

A Simple 1–1 Electrolyte: Volumetric Properties of Aqueous Solutions of Sulfuric Acid at Elevated Temperatures

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Cite This: *J. Chem. Eng. Data* 2021, 66, 3219–3225

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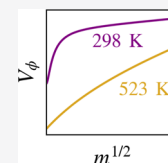


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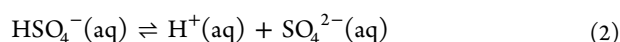
Supporting Information

ABSTRACT: Densities of aqueous solutions of sulfuric acid (H_2SO_4) have been measured by vibrating tube densimetry at molalities m varying from 0.02 to 3.0 mol·kg⁻¹, at temperatures over the range 323.15 ≤ T /K ≤ 523.15 at 10 MPa pressure. These results were used to calculate the corresponding apparent molar volumes $V_\phi(\text{H}_2\text{SO}_4, \text{aq})$ and appear to be the first-ever systematic study of the volumetric properties of this important acid at elevated temperatures. At $T \leq 373.15$ K, the present results aligned well with recent literature data and with values reported in the 1926 *International Critical Tables*. No reliable experimental data were found for comparison at higher temperatures. The present results confirm that at lower concentrations and temperatures, sulfuric acid solutions exist as a variable mixture of $\text{H}^+(\text{aq}) + \text{HSO}_4^-(\text{aq}) + \text{SO}_4^{2-}(\text{aq})$. However, at higher temperatures, the degree of association increases markedly such that at $T \geq 448.15$ K, sulfuric acid solutions behave like a simple 1:1 electrolyte [$\text{H}^+(\text{aq}) + \text{HSO}_4^-(\text{aq})$] even at low concentrations. The variation of $V_\phi(\text{H}_2\text{SO}_4, \text{aq})$ over the entire experimental region was well modelled using a simple Pitzer equation that specifically included (where appropriate) the effects of chemical speciation. Combination of this model with relevant literature data enabled estimation of the standard ionic volume $V^\circ(\text{HSO}_4^-, \text{aq})$ and the standard volume change $\Delta_r V^\circ$ for the reaction $\text{H}^+(\text{aq}) + \text{SO}_4^{2-}(\text{aq}) \rightarrow \text{HSO}_4^-(\text{aq})$ at temperatures up to 523 K.



INTRODUCTION

With major uses in fertilizer manufacture and in the hydrometallurgical processing of non-ferrous metals,^{1–3} the annual global production of sulfuric acid at ca. 260 Mt is higher than that of all other anthropogenic chemicals. While pure sulfuric acid is rarely employed, its aqueous solutions and/or its salts have a myriad of industrial and other uses. They are also of considerable environmental interest due to their presence throughout the biosphere,⁴ their roles in acid mine drainage,⁵ and in the formation of upper-atmospheric aerosols.⁶ In addition to their practical importance, aqueous solutions of sulfuric acid are also of fundamental scientific interest because of the status of $\text{H}_2\text{SO}_4(\text{aq})$ as the archetypal diprotic acid. Like all multiprotic acids in aqueous solution, sulfuric acid dissociates in a stepwise manner



The first dissociation step goes to completion except at very high acid concentrations and/or high temperatures⁴ and thus will not be considered further in this paper. On the other hand, as is well known, the second dissociation (eq 2) is relatively weak, with a standard equilibrium constant $K_a^\circ \approx 0.01$ at near-ambient conditions, becoming even weaker with increasing temperature.⁴

In this context, the volumetric properties of $\text{H}_2\text{SO}_4(\text{aq})$ are of particular interest because, as discussed in the classic monographs of Harned and Owen⁷ and of Robinson and Stokes⁸ and more recently by ourselves,⁹ they show an unusual

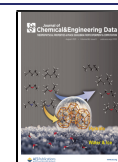
dependence on concentration. In essence, the observed apparent molar volumes (V_ϕ) of $\text{H}_2\text{SO}_4(\text{aq})$ are markedly affected as the acid changes from being diprotic [$2\text{H}^+(\text{aq}) + \text{SO}_4^{2-}(\text{aq})$] in dilute solutions to becoming monoprotic [$\text{H}^+(\text{aq}) + \text{HSO}_4^-(\text{aq})$] at higher concentrations. As the degree of dissociation (i.e., the value of K_a) varies with temperature,⁴ so too does the volumetric behavior of $\text{H}_2\text{SO}_4(\text{aq})$.⁹

Given their widespread application, it might be naively assumed that the volumetric properties of sulfuric acid solutions are very well characterized over wide ranges of concentration and temperature. In fact, such properties are almost unknown for any $\text{H}_2\text{SO}_4(\text{aq})$ solutions at $T > 373$ K. For example, in the two most recent comprehensive compilations of electrolyte solution densities, Sönel and Novotný¹⁰ list values for $\text{H}_2\text{SO}_4(\text{aq})$ only at $T \leq 373$ K, while Aseyev and Zaytsev¹¹ give densities up to 473 K but without citing references (implying that they may not be experimental values). Even the 1926 *International Critical Tables* (ICT),¹² which provide high quality density data for $\text{H}_2\text{SO}_4(\text{aq})$ up to 373 K,⁹ list only a few scattered values of low precision at higher temperatures. All of these data will be further discussed below but, to the best of our knowledge, they are the only

Received: April 22, 2021

Accepted: June 24, 2021

Published: July 7, 2021



densities available for sulfuric acid solutions at elevated temperatures ($T > 373$ K).

