Chemical speciation effects on the volumetric properties of aqueous sulfuric acid solutions

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A B S T R A C T

Densities of fifteen aqueous solutions of sulfuric acid (H_2SO_4) have been measured by vibrating-tube densimetry at solute molalities (m) from (0.01 to 3.0) $mol \cdot kg^{-1}$ over the temperature range $293.15 \leq T/K \leq 343.15$. These data have been used to calculate the corresponding apparent molar volumes $V_\phi(H_2SO_4,aq)$, which represent a significant expansion of the volumetric database for this industrially-important acid. At 298.15 K the present results agree well with literature data, notably with the century-old values given in the 1926 *International Critical Tables*. At other temperatures, where comparisons are possible agreement with the present V_ϕ values is also very satisfactory. Consistent with earlier studies, $V_\phi(H_2SO_4,aq)$ was found to exhibit an abnormally-large decrease at low concentrations ($m \leq 0.1$ $mol \cdot kg^{-1}$). This effect is consistent with a change in the chemical speciation of $H_2SO_4(aq)$, from an essentially 1:1 electrolyte ($H^+(aq) + HSO_4^-$ (aq)) at higher concentrations to a predominantly 1:2 electrolyte ($2H^+(aq) + SO_4^{2-}$ (aq)) in dilute solutions. The V_ϕ values were modelled using variants of Young's rule and the Pitzer formalism. Combination of these results with literature values for the standard volume $V°(SO_4^{2-},aq)$ enabled estimation of $V°(HSO_4^-,aq)$ and the standard volume change, $\Delta_r V°$, for the first protonation of the sulfate ion ($H^+(aq) + SO_4^{2-}(aq) \rightarrow HSO_4^-(aq)$) as functions of temperature. It is shown that $V°(HSO_4^-,aq)$ is sensitive to the value of the first protonation constant and probably cannot be determined to better than $\pm$ 0.3 $cm^3 \cdot mol^{-1}$ at present.

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1. Introduction

The global production of sulfuric acid, ca. 260 Mt per year, far exceeds that of all other anthropogenic chemicals. Its main uses are in the manufacture of phosphate-based fertilizers, which consume about 50% of production, and for various chemical and hydrometallurgical processes [1–3]. However, the importance of aqueous solutions of H_2SO_4 goes far beyond their industrial usage. For example, sulfuric acid is the major component in the environmental pollution arising from acid mine drainage from many past and present mine sites [4] and is known to play an important role in upper-atmospheric aerosols [5]. So diverse are the myriad applications of $H_2SO_4(aq)$ that its production has even been suggested as a surrogate measure of national economic development [6].

Given their ubiquitous usage it is to be expected that the properties of aqueous solutions of sulfuric acid are particularly well known. For example, it has been noted [7] that the second deprotonation of sulfuric acid:

$$HSO_4^-(aq) \rightleftharpoons SO_4^{2-}(aq) + H^+(aq) \qquad (1)$$
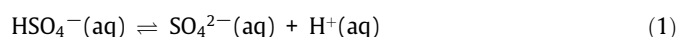
with equilibrium constant K_a, is the most widely investigated of all solution chemical equilibria apart from the self-ionization of water [8,9]. It is therefore surprising to find that the volumetric properties of $H_2SO_4(aq)$, while exceptionally well-established for some conditions (e.g., at 298.15 K and 0.101 MPa) show major gaps under others (see for example the JESS database of physico-chemical properties of electrolyte solutions [10]). Some of these poorly characterised regions are especially relevant for several important industrial applications [2].

Table 1 lists a *selection* of the high-quality density studies of $H_2SO_4(aq)$ under near-ambient conditions over the concentration range of interest. Of particular note is the comprehensive compilation presented in the *International Critical Tables* (ICT), published in 1926 [11]. This critical assessment of the then-available experimental data (most of it now more than one hundred years old) not only covers the widest ranges of temperature and concentration (Table 1) but, as will be seen below, proposes densities that are in near-quantitative agreement with the present study.

