The extrapolated value of ρ at infinite dilution, ρ° , was obtained at each temperature using a weighted linear least-squares analysis and each data point was weighted according to its estimated uncertainty.

To illustrate behavior of the ions at higher temperatures, the data from this study are presented with and without invoking hydrolysis of $\text{SO}_4^{2-}(\text{aq})$, reaction 10, and ion association (reactions 4–9). For example, in Figure 2, the values of ρ are plotted against the final ionic strength, I , under both sets of conditions.

The required enthalpy correction due to volume change of the liquid placed in the calorimeter as the result of introduction of the solute, δH_V , must be added to the extrapolated value of ρ , ρ° , in order to obtain the experimental standard state enthalpy. These standard state enthalpies at p_{sat} , $\Delta_{\text{sol}}\bar{H}^\circ(T, p_{\text{sat}})$, for solutions of sodium sulfate from 444.76 to 573.16 K and

their estimated propagated errors at each experimental temperature are summarized in Table 3.

The experimental enthalpies for the solution of sodium sulfate at p_{sat} , $\Delta_{\text{sol}}\bar{H}^\circ(T, p_{\text{sat}})$, from this study together with corresponding values from Gardner et al.⁶ from 273.15 to 368.16 K were empirically fitted to eq 13 (Figure 3):

$$\Delta_{\text{sol}}\bar{H}^\circ = a_1 + a_2T + a_3T^2 + a_4T^2/(a_5 - T)^2 + a_6T^2/(T - a_7)^2 \quad (13)$$

This equation, while purely empirical, has been used for enthalpies of solution of a wide variety of electrolytes^{13,19} and the extrapolated values of the enthalpy of solution up to 598.15 K are believed to be reliable. The resulting parameters are summarized in Table 4.

The standard state partial molal heat capacities of aqueous sodium sulfate are calculated from the following equation:

$$\bar{C}_{p,2}^\circ = C_p^\circ(\text{cr}) + (\partial\Delta_{\text{sol}}\bar{H}^\circ/\partial T)_{\text{sat}} + [\Delta_{\text{sol}}\bar{V}^\circ - T(\partial\Delta_{\text{sol}}\bar{V}^\circ/\partial T)_p](\partial p/\partial T)_{\text{sat}} \quad (14)$$

where the molar heat capacities of the solid, $C_p^\circ(\text{cr})$, are from literature⁴ and $(\partial p/\partial T)_{\text{sat}}$ is from Keenan et al.¹² These $\bar{C}_{p,2}^\circ$ are listed in table 5 and also plotted in Figure 4. The contribution to $\bar{C}_{p,2}^\circ$ from the molal volume, the third term in eq 14, indicates that a 10% uncertainty at 573.15 K in this term will introduce an error of approximately 2% to the overall value of $\bar{C}_{p,2}^\circ$. The probable error in the values of $\bar{C}_{p,2}^\circ$ for $\text{Na}_2\text{SO}_4(\text{aq})$ are estimated to be (15, 30, 120, 250) J mol⁻¹ K⁻¹ at temperatures of (473.15, 523.15, 573.15, 598.15) K, respectively.

The important standard state Gibbs free energies of solution of sodium sulfate are calculated from eq 15 together with eq 13, parameter values from Table 4, and the values of the standard state molal volume of solution, $\Delta_{\text{sol}}\bar{V}^\circ$:

$$\Delta_{\text{sol}}\bar{G}^\circ(T, p_{\text{sat}}) = T/T_r\Delta_{\text{sol}}\bar{G}^\circ(T_r, p_r) - T\int_{T_r}^T \Delta_{\text{sol}}\bar{H}^\circ(T, p_{\text{sat}})/T^2 dT + T\int_{T_r}^T \Delta_{\text{sol}}\bar{V}^\circ(T, p_{\text{sat}})/T(\partial p/\partial T)_{\text{sat}} dT \quad (15)$$

where T_r and p_r are the reference temperature (298.15 K) and the reference pressure (0.1 MPa) and $\Delta_{\text{sol}}\bar{G}^\circ(298.15 \text{ K}, 0.1 \text{ MPa})$ is calculated from NBS tables.²⁰