In view of this unsatisfactory situation, the first aim of this paper is to extend the existing database for the volumetric properties of $\text{H}_2\text{SO}_4(\text{aq})$ up to moderate concentrations and to elevated temperatures. The second aim is to determine the extent to which chemical speciation (the degree of dissociation) affects the volumetric behavior of sulfuric acid solutions at elevated temperatures and, thirdly, to model this behavior using a simple Pitzer equation.¹³

While measurement of the densities of such chemically aggressive solutions undoubtedly represents a significant experimental challenge, especially at elevated temperatures, the corrosive nature of $\text{H}_2\text{SO}_4(\text{aq})$ can be handled satisfactorily in our purpose-built high-temperature vibrating tube densimeter.¹⁴ Accordingly, this paper reports densities of $\text{H}_2\text{SO}_4(\text{aq})$ at concentrations $0.01 \leq m/\text{mol}\cdot\text{kg}^{-1} \leq 3$ over the temperature range $323.15 \leq T/\text{K} \leq 523.15$ and a pressure of $p = 10$ MPa. Note that the minimum temperature in this study was chosen to overlap with our previous investigation of the same solutions of $\text{H}_2\text{SO}_4(\text{aq})$ made at $293.15 \leq T/\text{K} \leq 343.15$.⁹ In contrast, the pressure was selected merely to ensure the solutions remained liquid over the temperature range of interest, remembering that modest differences in pressure have relatively minor effects on the volumetric behavior of aqueous solutions except at temperatures close to the critical point ($T \rightarrow 647$ K).^{9,15,16}

EXPERIMENTAL SECTION

Reagents. The preparation of the $\text{H}_2\text{SO}_4(\text{aq})$ stock solutions (Table 1) has been described previously.⁹ Working

Table 1. Sample Sources and Purities

chemical name	CASRN	source	initial mass fraction purity	purification method
sulfuric acid	7664-93-9	Merck	$\geq 0.98^a$	none
sulfuric acid	7664-93-9	VWR	$\geq 0.998^b$	none
sodium chloride	7647-14-5	Ajax Finechem	$\geq 0.999^c$	oven drying

^aAnalytical grade, major impurity is water; manufacturer's batch analysis indicates no other significant impurities. ^bConcentrated volumetric standard, used as supplied. ^cExcluding water, see text.

solutions were prepared from the stock solutions by weight dilution with ultra-pure water (Ibis Technology, Australia; resistivity ≥ 18 M Ω ·cm). Calibration solutions for the densimeter were prepared by weight using analytical grade sodium chloride (Table 1) dried at 423 K for ca. 72 h, which was then assumed to contain 0.0015 weight fraction of water.¹⁷ Buoyancy corrections were applied throughout.

Density Determinations. Sample solution densities were measured with a purpose-built flow-type vibrating tube densimeter that has been described in detail elsewhere.¹⁴ In the present context, its most important features are as follows. (1) Pt tubing for ingress and egress of the flowing liquids and a Pt-10% Rh vibrating tube, both of which are fully resistant to $\text{H}_2\text{SO}_4(\text{aq})$ over the entire concentration and temperature ranges of interest. (2) Optical detection of the vibrating tube frequency to enhance accuracy. (3) Several stages of passive and active heating of the incoming solution to produce stable measurement temperatures (± 0.005 K) up to 523 K. (4) High-pressure sample delivery and pressure-buffering systems that

allow continuous operation of the densimeter under flow conditions.

Density differences $\Delta\rho = \rho - \rho_w$, where the subscript w denotes a pure water value, were calculated from the square of the measured oscillation period (τ^2) of the vibrating tube as

$$\Delta\rho = K(\tau^2 - \tau_w^2) \quad (3)$$

where K is an instrument-specific and temperature- and pressure-dependent calibration constant. The densimeter was calibrated at each measurement temperature at 10 MPa pressure using a series of accurately prepared solutions of ca. 1, 3, 5, and 6 mol·kg⁻¹ NaCl(aq). Densities of these solutions were calculated from Archer's equation¹⁸ together with Hill's²⁰ equation of state for pure water. As an additional check, the densities of the calibrating solutions were also measured at 5 K intervals over the range $293.15 \leq T/\text{K} \leq 343.15$ and 0.1 MPa pressure (Table S1, Supporting Information), with a commercial vibrating glass-tube densimeter (Anton Paar DMA 5000 M, Graz, Austria), calibrated with water and air as recommended by the manufacturer. The densities of NaCl(aq) so obtained and the apparent molar volumes V_ϕ calculated from them were found to agree with Archer's equation, generally within $\pm 0.0023\%$ and ± 0.01 cm³·mol⁻¹, with maximum deviations of +0.0050% and -0.05 cm³·mol⁻¹, respectively.

The accuracy of the present results for $\text{H}_2\text{SO}_4(\text{aq})$ relies on that of Archer's equation.¹⁸ As has been observed previously,¹⁹ $\Delta\rho$ values calculated from Archer's equation should be accurate to better than 0.1% at $T < 473$ K and to 0.15–0.20% in the range $473 \leq T/\text{K} \leq 523$.¹⁹ The raw data for both NaCl(aq) and $\text{H}_2\text{SO}_4(\text{aq})$ have been included in Supporting Information (Tables S2 and S3) to facilitate future recalculation if more accurate data for NaCl(aq) become available.

RESULTS AND DISCUSSION

Densities and Apparent Molar Volumes. Density differences, $\Delta\rho$, were measured for 12 to 14 solutions of $\text{H}_2\text{SO}_4(\text{aq})$ at concentrations $0.02 \leq m/\text{mol}\cdot\text{kg}^{-1} \leq 3.0$, over the temperature range $323.15 \leq T/\text{K} \leq 523.15$ (mostly at 25 K intervals) at a constant pressure $p = 10$ MPa. Values of $\Delta\rho$ were converted to apparent molar volumes, V_ϕ , using the usual equation

$$V_\phi = \frac{M}{\Delta\rho + \rho_w} - \frac{\Delta\rho}{m\rho_w(\Delta\rho + \rho_w)} \quad (4)$$

where M ($= 98.072$ g·mol⁻¹) is the molar mass of anhydrous (pure) sulfuric acid, calculated from current IUPAC atomic weights,²² and m is the stoichiometric (total) sulfuric acid concentration (mol H_2SO_4)·(kg H_2O)⁻¹. Densities of pure water, for the target conditions were calculated from the IAPWS-95 equation-of-state.²¹ The present experimental $\Delta\rho$ values, along with the calculated V_ϕ values and their respective uncertainties (estimated in accordance with the GUM guidelines²³), are given in Table 2. The values given are averages of repeat measurements. As stated above, the raw data for these results are given in Table S3 (Supporting Information).