Table 1
Selected density data for H_2SO_4(aq) at near-ambient conditions.[a]

Author(s)	Year	Method(s)	m/mol·kg^{-1}	T/K
ICT [11]	1926	compilation	0.1 - pure H_2SO_4	273–413
Klotz & Eckert [18]	1942	sinker	0.01–3.0	298
Khare [19]	1961	pycnometer	0.03–4.0	303
Lindstrom & Wirth [20]	1969	sinker, dilatometer	0.001–2.3	298
Larson et al. [21]	1982	vibrating tube	0.05–0.6	298
Hovey & Hepler [22]	1990	vibrating tube	0.1–1.0	283–328
Zhao et al. [23]	2006	pycnometer	1.1–4.4	293–343
Li et al. [24]	2019	vibrating tube	0.05–0.5[b]	283–318

[a] Pressures not stated but assumed to be 0.1 MPa at $T \leq 373.15$ K and saturation vapor pressure at $T > 373.15$ K.
[b] Measurements at 293 and 303 K extended to $m \leq 3.7$ mol·kg^{-1}.

Noteworthy by their omission from Table 1 are the more recent density compilations of Söhnel and Novotny [12] and of Asayev and Zaytsev [13]. As found for a number of other electrolyte systems, these modern compilations often exhibit significant departures from high-quality experimental data and show many internal inconsistencies [14]. Accordingly they, along with a number of less-reliable measurements, e.g. [15–17], will not be considered further in this paper.

2. Experimental

2.1. Reagents

Details of the reagents used in the present study are given in Table 2. Briefly, two stock solutions of sulfuric acid were prepared. The first was a commercial Concentrated Volumetric Standard (CVS) ampoule with a stated accuracy of ± 0.2%. The second was prepared by diluting analytical grade concentrated sulfuric acid; its concentration was determined by density comparison with the CVS solution. Working solutions were prepared by weight dilutions using high-purity de-ionized water (Ibis Technology, Australia). Buoyancy corrections were applied throughout.

2.2. Density determinations

Densities were determined with an Anton-Paar (Graz, Austria) DMA 5000 M vibrating-glass-tube densimeter. The measurement protocol and the calibration of this instrument with water and air have been described in detail elsewhere [25]. Measurements were performed isoplethically over the temperature range $293.15 \leq T/K \leq 343.15$ in 5 K intervals. Temperatures of solutions in the densimeter tube were controlled to ± 0.002 K using the in-built thermostat. The experimental pressure of (0.101 ± 0.001) MPa was obtained from the internal sensor of the densimeter. Reproducibility of the measured densities was generally within ± 10 μg·cm^{-3}.

3. Results and discussion

3.1. Densities and apparent molar volumes

Experimental density differences, $\Delta\rho = \rho - \rho_{w,exp}$ (where ρ and $\rho_{w,exp}$ are, respectively, the experimental densities of the solution and of pure water at the target conditions) were converted to apparent molar volumes, V_ϕ, using the usual equation

$$V_\phi = \frac{M}{\Delta\rho + \rho_w} - \frac{\Delta\rho}{m\rho_w(\Delta\rho + \rho_w)} \qquad (2)$$

where M is the molar mass of anhydrous (pure) sulfuric acid, 98.072 g·mol^{-1}, calculated from the 2013 IUPAC atomic weights [26], and m is the stoichiometric (total) sulfuric acid molality

(mol H_2SO_4)·(kg H_2O)$^{-1}$. Here, the pure water densities ρ_w were calculated from the IAPWS-95 equation of state [27] and for convenience are included in Table 3.

The values of $\Delta\rho$ and V_ϕ obtained for 15 sulfuric acid concentrations spanning the range $0.01 \leq m$/mol·kg$^{-1} \leq 3$ are listed in Table 3. Also given in Table 3 are the standard uncertainties in the density difference $u(\Delta\rho)$ and the combined standard uncertainties in the apparent molar volumes $u_c(V_\phi)$, estimated in accordance with the GUM guidelines [28].