The uncertainty associated with the calculation of $\Delta_{\text{sol}}\bar{G}^\circ(T, p_{\text{sat}})$ from the above equation is mainly due to the uncertainty in estimation of the standard state partial molal volume, \bar{V}_2° , at p_{sat} . Fortunately, even a 10% uncertainty in \bar{V}_2° will result in

TABLE 7: Stoichiometric Activity Coefficients for Aqueous Solutions of Sodium Sulfate Calculated from Meissner–Lindsay²² Model at p_{sat}

m (mol kg ⁻¹)	298.15 K	323.15 K	373.15 K	423.15 K	473.15 K	523.15 K	573.15 K
0.10	0.4324	0.4168	0.3742	0.3233	0.2586	0.1890	0.1122
0.25	0.3295	0.3159	0.2747	0.2254	0.1656	0.1068	0.0504
0.50	0.2637	0.2532	0.2150	0.1684	0.1145	0.0655	0.0246
0.75	0.2308	0.2225	0.1866	0.1419	0.0916	0.0485	0.0157
1.00	0.2099	0.2033	0.1692	0.1259	0.0783	0.0392	0.0114
1.50	0.1837	0.1797	0.1480	0.1067	0.0627	0.0288	0.0072
2.00	0.1667	0.1648	0.1351	0.0948	0.0530	0.0226	0.0049
2.50	0.1543	0.1543	0.1261	0.0865	0.0463	0.0185	0.0035
3.00	0.1448	0.1464	0.1194	0.0802	0.0414	0.0155	0.0026

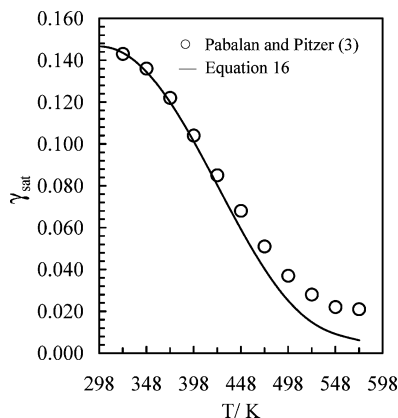


Figure 5. Activity coefficient of solid-saturated aqueous sodium sulfate at p_{sat} .

less than 0.2% error in $\Delta_{\text{sol}}\bar{G}^{\circ}(T, p_{\text{sat}})$ at the highest temperature because the contribution of \bar{V}_2° to the second and third terms in eq 15 has the opposite sign and comparable magnitude. Consequently, as the result of this partial cancellation of the effect of \bar{V}_2° , the total contribution of \bar{V}_2° at the highest temperature of this study is less than 4% of $\Delta_{\text{sol}}\bar{G}^{\circ}(T, p_{\text{sat}})$.

It is important to note that $\Delta_{\text{sol}}\bar{G}^{\circ}(T, p_{\text{sat}})$ derived from these thermal measurements unambiguously defines the activity of the solute in a solid-saturated solution of the electrolyte at any temperature:

$$\Delta_{\text{sol}}\bar{G}^{\circ} = -RT \ln(4\gamma_{\text{sat}}^3 m_{\text{sat}}^3) \quad (16)$$

where γ_{sat} and m_{sat} are the stoichiometric activity coefficient and the solubility of the solid-saturated solution at temperature T , respectively.

The values of γ_{sat} for solutions of sodium sulfate at p_{sat} up to 598.15 K were calculated from eq 16 using solubility data from literature²¹ and are given in Table 6 and Figure 5. These stoichiometric activity coefficients at the solid-saturated solutions, γ_{sat} , can also be extended to all concentrations using the Meissner–Lindsay model.²² This model is a simple empirical equation of an extended Debye–Hückel form which provides the stoichiometric activity coefficients for all concentrations at a given T and p when experimental value at only one concentration is given at the same T and p . The stoichiometric activity coefficients of aqueous solutions of sodium sulfate for all concentrations ($0 \leq m \leq m_{\text{sat}}$) at p_{sat} calculated from this study are given in Table 7 and comparison with literature values are summarized in Figure 6.