Apparent molar volumes $V_\phi(\text{H}_2\text{SO}_4, \text{aq})$ calculated from the present density data via eq 4 are shown in Figure 1 as a function of concentration (as $m^{1/2}$) at several temperatures. The most notable feature of these data is the very sharp

Table 2. Experimental Density Differences $\Delta\rho$ and Apparent Molar Volumes V_ϕ of $\text{H}_2\text{SO}_4(\text{aq})$ at Molalities m , Temperatures T , and 10 MPa Pressure^a

$m/(\text{mol}\cdot\text{kg}^{-1})$	$\Delta\rho/(\text{kg}\cdot\text{m}^{-3})$	$V_\phi/(\text{cm}^3\cdot\text{mol}^{-1})$	$m/(\text{mol}\cdot\text{kg}^{-1})$	$\Delta\rho/(\text{kg}\cdot\text{m}^{-3})$	$V_\phi/(\text{cm}^3\cdot\text{mol}^{-1})$
$T = 323.15 \text{ K}, \rho_w = 988.427 \text{ kg}\cdot\text{m}^{-3}$			$T = 448.15 \text{ K}, \rho_w = 892.352 \text{ kg}\cdot\text{m}^{-3}$		
0.02000	1.325(8)	31.50(54)	0.06000	3.790(11)	30.77(52)
0.04000	2.546(8)	34.12(28)	0.1000	6.256(9)	31.44(24)
0.06000	3.755(8)	35.15(20)	0.2000	12.339(12)	32.28(16)
0.1000	6.120(8)	36.47(14)	0.4000	24.139(19)	33.49(13)
0.2000	12.012(8)	37.39(10)	0.5999	35.674(27)	34.13(12)
0.4000	23.477(9)	38.33(9)	0.8000	46.857(34)	34.78(11)
0.5999	34.735(11)	38.69(8)	1.000	57.819(42)	35.26(11)
0.8000	45.705(13)	39.02(8)	1.500	84.213(86)	36.21(14)
1.000	56.478(15)	39.25(8)	2.000	108.998(111)	37.12(13)
1.500	82.590(20)	39.63(7)	2.500	132.594(134)	37.86(12)
2.000	107.281(25)	40.03(7)	3.000	155.016(157)	38.50(11)
2.500	130.940(31)	40.33(7)	$T = 473.15 \text{ K}, \rho_w = 864.234 \text{ kg}\cdot\text{m}^{-3}$		
3.000	153.362(50)	40.64(9)	0.02000	1.346(8)	23.87(123)
$T = 373.15 \text{ K}, \rho_w = 958.771 \text{ kg}\cdot\text{m}^{-3}$			0.04000	2.666(6)	24.67(51)
0.02000	1.213(8)	36.37(71)	0.1000	6.559(8)	25.96(27)
0.04000	2.393(8)	37.25(36)	0.2000	12.909(9)	27.12(17)
0.07999	4.713(8)	38.12(20)	0.4000	25.187(11)	28.77(13)
0.1000	5.859(8)	38.44(17)	0.5999	37.130(15)	29.76(12)
0.2000	11.577(9)	38.95(11)	0.8000	48.692(18)	30.67(11)
0.4000	22.736(13)	39.62(10)	1.000	59.993(31)	31.37(15)
0.5999	33.687(18)	39.90(9)	1.500	87.142(43)	32.75(14)
0.8000	44.359(22)	40.20(9)	2.000	112.552(55)	34.01(13)
1.000	54.870(27)	40.38(8)	2.500	136.694(66)	35.04(13)
1.500	80.243(55)	40.76(11)	3.000	159.590(77)	35.91(12)
2.000	104.300(71)	41.14(10)	$T = 498.15 \text{ K}, \rho_w = 832.302 \text{ kg}\cdot\text{m}^{-3}$		
2.500	127.302(86)	41.46(10)	0.02000	1.436(5)	14.97(104)
3.000	149.193(101)	41.75(10)	0.04000	2.843(8)	16.02(75)
$T = 398.15 \text{ K}, \rho_w = 939.415 \text{ kg}\cdot\text{m}^{-3}$			0.1000	6.982(9)	17.72(33)
0.02000	1.215(8)	35.68(80)	0.2000	13.662(13)	19.67(21)
0.04000	2.403(8)	36.39(41)	0.4000	26.485(23)	22.26(16)
0.06000	3.580(8)	36.80(28)	0.5999	38.934(33)	23.73(15)
0.1000	5.908(8)	37.38(19)	0.8000	50.937(60)	25.05(20)
0.2000	11.683(10)	37.88(13)	1.000	62.719(73)	25.98(19)
0.4000	22.948(15)	38.58(10)	1.500	90.652(105)	28.11(17)
0.5999	33.995(21)	38.91(10)	2.000	116.747(135)	29.89(16)
0.8000	44.748(27)	39.27(9)	2.500	141.492(164)	31.31(15)
1.000	55.310(33)	39.52(9)	3.000	164.872(191)	32.52(14)
1.500	80.834(67)	40.00(12)	$T = 523.15 \text{ K}, \rho_w = 795.347 \text{ kg}\cdot\text{m}^{-3}$		
2.000	104.926(86)	40.51(11)	0.02000	1.583(6)	-0.23(131)
2.500	127.973(105)	40.91(11)	0.1000	7.560(13)	5.22(37)
3.000	149.898(122)	41.27(10)	0.2000	14.730(29)	8.13(32)
$T = 423.15 \text{ K}, \rho_w = 917.305 \text{ kg}\cdot\text{m}^{-3}$			0.4000	28.384(55)	11.99(26)
0.02000	1.241(8)	33.34(92)	0.5999	41.540(80)	14.33(23)
0.04000	2.456(8)	34.09(47)	0.8000	54.148(147)	16.37(31)
0.07999	4.855(8)	34.81(25)	1.000	66.442(180)	17.91(29)
0.1000	6.047(8)	35.04(21)	1.500	95.649(260)	21.01(25)
0.2000	11.943(10)	35.68(14)	2.000	122.748(333)	23.57(23)
0.4000	23.443(15)	36.52(11)	2.500	148.309(402)	25.63(20)
0.5999	34.662(21)	37.03(10)	3.000	172.388(468)	27.36(19)
0.8000	45.592(27)	37.50(10)			
1.000	56.315(46)	37.83(13)			
1.500	82.163(66)	38.52(12)			
2.000	106.503(85)	39.20(12)			
2.500	129.770(103)	39.73(11)			
3.000	151.880(121)	40.20(11)			
$T = 448.15 \text{ K}, \rho_w = 892.352 \text{ kg}\cdot\text{m}^{-3}$					
0.02000	1.297(8)	28.76(106)			
0.04000	2.541(8)	30.36(54)			

^aNumbers in brackets are the combined standard uncertainties u_c in the last digits of each entry. $\Delta\rho = \rho - \rho_w$ where ρ is the solution density and ρ_w is the pure water density under the same conditions. Values for ρ_w were calculated from the IAPWS-95 equation of state.²¹ Standard uncertainties: $u_c(m) = 0.002$, $u_c(T) = 0.02 \text{ K}$, $u_c(p) = 0.01 \text{ MPa}$. Non-significant figures have been retained to avoid round-off errors.