3.2. Comparisons with literature data

Fig. 1 plots the present and selected literature values of V_ϕ as a function of the stoichiometric (total) sulfuric acid concentration (as $m^{1/2}$) at 298.15 K and 0.101 MPa, where by far the greatest amount of reliable data exists. The agreement among the various studies is excellent with an average spread of just ± 0.3 cm^3·mol^{-1} over the whole concentration range. This is comparable with well characterized electrolyte systems such as NaCl(aq), HCl(aq) and NaBr (aq) [29]. The concordance with the ICT data [11] (with an average difference of ± 0.1 cm^3·mol^{-1}) is especially notable. There are too few data at other temperatures to justify plots analogous to Fig. 1 but a more general comparison with the better quality literature data (Table 1) over wide ranges of T and m (Fig. 2) shows a high level of agreement. Fig. 2 also shows how the present results have expanded the volumetric database of H_2SO_4(aq) especially in the dilute range (m/mol·kg$^{-1} \leq 0.1$) at T/K > 298.15.

Although the uncertainty in V_ϕ increases rapidly as $\rho \rightarrow \rho_w$ (cf. Eq. (2)), the observed agreement (Figs. 1 and 2) amongst the independent investigations confirms the unusual decrease in the $V_\phi(m^{1/2})$ values for H_2SO_4(aq) at low solute concentrations ($m \leq 0.1$ mol·kg^{-1}). While this phenomenon has not been widely studied (Table 1) its characteristics, at least at 298.15 K, based mainly on the data of Klotz and Eckert [18], were discussed at length in Robinson and Stokes' classic monograph [30]. In essence, the dramatic decrease in V_ϕ at low m is consistent with a change in the chemical speciation of the sulfuric acid, which alters from being a mainly 1:1 electrolyte (H$^+$(aq) + HSO$_4^-$ (aq)) to become a predominantly 1:2 electrolyte (2H$^+$(aq) + SO$_4^{2-}$(aq)) with increasing dilution (cf. Eq. (1)). This effect shifts to lower concentrations at higher temperatures (Fig. 2) as HSO$_4^-$ (aq) becomes a weaker acid, ie, as Eq. (1) shifts to the left [31].

3.3. Standard molar volumes

The standard (infinite dilution) molar volume of the sulfate ion $V°$(SO$_4^{2-}$,aq), hereafter $V_2°$, can be calculated over the temperature range of interest using the $V°$ values of well characterised 1:2 sulfate salts by assuming ionic additivity. On the other hand, the estimation of $V°$(HSO$_4^-$,aq), hereafter $V_1°$, and the standard molar volume change for Eq. (1), from left to right, $\Delta_r V°$, is much less

Table 2

Sample sources and purities.

chemical name	CASRN	source	initial mass fraction purity	purification method
sulfuric acid	7664–93–9	Merck	≥ 0.98[a]	none
sulfuric acid	7664–93–9	VWR	≥ 0.998[b]	none

[a] Analytical grade, as supplied, has no significant impurities other than water

[b] Concentrated volumetric standard.

Table 3

Experimental density differences, $\Delta\rho = \rho - \rho_{w,exp}$,[a] and apparent molar volumes, V_ϕ, at molalities m[b], temperatures T and pressure p = 0.101 MPa.[c]