For convenience of the reader, the standard state thermodynamic properties for Na₂SO₄(aq) from 298.15 to 598.15 K are listed in Table 8. The auxiliary data for Na₂SO₄(cr) are from JANAF tables.⁴

4. Discussion

As previously noted, the comprehensive set of equations for the thermodynamic properties of Na₂SO₄(aq) at temperatures from 298.15 to 573.15 K reported by Pabalan and Pitzer³ did not explicitly include any corrections for hydrolysis of sulfate ion or ion association in their model. The extent of hydrolysis of SO₄²⁻(aq) and ion association to form NaSO₄⁻(aq), Na₂SO₄^o(aq), HSO₄⁻(aq), H₂SO₄^o(aq), and NaHSO₄(aq) as a function of concentration can now be evaluated from recently reported conductance measurements.^{2a} For example, the degree of association, $\alpha_{\text{NaSO}_4^-}$, was

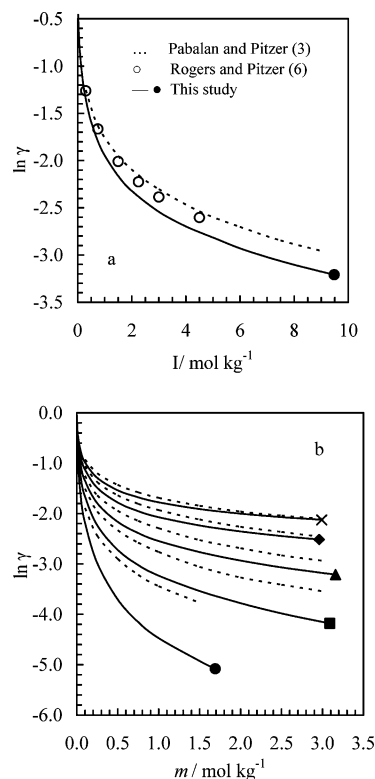


Figure 6. Comparison of stoichiometric mean activity coefficient of aqueous sodium sulfate at p_{sat} (a) at 473.15 K and (b) at different temperatures (from top to bottom, 373.15, 423.15, 473.15, 523.15, 573.15 K): solid lines, this study; dashed lines, Pabalan and Pitzer;³ solid symbols, this study at saturation.

calculated from the association constant of SO₄²⁻(aq) with Na⁺(aq) from 373.15 to 573.15 K ($m \leq 0.01$) and is listed in Table 9. These results indicate that at $m \geq 0.01$ ion association in aqueous solutions of sodium sulfate cannot be ignored at temperatures greater than 373.15 K.

The standard state partial molal heat capacities of Na₂SO₄(aq) from this study are compared with the literature values^{3,6} in Table 5 and Figure 4. The agreement is good only up to 373.15 K. As expected, at 473.15 K the result of the present study differs by approximately 60% from those reported by Pabalan and Pitzer.³ The lowest concentration of their study was 0.05 m and, from the above discussion, the lack of ion association in their model is believed to be mainly responsible for these differences. For the sake of comparison of their data at high temperatures, the results from the present study have also been analyzed without invoking ion association or hydrolysis of SO₄²⁻(aq) ion and are included in Table 5. From these data a similar conclusion to the above can be reached regarding the Pabalan and Pitzer³ values of $\bar{C}_{p,2}^{\circ}$. The lowest concentration in the present study is ($10^{-4} m$), as compared to 0.05 m in their study.³ The difficulties involving the extrapolations of various thermodynamic functions from regions outside the validity of a simple limiting law (Debye–Hückel) have been discussed in more detail elsewhere.²³ The comparison of $\bar{C}_{p,2}^{\circ}$ values for Na₂SO₄(aq) from Pabalan and Pitzer³ with those of NaCl(aq)^{13a} indicates that as a result of high concentration ($m \geq 0.05$) their apparent molar heat capacities at temperatures greater than 373.15 K were not extrapolated correctly to the standard state of completely ionized sodium sulfate, Na₂SO₄(aq). For example, at 573.15 K their absolute value for $\bar{C}_{p,2}^{\circ}$ of Na₂SO₄(aq) is only 20% larger than that of NaCl(aq).^{13a}