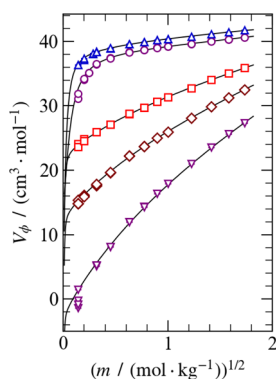


Figure 1. Present results for the apparent molar volume V_ϕ of $\text{H}_2\text{SO}_4(\text{aq})$ as a function of concentration (as $m^{1/2}$) at representative temperatures $T/\text{K} = 323.15$ (circles), 373.15 (triangles up), 473.15 (squares), 498.15 (diamonds), and 523.15 (triangles down) and 10 MPa pressure. Lines were calculated via eq 6 using the parameter values given in Table 3.

decrease in $V_\phi(m^{1/2})$ at lower concentrations and temperatures (e.g., the two uppermost curves in Figure 1). These results are in keeping with earlier observations^{9,24–26} and, as discussed at length by Robinson and Stokes⁸ and ourselves,⁹ are consistent with a shift in position of equilibrium 2 at these temperatures. At higher temperatures, this feature dissipates, such that at $T \gtrsim 448$ K the V_ϕ values exhibit (see the three lowermost curves in Figure 1) a smooth approach to the Debye–Hückel limiting law (DHLL) behavior of a typical 1–1 electrolyte, noting that the DHLL slope itself increases considerably with temperature.²⁷

Alignment with Lower Temperature Data. A more-or-less direct comparison between the present results and previous work⁹ can be made only at 323.15 K. Surprisingly, the differences between the present and previous values,⁹ that is, $V_\phi(10 \text{ MPa}) - V_\phi(0.1 \text{ MPa})$ at equal concentrations at this temperature are well within the estimated experimental uncertainties, averaging $-0.09 \text{ cm}^3 \cdot \text{mol}^{-1}$ over the whole concentration range, with a maximum difference of $-0.7 \text{ cm}^3 \cdot \text{mol}^{-1}$. The absence of the expected variation of V_ϕ with pressure, bearing in mind that the volume change of the deprotonation reaction is rather large (Table 3), is almost certainly due to a shift in eqm 2. Although no further direct comparisons are possible, it is obvious from Figure 2 that the present results for $V_\phi(\text{H}_2\text{SO}_4, \text{aq})$ align almost perfectly with our previous data at $T \leq 343.15$ K⁹ despite the pressure difference.

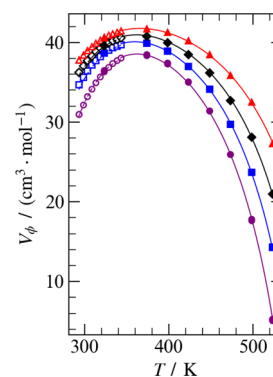


Figure 2. Apparent molar volumes V_ϕ of $\text{H}_2\text{SO}_4(\text{aq})$ as a function of temperature T at concentrations $m/\text{mol} \cdot \text{kg}^{-1} = 0.1, 0.6, 1.5, 3.0$ (bottom to top) at 10 MPa pressure. Filled symbols, this work; unfilled symbols, our previous work at $293.15 \leq T/\text{K} \leq 343.15$ and 0.1 MPa pressure.⁹ The lines are a visual guide only.

As is typical for aqueous electrolyte solutions,²⁸ the values of $V_\phi(\text{H}_2\text{SO}_4, \text{aq})$ show a clear maximum at ~ 370 K that is almost independent of concentration (Figure 2). While changes in V_ϕ with concentration and temperature are relatively small below this maximum, the effects of both parameters increase significantly at higher temperatures (Figure 2). Such changes reflect the increasing compressibility of the solvent (and hence of the solutions) along with increasing electrostriction of the solvent by the solute ions.

Comparison with Literature Data. The present V_ϕ values are compared, in the form of a deviation plot, with the available literature data at high temperatures ($T \geq 373$ K) in Figure 3. The deviations were calculated relative to the present isothermal fits (eq 6 and Table 3). At 373.15 K, as observed at lower temperatures,⁹ the century-old values listed in the 1926 ICT¹² are in good agreement with the present results (Figure 3), especially given that at least some of the small systematic difference (ca. $-0.6 \text{ cm}^3 \cdot \text{mol}^{-1}$) is likely due to the higher pressure used in the present work. Also at 373.15 K, the values reported by Aseyev and Zaytsev¹¹ and Söhnel and Novotný¹⁰ show somewhat larger deviations, of the order of -0.5 to $-2.5 \text{ cm}^3 \cdot \text{mol}^{-1}$. In part, these differences arise from the limited number of significant figures given for density data in both compilations. As noted in the Introduction section, almost no meaningful comparisons with literature data are possible at $T > 373$ K. The few results listed in the ICT¹² (not shown) at $373 < T/\text{K} \leq 413$ vary erratically, while the values of Aseyev and Zaytsev at $373 < T/\text{K} \leq 473$ (Figure 3) differ

Table 3. Literature Values of $V_2^\circ(\text{SO}_4^{2-})$ and Present Values of $V_1^\circ(\text{HSO}_4^-)$ and of $\Delta_r V^\circ$ for the Protonation of Sulfate (Reverse of Eq 2) at $323.15 \leq T/\text{K} \leq 523.15$ at 10 MPa Pressure^a