m/mol·kg^{-1}	$\Delta\rho$/kg·m^{-3} T = 293.15 K, ρ_w = 998.207 kg·m^{-3}	V_ϕ/cm^3·mol^{-1}	$\Delta\rho$/kg·m^{-3} T = 298.15 K, ρ_w = 997.047 kg·m^{-3}	V_ϕ/cm^3·mol^{-1}
0.01028	0.744(2)	22.65(26)	0.757(3)	24.26(33)
0.01028	0.773(2)	22.75(31)	0.755(4)	24.45(42)
0.01028	0.776(4)	22.46(40)	0.763(10)	23.67(99)
0.02000	1.446(2)	25.68(19)	1.413(4)	27.26(25)
0.04000	2.794(2)	28.08(15)	2.732(6)	29.59(20)
0.06000	4.111(4)	29.37(15)	4.026(3)	30.74(14)
0.06000	4.085(2)	29.79(14)	4.012(6)	30.98(17)
0.07999	5.406(1)	30.26(14)	5.305(1)	31.49(13)
0.07999	5.418(4)	30.11(14)	5.311(5)	31.41(15)
0.1000	6.683(1)	30.99(13)	6.563(3)	32.15(13)
0.2000*	12.972(1)	32.74(13)	12.757(10)	33.77(14)
0.4000*	25.228(2)	34.10(12)	24.824(9)	35.07(12)
0.5999	37.201(2)	34.73(12)	36.613(2)	35.67(12)
0.8000*	48.764(2)	35.36(12)	48.030(1)	36.23(12)
1.000*	60.311(2)	35.58(11)	59.414(2)	36.44(11)
1.500*	87.872(2)	36.27(11)	86.638(6)	37.05(11)
2.000*	113.929(1)	36.87(10)	112.394(1)	37.59(10)
2.500*	138.787(1)	37.35(10)	137.003(1)	38.02(10)
3.000*	162.234(7)	37.83(9)	160.242(11)	38.46(9)
	T = 303.15 K, ρ_w = 995.649 kg·m^{-3}		T = 308.15 K, ρ_w = 994.033 kg·m^{-3}	
0.01028	0.740(1)	25.85(19)	0.729(1)	26.86(19)
0.01028	0.738(3)	26.05(34)	0.728(3)	26.96(34)
0.01028	0.750(9)	24.87(90)	0.735(10)	26.27(100)
0.02000	1.388(4)	28.45(25)	1.365(4)	29.55(25)
0.04000	2.677(1)	30.92(14)	2.629(2)	32.07(14)
0.06000	3.952(3)	31.93(14)	3.888(3)	32.96(14)
0.06000	3.936(1)	32.20(13)	3.875(1)	33.18(13)
0.07999	5.214(1)	32.58(13)	5.130(1)	33.59(13)
0.07999	5.217(5)	32.55(15)	5.135(5)	33.53(14)
0.1000	6.453(4)	33.21(14)	6.354(4)	34.15(13)
0.2000*	12.560(11)	34.72(14)	12.385(10)	35.55(13)
0.4000*	24.464(9)	35.93(12)	24.151(9)	36.67(12)
0.5999	36.102(2)	36.48(12)	35.660(2)	37.18(12)
0.8000*	47.379(1)	37.01(11)	46.814(1)	37.67(11)
1.000*	58.632(1)	37.18(11)	57.951(2)	37.82(11)
1.500*	85.548(7)	37.74(11)	84.599(7)	38.33(11)
2.000*	111.037(1)	38.23(10)	109.850(1)	38.78(10)
2.500*	135.420(2)	38.61(10)	134.028(4)	39.14(10)
3.000*	158.472(11)	39.01(9)	156.911(9)	39.50(9)
	T = 313.15 K, ρ_w = 992.216 kg·m^{-3}		T = 318.15 K, ρ_w = 990.212 kg·m^{-3}	
0.01028	0.726(3)	27.07(34)	0.716(1)	27.97(20)
0.01028	0.715(5)	28.16(52)	0.715(3)	28.07(34)
0.01028	0.722(4)	27.47(43)	0.711(7)	28.47(71)
0.02000	1.346(6)	30.44(34)	1.326(3)	31.38(21)
0.04000	2.592(3)	32.95(15)	2.559(1)	33.72(13)
0.06000	3.831(9)	33.86(20)	3.779(4)	34.68(15)
0.06000	3.819(1)	34.06(13)	3.769(2)	34.85(13)
0.07999	5.053(1)	34.51(13)	4.991(2)	35.24(13)
0.07999	5.064(5)	34.37(14)	4.997(5)	35.16(14)
0.1000	6.266(1)	34.99(13)	6.188(2)	35.73(13)
0.2000*	12.229(11)	36.29(13)	12.098(8)	36.91(13)
0.4000*	23.878(5)	37.31(12)	23.640(5)	37.87(12)
0.5999	35.283(1)	37.77(12)	34.952(1)	38.28(11)
0.8000*	46.327(1)	38.24(11)	45.905(2)	38.73(11)
1.000*	57.362(4)	38.37(11)	56.854(3)	38.84(11)
1.500*	83.772(5)	38.84(10)	83.058(6)	39.28(10)
2.000*	108.819(1)	39.26(10)	107.919(1)	39.68(10)

Table 3 (*continued*)