The stoichiometric activity coefficients for saturated solutions of aqueous sodium sulfate up to 573.15 K are compared with

TABLE 8: Standard State Thermodynamic Properties of Completely Ionized Na₂SO₄(aq)^a

T (K)	($\bar{H}_2^\circ(T) - \bar{H}_2^\circ(T_r)$) ^b (kJ mol ⁻¹)	($\bar{G}_2^\circ(T) - \bar{G}_2^\circ(T_r)$) ^c (kJ mol ⁻¹)	\bar{S}_2° ^d (J mol ⁻¹ K ⁻¹)	$\bar{C}_{p,2}^\circ$ ^e (J mol ⁻¹ K ⁻¹)	\bar{V}_2° ^f (cm ³ mol ⁻¹)	(d \bar{V}_2° /dT) _p ^f (cm ³ mol ⁻¹ K ⁻¹)	(d \bar{V}_2° /dp) _T ^f (cm ³ mol ⁻¹ MPa ⁻¹)
298.15	0.000	0.000	138.1 ^g	-195.7	14.0	-9.637 × 10 ⁻⁰²	1.788 × 10 ⁻⁰¹
323.15	-3.808	-3.219	125.6	-123.5	10.9	-1.492 × 10 ⁻⁰¹	1.974 × 10 ⁻⁰¹
348.15	-6.718	-6.185	116.7	-119.0	6.5	-2.051 × 10 ⁻⁰¹	2.249 × 10 ⁻⁰¹
373.15	-10.233	-8.930	106.9	-172.3	0.5	-2.809 × 10 ⁻⁰¹	2.665 × 10 ⁻⁰¹
398.15	-15.833	-11.378	92.2	-288.1	-7.8	-3.922 × 10 ⁻⁰¹	3.323 × 10 ⁻⁰¹
423.15	-25.163	-13.373	69.4	-474.4	-19.5	-5.634 × 10 ⁻⁰¹	4.422 × 10 ⁻⁰¹
448.15	-40.066	-14.673	35.2	-741.6	-36.5	-8.379 × 10 ⁻⁰¹	6.363 × 10 ⁻⁰¹
473.15	-62.380	-14.965	-13.2	-1104.4	-62.2	-1.303 × 10 ⁰⁰	1.002 × 10 ⁰⁰
498.15	-94.996	-13.866	-80.2	-1585.1	-102.8	-2.147 × 10 ⁰⁰	1.749 × 10 ⁰⁰
523.15	-129.469	-10.944	-147.9	-2217.7	-171.4	-3.837 × 10 ⁰⁰	3.444 × 10 ⁰⁰
548.15	-190.510	-5.769	-261.9	-3136.0	-298.1	-7.722 × 10 ⁰⁰	7.894 × 10 ⁰⁰
573.15	-271.044	1.938	-404.4	-4742.6	-565.7	-1.876 × 10 ⁰¹	2.262 × 10 ⁰¹
598.15	-375.190	11.664	-577.9	-8305.4	-1284.8	-5.310 × 10 ⁰¹	9.698 × 10 ⁰¹

^a T_r = 298.15 K. ^b Equation 13. ^c Equation 15. ^d $\bar{S}_2^\circ(T) = [(\bar{H}_2^\circ(T) - \bar{H}_2^\circ(T_r)) - (\bar{G}_2^\circ(T) - \bar{G}_2^\circ(T_r))]/T + T_r \bar{S}_2^\circ(T_r)/T$. ^e Equation 14. ^f Calculated from unified theory of electrolytes.¹⁷ ^g From NBS tables.²⁰

TABLE 9: Degree of Association, α, of Na⁺(aq) with SO₄²⁻(aq) at Different T and m Calculated from Conductance Data^{2a}

T (K)	m/mol kg ⁻¹	α
573.15	0.001	0.318
573.15	0.005	0.520
573.15	0.010	0.571
523.15	0.001	0.119
523.15	0.005	0.289
523.15	0.010	0.359
473.15	0.001	0.041
473.15	0.005	0.137
473.15	0.010	0.197
423.15	0.001	0.017
423.15	0.005	0.066
423.15	0.010	0.106
373.15	0.001	0.009
373.15	0.005	0.038
373.15	0.010	0.065

the results of Pabalan and Pitzer³ in Figure 5. As expected, the agreement is satisfactory only up to 373.15 K. The stoichiometric activity coefficients of aqueous solutions of sodium sulfate at all concentrations (0 ≤ m ≤ m_{sat}) at p_{sat} calculated from the Meissner-Lindsay model²² are also compared with Pabalan and Pitzer³ in Figure 6. The two sets of data only agree to within combined uncertainties up to 423.15 K.