T/K	$V_2^\circ(\text{SO}_4^{2-})^b/(\text{cm}^3 \cdot \text{mol}^{-1})$	$V_1^\circ(\text{HSO}_4^-)/(\text{cm}^3 \cdot \text{mol}^{-1})$	$\Delta_r V^\circ/(\text{cm}^3 \cdot \text{mol}^{-1})$	$10^5 \cdot \beta_1^{V(0)}/(\text{kg} \cdot \text{mol}^{-1} \cdot \text{MPa}^{-1})$
323.15	15.44	38.92(38)	23.48	6.04(54)
373.15	9.42	38.26(22)	28.84	1.69(54)
398.15	3.63	36.37(20)	32.75	1.82(54)
423.15	-4.72	33.35(18)	38.07	2.59(55)
448.15	-16.63	28.95(19)	45.58	3.56(55)
473.15	-32.85	22.36(22)	55.20	4.91(57)
498.15	-57.03	12.78(24)	69.81	6.55(67)
523.15	-92.11	-2.49(28)	89.61	7.33(88)

^aNumbers in brackets are the combined standard uncertainties $u_c(V_1^\circ)$ and standard uncertainties $u(\beta_1^{V(0)})$. All $V^\circ(\text{ion})$ values are based on $V^\circ(\text{H}^+, \text{aq}) \equiv 0$ at all T . ^bDerived from literature data as described in the text.

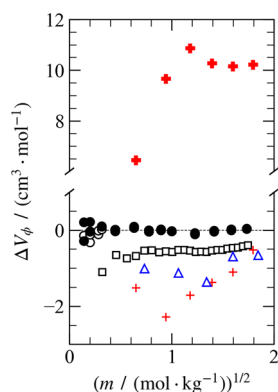


Figure 3. Deviations $\Delta V_{\phi} = V_{\phi, \text{exp}} - V_{\phi, \text{calc}}$ of experimental apparent molar volumes of $\text{H}_2\text{SO}_4(\text{aq})$ from the present isothermal fits (eq 6 and Table 3): circles are present results at 373.15 K (unfilled) and 473.15 K (filled) and $p = 10$ MPa; squares, ICT¹² at 373.15 K and $p = 0.1$ MPa; upward triangles, Söhnel and Novotný¹⁰ at 373.15 K; crosses, Aseyev and Zaytsev¹¹ at 373.15 K (thin) and 473.15 K (thick). Note break in the y -axis scale.

increasingly from the present values such that at 473.15 K they are higher by more than $10 \text{ cm}^3 \cdot \text{mol}^{-1}$. The absence of cited references for these values may mean that they are extrapolated rather than measured.

Standard Molar Ionic Volumes. The present results can be used to estimate the standard (infinite dilution) molar volume of the hydrogen sulfate ion $V_1^\circ(\text{HSO}_4^-, \text{aq})$, hereafter V_1° , providing estimates are available for the corresponding values of the sulfate ion, $V_2^\circ(\text{SO}_4^{2-}, \text{aq})$, hereafter V_2° . As in previous work,^{9,29} the values of V_2° , based on the usual convention that $V^\circ(\text{H}^+, \text{aq}) \equiv 0$ at all T , were calculated from the known standard volumes of the dissociated electrolytes $\text{Na}_2\text{SO}_4(\text{aq})$,³⁰ $\text{NaCl}(\text{aq})$,¹⁸ and $\text{HCl}(\text{aq})$ ³¹ by assuming ionic additivity

$$V_2^\circ(\text{SO}_4^{2-}, \text{aq}) = V^\circ(\text{Na}_2\text{SO}_4, \text{aq}) - 2V^\circ(\text{NaCl}, \text{aq}) + 2V^\circ(\text{HCl}, \text{aq}) - 2V^\circ(\text{H}^+, \text{aq}) \quad (5)$$

The values so obtained at $323.15 \leq T/\text{K} \leq 523.15$ are collected in Table 3. Values of V_1° were then determined by fitting each experimental isotherm with a simple Pitzer model¹³

$$V_{\phi} = (1 - \alpha)V_1^\circ + \alpha V_2^\circ + A_V(1 + 2\alpha) \frac{\ln(1 + bI^{1/2})}{b} + 2RT(1 - \alpha^2)m\beta_1^{V(0)} \quad (6)$$

where α is the degree of dissociation of $\text{HSO}_4^-(\text{aq})$ (cf. eq 2), A_V is the DHLL slope for volumes,²⁷ $b = 1.2 \text{ kg}^{1/2} \cdot \text{mol}^{-1/2}$ is a constant, $I = (1 + 2\alpha)m$ is the actual ionic strength, m is the stoichiometric molality of $\text{H}_2\text{SO}_4(\text{aq})$, R is the gas constant, and $\beta_1^{V(0)}$ is an adjustable parameter.¹³

As in our previous work,⁹ α was calculated from the equation given for $\ln K_a^\circ$ by Dickson et al.³² in combination with the Pitzer variant of the DHLL for activity coefficients.¹³ Since the $\ln K_a^\circ$ values are given³² at the saturation vapor pressure of pure water p_{sat} , a simple correction to 10 MPa pressure

$$\ln K_a^\circ(p) \approx \ln K_a^\circ(p_{\text{sat}}) + \frac{\Delta_r V^\circ}{RT}(p - p_{\text{sat}}) \quad (7)$$

was applied, where $\Delta_r V^\circ = V_1^\circ - V_2^\circ$ is the standard volume change for the protonation of the sulfate ion (the reverse of eq 2). Relevant values of $\Delta_r V^\circ$ are listed in Table 3. The pressure dependence of $\Delta_r V^\circ$ was assumed negligible under the studied conditions and was thus omitted from eq 7. No other interactions were taken into account in the calculations, and it was assumed that any systematic errors in the calculated α values were small and mostly compensated by the $\beta_1^{V(0)}$ parameter at higher concentrations. Optimized values of V_1° and $\beta_1^{V(0)}$ over the present temperature range are given in Table 3.