$m/\text{mol·kg}^{-1}$	$\Delta\rho/\text{kg·m}^{-3}$	$V_\phi/\text{cm}^3\text{·mol}^{-1}$	$\Delta\rho/\text{kg·m}^{-3}$	$V_\phi/\text{cm}^3\text{·mol}^{-1}$
2.500*	132.812(4)	39.59(10)	131.750(5)	39.98(9)
3.000*	155.550(4)	39.92(9)	154.345(6)	40.30(9)
	T = 323.15 K, ρ_w = 988.034 kg·m^{-3}		T = 328.15 K, ρ_w = 985.693 kg·m^{-3}	
0.01028	0.694(5)	30.07(53)	0.686(2)	30.78(26)
0.01028	0.705(2)	28.98(26)	0.692(2)	30.18(27)
0.01028	0.698(5)	29.67(53)	0.690(5)	30.38(53)
0.02000	1.309(4)	32.17(25)	1.294(4)	32.86(25)
0.04000	2.533(1)	34.32(13)	2.502(1)	35.04(13)
0.06000	3.733(6)	35.40(16)	3.698(5)	35.93(15)
0.06000	3.723(2)	35.57(13)	3.684(1)	36.17(13)
0.07999	4.934(3)	35.90(13)	4.887(5)	36.44(14)
0.07999	4.942(1)	35.80(13)	4.898(4)	36.30(14)
0.1000	6.121(4)	36.35(13)	6.063(1)	36.88(12)
0.2000*	11.981(3)	37.45(12)	11.881(3)	37.90(12)
0.4000*	23.443(5)	38.32(12)	23.269(3)	38.71(12)
0.5999	34.674(3)	38.70(11)	34.438(1)	39.06(11)
0.8000*	45.543(2)	39.15(11)	45.238(1)	39.49(11)
1.000*	56.422(1)	39.23(11)	56.054(3)	39.56(11)
1.500*	82.445(2)	39.66(10)	81.922(1)	39.97(10)
2.000*	107.149(1)	40.03(10)	106.486(1)	40.33(10)
2.500*	130.832(2)	40.32(9)	130.042(2)	40.61(9)
3.000*	153.303(7)	40.62(9)	152.404(5)	40.89(9)
	T = 333.15 K, ρ_w = 983.195 kg·m^{-3}		T = 338.15 K, ρ_w = 980.550 kg·m^{-3}	
0.01028	0.680(1)	31.29(20)	0.673(1)	31.89(21)
0.01028	0.677(2)	31.59(27)	0.670(4)	32.20(44)
0.01028	0.679(1)	31.39(20)	0.671(1)	32.10(21)
0.02000	1.277(5)	33.65(30)	1.265(4)	34.19(25)
0.04000	2.482(1)	35.48(13)	2.460(1)	35.98(13)
0.06000	3.669(3)	36.36(14)	3.645(3)	36.70(14)
0.06000	3.648(1)	36.72(13)	3.623(2)	37.08(13)
0.07999	4.841(3)	36.97(13)	4.809(5)	37.31(14)
0.07999	4.862(1)	36.70(13)	4.827(2)	37.08(13)
0.1000	6.011(1)	37.35(12)	5.969(1)	37.72(12)
0.2000*	11.799(1)	38.27(12)	11.731(1)	38.56(12)
0.4000*	23.128(2)	39.02(12)	23.013(1)	39.26(12)
0.5999	34.240(2)	39.34(11)	34.083(3)	39.56(11)
0.8000*	44.982(2)	39.77(11)	44.774(1)	39.99(11)
1.000*	55.747(3)	39.83(11)	55.492(3)	40.05(11)
1.500*	81.484(2)	40.23(10)	81.119(1)	40.44(10)
2.000*	105.925(1)	40.58(10)	105.458(1)	40.78(10)
2.500*	129.374(1)	40.85(9)	128.814(2)	41.04(9)
3.000*	151.640(4)	41.12(9)	150.995(1)	41.31(9)
	T = 343.15 K, ρ_w = 977.764 kg·m^{-3}			
0.01028	0.666(2)	32.50(27)		
0.01028	0.665(3)	32.60(36)		
0.01028	0.664(1)	32.71(21)		
0.02000	1.251(2)	34.83(18)		
0.04000	2.438(1)	36.47(13)		
0.06000	3.622(2)	37.03(13)		
0.06000	3.599(1)	37.43(13)		
0.07999	4.777(5)	37.66(14)		
0.07999	4.797(1)	37.40(13)		
0.1000	5.932(2)	38.04(13)		
0.2000*	11.678(1)	38.77(12)		
0.4000*	22.919(1)	39.45(12)		
0.5999	33.952(3)	39.73(11)		
0.8000*	44.606(1)	40.16(11)		
1.000*	55.290(2)	40.21(11)		
1.500*	80.826(1)	40.59(10)		
2.000*	105.077(1)	40.94(10)		
2.500*	128.358(1)	41.20(9)		
3.000*	150.460(1)	41.47(9)		

[a] Where ρ is the experimental sample density and $\rho_\text{w,exp}$ is the experimental water density at the same T, p. The values ρ_w listed in this Table are calculated using IAPWS-95 equation-of-state [27].