In Figure 7, the standard state partial molal volume, $\bar{V}_2^\circ(\text{Na}_2\text{SO}_4, \text{aq})$, at 10 MPa, calculated from the unified theory of electrolytes,¹⁷ using the results from the present study and

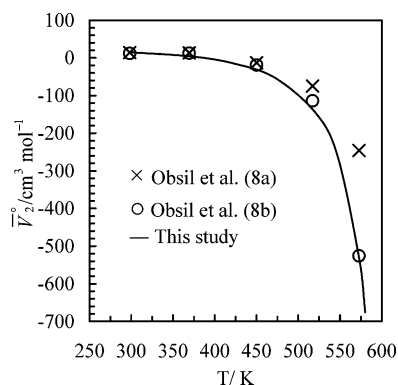


Figure 7. Standard state partial molal volume of aqueous sodium sulfate at 10 MPa: Obsil et al.,^{8a} no corrections for hydrolysis or ion association; Obsil et al.,^{8b} corrected only for the first step association of sodium with sulfate ion.

dielectric properties from Archer and Wang,²⁴ are compared with the experimental values in literature. Reasonable agreement is observed with the results of Obsil et al.^{8b} up to 573.15 K; however, these authors^{8b} corrected their $\bar{V}_2^\circ(\text{Na}_2\text{SO}_4, \text{aq})$ only for the first step association of Na⁺(aq) with SO₄²⁻(aq) ion.

5. Conclusion

The standard state thermodynamic properties for completely ionized sodium sulfate, Na₂SO₄(aq), from the present study are recommended over the data of Pabalan and Pitzer.³ The results from the present study are based on measurements down to 10⁻⁴ m, from where more reliable extrapolations to standard state conditions are possible, and the measured values are corrected for ion association and hydrolysis of SO₄²⁻(aq) using available auxiliary literature data.^{2a}

The standard state partial molal volumes calculated in this study are in good agreement with the published literature when ion association is not ignored.⁸

Acknowledgment. We thank Ms. Irina Chukhray and Dr. Peter Turner for critical reading of the manuscript. This work was supported by funds from Electric Power Research Institute and San Diego State University Research Foundation.

Supporting Information Available: Enthalpies and equilibrium constants for hydrolysis of SO₄²⁻(aq) and association of Na⁺(aq) with SO₄²⁻(aq) and NaSO₄⁻(aq) at p_{sat}. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References and Notes

- (1) (a) Hnedkovsky, L.; Hynek, V.; Majer, V.; Wood, R. H. *J. Chem. Thermodyn.* **2002**, *34*, 755–782. (b) Rogers, P. S. Z.; Duffy, C. J. *J. Chem. Thermodyn.* **1989**, *21*, 595–614.
- (2) (a) Hnedkovsky, L.; Wood, R. H.; Balashov, V. N. *J. Phys. Chem. B* **2005**, *109*, 9034–9046. (b) Oscarson, J. L.; Izatt, R. M.; Brown, P. R.; Pawlak, Z.; Gillespie, S. E.; Christensen, J. J. *J. Solution Chem.* **1988**, *17*, 841–863. (c) Pokrovski, G. S.; Schott, J.; Sergeev, A. S. *Chem. Geol.* **1995**, *124*, 253–265.
- (3) Pabalan, R. T.; Pitzer, K. S. *Geochim. Cosmochim. Acta* **1988**, *52*, 2393–2404.
- (4) Chase, M. W., Jr.; Davies, C. A.; Downey, J. R., Jr.; Frurip, D. J.; Donald, R. A.; Syverud, A. N. *J. Phys. Chem. Ref. Data* **1985**, *14*, Suppl. No. 1.
- (5) Gardner, W. L.; Jekel, E. C.; Cobble, J. W. *J. Phys. Chem.* **1969**, *73*, 2017–2020.
- (6) Rogers, P. S. Z.; Pitzer, K. *J. Phys. Chem.* **1981**, *85*, 2886–2895.
- (7) Holmes, H. F.; Mesmer, R. E. *J. Solution Chem.* **1986**, *15*, 495–518.