At $T \geq 448.15$ K, the above calculation scheme gave essentially identical results to a more conventional fit assuming $\text{H}_2\text{SO}_4(\text{aq})$ to be a simple 1–1 electrolyte (i.e., $\alpha = 0$ in eq 6). This is of course equivalent to stating that $\text{H}_2\text{SO}_4(\text{aq})$ at high T is a simple monoprotic acid.

To the best of our knowledge, no previous estimates of V_1° at $T > 343$ K are available.⁹ The results obtained for V_1° via the present approach are listed in Table 3 and plotted in Figure 4,

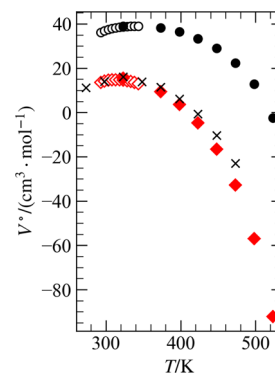


Figure 4. Standard molar ionic volumes $V_1^\circ(\text{HSO}_4^-, \text{aq})$ and $V_2^\circ(\text{SO}_4^{2-}, \text{aq})$ as a function of temperature T : filled circles, present V_1° at 10 MPa; unfilled circles, V_1° of Vielma et al. at 0.1 MPa;⁹ filled diamonds, V_2° at 10 MPa, calculated from literature data (Table 3); unfilled diamonds, V_2° at 0.1 MPa, calculated from literature data;^{9,30,35,36} crosses, V_2° given by Millero.²⁸

along with the corresponding V_2° value. Also included in Figure 4 are the widely spaced V_2° values of Millero²⁸ (adopted by Marcus^{33,34}), which agree well with the present results at $T \leq 373.15$ K but differ increasingly at higher temperatures (Figure 4). Typical of most ions in aqueous solution,^{28,33,34} both V_1° and V_2° pass through a shallow maximum, albeit at somewhat different temperatures: ~ 340 K for V_1° and ~ 315 K for V_2° . At higher temperatures, both V_1° and, especially, V_2° decrease markedly for the reasons outlined above. As would be expected from the greater electrostriction of the solvent due to the higher charge of the sulfate ion, $V_2^\circ \ll V_1^\circ$, especially at higher temperatures (Figure 4).

Volumetric Pitzer Model for $\text{H}_2\text{SO}_4(\text{aq})$ at Elevated Temperatures. Because of the relative simplicity of the behavior of $V_{\phi}(\text{H}_2\text{SO}_4, \text{aq})$ at higher temperatures, compared with that at $T \lesssim 343$ K,⁹ it is useful for practical applications to derive a temperature-dependent volumetric Pitzer model (based on eq 6) over the present experimental ranges. To achieve this, values of V_1° , V_2° , and $\beta_1^{V(0)}$ were given general temperature and pressure dependences

$$X(T, p) = \sum_i a f_i(T, p) \quad (8)$$

where a_i are adjustable parameters and f_i are basis functions selected from a large bank of terms following the structural optimization scheme of Setzmann and Wagner.³⁷ The selected basis functions and the corresponding values of a_i are given in Table 4, along with their estimated uncertainties. The fit using

Table 4. Basis Functions $f_i(T,p)$ and Fitting Parameters a_i for Eqs 6 and 8^a

X	$f_i(T,p)$	a_i	$u(a_i)$
V_1°	$\tau^{-1.5}\kappa_T$	-5.404541×10^4	0.01570364×10^4
	1	50.76165	0.07494659
	$\tau^{7.5}$	-2.009760×10^{-2}	$0.04598639 \times 10^{-2}$
V_2°	τ^{-3}	-88.683422	0.868752
	τ^{-1}	94.114300	0.338465
	κ_T	-9.974262×10^4	0.0242982×10^4
	τ	11.324729	0.079574
	$\tau^3\kappa_T$	0.1301293	0.01321939
$\beta_1^{V(0)}$	$\tau^4\kappa_T$	-8.039683×10^{-3}	0.9342449×10^{-2}
	τ^{10}	1.617689×10^{-7}	0.2043732×10^{-7}

^a $\tau = T_c/T$, where $T_c = 647.096$ K is the critical temperature of pure water²¹ and κ_T is the isothermal compressibility of pure water in units of MPa^{-1} .²¹

these parameters reproduces the experimental values of $V_\phi(\text{H}_2\text{SO}_4, \text{aq})$ at $m \leq 3.0$ mol·kg⁻¹, $323 \leq T/\text{K} \leq 523$, and 10 MPa pressure essentially within their estimated uncertainties. It should be noted, however, that more precise interpolation of the present results along the experimental isotherms can be achieved by using the isothermal fitting parameters given in Table 3.

Nature of Aqueous Sulfuric Acid Solutions. It is interesting to compare the present results for $\text{H}_2\text{SO}_4(\text{aq})$ with the corresponding values of common strong monoprotic acids. Figure 5 plots relevant data for the aqueous solutions of H_2SO_4

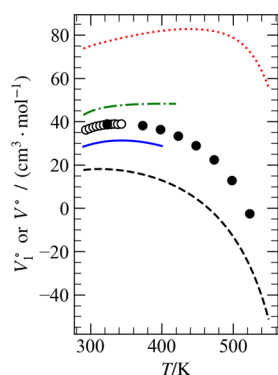


Figure 5. Standard molar volumes of sulfuric acid and strong monoprotic inorganic acids as functions of temperature: filled circles, present $V_1^*(\text{HSO}_4^-, \text{aq})$ values at 10 MPa; unfilled circles, $V_2^*(\text{HSO}_4^-, \text{aq})$ at 0.1 MPa;⁹ solid line, $V^*(\text{HNO}_3, \text{aq})$ at 0.35 MPa;³⁹ dashed line, $V^*(\text{HCl}, \text{aq})$ at 10 MPa;³¹ dash-dot line, $V^*(\text{HClO}_4, \text{aq})$ at 10 MPa;³⁸ dotted line, $V^*(\text{HTf}, \text{aq})$ at saturation pressure.⁴⁰

(present work), HCl ,³¹ HClO_4 ,³⁸ HNO_3 ,³⁹ and HTf (trifluoromethanesulfonic acid)⁴⁰ as functions of temperature. These data support, in a qualitative way, the notion that sulfuric acid does indeed behave as a 1:1 electrolyte in aqueous solution up to high temperatures.

CONCLUSIONS

The present density measurements and the apparent molar volumes $V_\phi(\text{H}_2\text{SO}_4, \text{aq})$ derived from them considerably expand the existing database of the volumetric properties of the aqueous solutions of sulfuric acid at elevated temperatures. The data obtained confirm previous findings that at relatively low concentrations and temperatures, sulfuric acid solutions behave as a variable mixture of the 1:2 electrolyte [$2\text{H}^+(\text{aq}) + \text{SO}_4^{2-}(\text{aq})$] and the 1:1 electrolyte [$\text{H}^+(\text{aq}) + \text{HSO}_4^-(\text{aq})$]. Due to changing chemical speciation, at higher temperatures ($T \geq 448$ K), sulfuric acid behaves as a simple 1:1 electrolyte at all measured concentrations. The values of $V_\phi(\text{H}_2\text{SO}_4)$ were well-fitted using a simple Pitzer model that included chemical speciation and, in combination with relevant literature data, enabled estimation of the standard ionic volume $V^\circ(\text{HSO}_4^-, \text{aq})$ and the standard volume change $\Delta_i V^\circ$ for the reaction $\text{H}^+(\text{aq}) + \text{SO}_4^{2-}(\text{aq}) \rightarrow \text{HSO}_4^-(\text{aq})$ at $T \leq 523$ K.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jced.1c00291>.

Density data for the calibration $\text{NaCl}(\text{aq})$ solutions and calibration data and raw measurement data for the high-temperature densimeter (PDF)

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was funded by the Finnish Cultural Foundation (T.V.) and Murdoch University. The research visit of T.V. to Murdoch University was funded by the Walter Ahlström Foundation (Finland).

REFERENCES

- (1) Müller, H. *Ullmann's Encyclopedia of Industrial Chemistry*; Ullmann, F., Gerhartz, W., Eds.; Wiley-VCH: Weinheim, Germany, 2000.
- (2) Crundwell, F. K.; Moats, M. S.; Ramachandran, V.; Robinson, T. G.; Davenport, W. G. *Extractive Metallurgy of Nickel, Cobalt and Platinum-Group Metals*; Elsevier: Oxford, U.K., 2011.
- (3) Sinclair, R. J. *The Extractive Metallurgy of Zinc*; AUSSIM: Carlton, Australia, 2005.
- (4) Hefter, G.; Gumiński, C. Remarks on the evaluation of thermodynamic data for sulfate ion protonation. *J. Solution Chem.* **2019**, *48*, 1657–1670.