- (8) (a) Obsil, M.; Majer, V.; Grolier, J. E.; Hefter, G.; Hynek, V. *J. Chem. Eng. Data* **1997**, *42*, 137–142. (b) Obsil, M.; Majer, V.; Grolier, J. E.; Hefter, G. *J. Chem. Soc. Faraday Trans.* **1996**, *92*, 4445–4451.
- (9) (a) Ellis, A. J. *J. Chem. Soc. A* **1968**, 1138. (b) Phutela, R. C.; Pitzer, K. S. *J. Chem. Eng. Data* **1988**, *31*, 320–327.
- (10) Chen, K. Ph.D. Dissertation. University of California, San Diego, and San Diego State University, 1987.
- (11) Criss, C. M.; Cobble, J. W. *J. Am. Chem. Soc.* **1961**, *83*, 3223–3228.
- (12) Keenan, J. H.; Keyes, F. G.; Hill, P. G.; Moore, J. G. *Steam Tables: International System of Units Volume*; John Wiley and Sons: New York, 1978.
- (13) (a) Djamali, E.; Cobble, J. W. *J. Phys. Chem. B* **2009**, *113*, 5200–5207. (b) Djamali, E. *J. Chem. Thermodyn.* **2009**, *41*, 872–879.
- (14) Stoer, J.; Bulirsch, R. *Introduction to Numerical Analysis*; Springer-Verlag, New York, 1980.
- (15) Marshall, W. L.; Franck, E. U. *J. Phys. Chem. Ref. Data* **1981**, *10*, 295–304.
- (16) Pitzer, K. S.; Kim, J. J. *J. Am. Chem. Soc.* **1974**, *96*, 5701–5707.
- (17) Djamali, E.; Cobble, J. W. *J. Phys. Chem. B* **2005**, *113*, 2398–2404.
- (18) Weast, R. C. *Handbook of Chemistry and Physics*; The Chemical Rubber Co.: Cleveland, OH, 1971.
- (19) Djamali, E.; Cobble, J. W. *J. Phys. Chem. B* **2009**, *113*, 2404–2409.
- (20) Wagman, D. D.; Evans, W. H.; Parker, V. B.; Schumm, R. H.; Halow, I.; Bailey, S. M.; Churney, K. L.; Nuttall, R. L. *J. Phys. Chem. Ref. Data* **1982**, *11*, Suppl. No. 2.
- (21) Linke, W. F.; Seidell, A. *Solubilities of Inorganic and Metal Organic Compounds*, 4th ed.; American Chemical Society: Washington, DC, 1965; Vol. 1; Vol. 2.
- (22) (a) Lindsay, W. T., Jr. In *The ASME Handbook on Water Technology for Thermal Power Systems*; Cohen, P., Ed.; American Society of Mechanical Engineers: New York, 1987; pp 341–544. (b) Meissner, H. P. In *Thermodynamics of Aqueous Systems with Industrial Applications*; Newman, S. A., Ed.; ACS Symposium Series 133; American Chemical Society, Washington, DC, 1980.
- (23) (a) Djamali, E. Ph.D. Dissertation. University of California, San Diego, and San Diego State University: San Diego, 2005. (b) Gates, J. A.; Tillett, D. M.; White, D. E.; Wood, R. H. *J. Chem. Thermodyn.* **1987**, *19*, 131–146. (c) Gates, J. A. Ph.D. Dissertation. University of Delaware, DE, 1985.
- (24) Archer, D. G.; Wang, P. *J. Phys. Chem. Ref. Data* **1990**, *19*, 371–411.

JP9049236