- (5) Jacobs, J. A.; Lehr, J. H.; Testa, S. M. *Acid Mine Drainage, Rock Drainage, and Acid Sulfate Soils: Causes, Assessment, Prediction, Prevention, and Remediation*; Wiley-Blackwell: Hoboken, USA, 2014.
- (6) Sipilä, M.; Berndt, T.; Petäjä, T.; Brus, D.; Vanhanen, J.; Stratmann, F.; Patokoski, J.; Mauldin, R. L.; Hyvärinen, A.-P.; Lihavainen, H.; Kulmala, M. The role of sulfuric acid in atmospheric nucleation. *Science* **2010**, *327*, 1243–1246.
- (7) Harned, H.; Owen, B. *The Physical Chemistry of Electrolytic Solutions*, 3rd ed.; American Chemical Society: New York, 1958; pp 404–406.
- (8) Robinson, R. A.; Stokes, R. H. *Electrolyte Solutions*, 2nd ed.; Butterworths: London, 1970; pp 383–391.
- (9) Vielma, T.; Hnědkovský, L.; Hefter, G. Chemical speciation effects on the volumetric properties of aqueous sulfuric acid solutions. *J. Chem. Thermodyn.* **2021**, *158*, 106408.
- (10) Söhnel, O.; Novotný, P. *Densities of Aqueous Solutions of Inorganic Substances*; Elsevier: New York, 1985.
- (11) Aseyev, G. G.; Zaytsev, I. D. *Volumetric Properties of Electrolyte Solutions; Estimation Methods and Experimental Data*; Begell House: New York, USA, 1996.
- (12) *International Critical Tables of Numerical Data, Physics, Chemistry and Technology*; Washburn, E. W., Ed.; McGraw-Hill: New York, 1926.
- (13) Pitzer, K. S. *Activity Coefficients in Electrolyte Solutions*, 2nd ed.; Pitzer, K. S., Ed.; CRC Press: Boca Raton, USA, 1991; pp 75–153.
- (14) Hnědkovský, L.; Königsberger, E.; Cibulka, I.; Königsberger, L.-C.; Schrödle, S.; May, P. M.; Hefter, G. Densities of NaOH (aq) at temperatures from (323 to 573) K and 10 MPa pressure. *J. Chem. Eng. Data* **2007**, *52*, 2237–2244.
- (15) Obšil, M.; Majer, V.; Grolier, J.-P. E.; Hefter, G. T. Volumetric properties of, and ion-pairing in, aqueous solutions of alkali-metal sulfates under superambient conditions. *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 4445–4451.
- (16) Majer, V.; Hui, L.; Crovetto, R.; Wood, R. H. Volumetric properties of aqueous 1-1 electrolyte solutions near and above the critical temperature of water I. Densities and apparent molar volumes of NaCl (aq) from 0.0025 mol·kg⁻¹ to 3.1 mol·kg⁻¹, 604.4 K to 725.5 K, and 18.5 MPa to 38.0 MPa. *J. Chem. Thermodyn.* **1991**, *23*, 213–229.
- (17) Albright, J. G.; Rard, J. A.; Serna, S.; Summers, E. E.; Yang, M. C. Isopiestic determination of the osmotic and activity coefficients of ZnSO₄(aq) at T = 298.15 K, and the standard potential of the electrochemical cell ZnHg_x(two phase)—ZnSO₄(aq)—PbSO₄(s)—PbHg_x(two phase). *J. Chem. Thermodyn.* **2000**, *32*, 1447–1487.
- (18) Archer, D. G. Thermodynamic properties of the NaCl + H₂O system II. Thermodynamic properties of NaCl(aq), NaCl · 2H₂O(cr), and phase equilibria. *J. Phys. Chem. Ref. Data* **1992**, *21*, 793–829.
- (19) Hynek, V.; Hnědkovský, L.; Cibulka, I. A new design of a vibrating tube densimeter and partial molar volumes of phenol (aq) at temperatures from 298 K to 573 K. *J. Chem. Thermodyn.* **1997**, *29*, 1237–1252.
- (20) Hill, P. G. A unified fundamental equation for the thermodynamic properties of H₂O. *J. Phys. Chem. Ref. Data* **1990**, *19*, 1233–1274.
- (21) Wagner, W.; Pruß, A. The IAPWS formulation 1995 for the thermodynamic properties of ordinary water substance for general and scientific use. *J. Phys. Chem. Ref. Data* **2002**, *31*, 387–535.
- (22) Meija, J.; Coplen, T. B.; Berglund, M.; Brand, W. A.; De Bièvre, P.; Gröning, M.; Holden, N. E.; Irrgeher, J.; Loss, R. D.; Walczyk, T.; Prohaska, T. Atomic weights of the elements 2013. *Pure Appl. Chem.* **2016**, *88*, 265–291.
- (23) Joint Committee for Guides in Metrology. *Evaluation of Measurement Data—Guide to the Expression of Uncertainty in Measurement*; International Bureau of Weights and Measures: Saint-Cloud: France, 1995.
- (24) Klotz, I. M.; Eckert, C. F. The apparent molal volumes of aqueous solutions of sulfuric acid at 25°. *J. Am. Chem. Soc.* **1942**, *64*, 1878–1880.
- (25) Khare, P. L. Compressibility of dilute solutions of sulphuric acid. *Trans. Faraday Soc.* **1961**, *58*, 363–367.
- (26) Lindstrom, R. E.; Wirth, H. E. Estimation of the bisulfate ion dissociation in solutions of sulfuric acid and sodium bisulfate. *J. Phys. Chem.* **1969**, *73*, 218–223.
- (27) Fernández, D. P.; Goodwin, A. R. H.; Lemmon, E. W.; Levelt Sengers, J. M. H.; Williams, R. C. A formulation for the static permittivity of water and steam at temperatures from 238 K to 873 K at pressures up to 1200 MPa, including derivatives and Debye–Hückel coefficients. *J. Phys. Chem. Ref. Data* **1997**, *26*, 1125–1166.
- (28) Millero, F. J. Molal volumes of electrolytes. *Chem. Rev.* **1971**, *71*, 147–176.
- (29) Hovey, J. K.; Hepler, L. G. Thermodynamics of sulphuric acid: apparent and partial molar heat capacities and volumes of aqueous HSO₄⁻ from 10–55 °C and calculation of the second dissociation constant to 350 °C. *J. Chem. Soc., Faraday Trans.* **1990**, *86*, 2831–2839.
- (30) Obšil, M.; Majer, V.; Hefter, G. T.; Hynek, V. Densities and apparent molar volumes of Na₂SO₄ (aq) and K₂SO₄ (aq) at temperatures from 298 K to 573 K and at pressures up to 30 MPa. *J. Chem. Eng. Data* **1997**, *42*, 137–142.
- (31) Sharygin, A. V.; Wood, R. H. Volumes and heat capacities of aqueous solutions of hydrochloric acid at temperatures from 298.15 K to 623 K and pressures to 28 MPa. *J. Chem. Thermodyn.* **1997**, *29*, 125–148.
- (32) Dickson, A. G.; Wesolowski, D. J.; Palmer, D. A.; Mesmer, R. E. Dissociation constant of bisulfate ion in aqueous sodium chloride solutions to 250 °C. *J. Phys. Chem.* **1990**, *94*, 7978–7985.
- (33) Marcus, Y. The standard partial molar volumes of ions in solution. Part 4. Ionic volumes in water at 0–100 °C. *J. Phys. Chem. B* **2009**, *113*, 10285–10291.
- (34) Marcus, Y. The standard partial molar volumes of ions in solution. Part 5. Ionic volumes in water at 125–200 °C. *J. Phys. Chem. B* **2012**, *116*, 7232–7239.
- (35) Clegg, S. L.; Wexler, A. S. Densities and apparent molar volumes of atmospherically important electrolyte solutions. 1. The solutes H₂SO₄, HNO₃, HCl, Na₂SO₄, NaNO₃, NaCl, (NH₄)₂SO₄, NH₄NO₃, and NH₄Cl from 0 to 50 °C, including extrapolations to very low temperature and to the pure liquid state, and NaHSO₄, NaOH, and NH₃ at 25 °C. *J. Phys. Chem. A* **2011**, *115*, 3393–3460.
- (36) Hu, B.; Hnědkovský, L.; Hefter, G. Densities and apparent molar volumes of aqueous solutions of Li₂SO₄ and LiCF₃SO₃ at temperatures from 293 to 343 K. *J. Chem. Eng. Data* **2016**, *61*, 3618–3626.
- (37) Setzmann, U.; Wagner, W. A new method for optimizing the structure of thermodynamic correlation equations. *Int. J. Thermophys.* **1989**, *10*, 1103–1126.
- (38) Hakin, A. W.; Lukacs, M. J.; Lian Liu, J. Densities and apparent molar volumes of HClO₄ (aq) and Yb(ClO₄)₃ (aq) at elevated temperatures and pressures. *J. Chem. Thermodyn.* **2004**, *36*, 759–772.
- (39) Patterson, B. A.; Woolley, E. M. Thermodynamics of ionization of water at temperatures 278.15 ≤ T/K ≤ 393.15 and at the pressure p = 0.35 MPa: apparent molar volumes and apparent molar heat capacities of aqueous solutions of potassium and sodium nitrates and nitric acid. *J. Chem. Thermodyn.* **2002**, *34*, 535–556.
- (40) Xiao, C.; Tremaine, P. R. Apparent molar volumes of aqueous sodium trifluoromethanesulfonate and trifluoromethanesulfonic acid from 283 K to 600 K and pressures up to 20 MPa. *J. Solution Chem.* **1997**, *26*, 277–294.