[b] m marked with "*" refer to solutions prepared from a stock solution, itself prepared from concentrated sulfuric acid. Unmarked m refer to solutions prepared from the concentrated volumetric standard.

[c] Standard uncertainties $u_\text{r}(m)$ = 0.002, $u(T)$ = 0.002 K, $u(p)$ = 0.001 MPa and $u(\rho_\text{w})$ = 0.001 kg·m^{-3} [27]. Numbers in brackets are standard uncertainties in the density difference $u(\Delta\rho)$ and combined standard uncertainties in the apparent molar volume $u_\text{c}(V_\phi)$. The values of these uncertainties refer to the corresponding last digits of the relevant values.
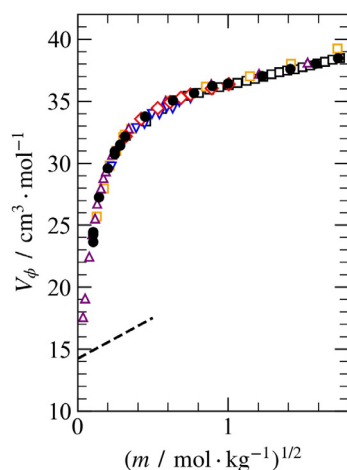
Fig. 1. Apparent molar volumes (V_ϕ) of H_2SO_4(aq) as a function of solute molality (as $m^{1/2}$) at 298.15 K and 0.101 MPa pressure. Black dots, this work; black squares [11]; orange squares [18]; purple triangles [20]; blue downward triangles [21]; red diamonds [22]; the dashed line is the Debye-Hückel limiting law slope for a 1:2 electrolyte. (For interpretation of the references to colour in this Figure legend, the reader is referred to the web version of this article.)
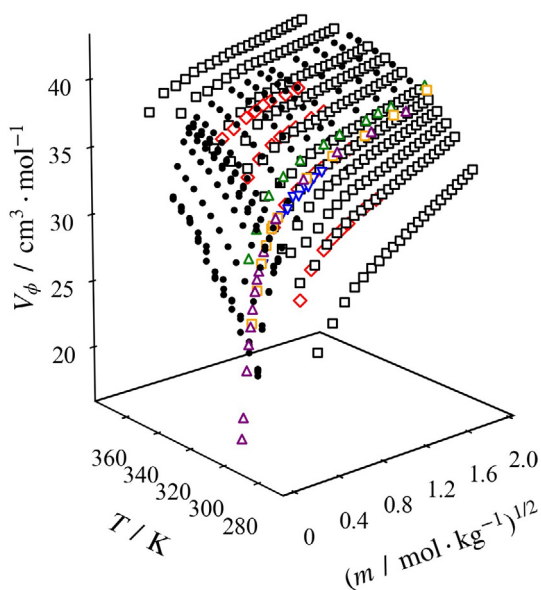

Fig. 2. Apparent molar volumes (V_ϕ) of H_2SO_4(aq) as a function of solute molality (as $m^{1/2}$) and temperature T at 0.101 MPa pressure: black dots, present results; black squares [11]; orange squares [18]; green triangles [19]; purple triangles [20]; blue downward triangles [21]; red diamonds [22]. (For interpretation of the references to colour in this Figure legend, the reader is referred to the web version of this article.)

Table 4
Summary of literature values for $V°(HSO_4^-,aq)$ and $\Delta_r V°$.

Quantity	T/K	V/cm^3 mol^{-1}	Refs.
$V°(HSO_4^-,aq)$	298.15	34.52 ± 0.39	Hovey and Hepler [22]
	298.15	35.1	Klotz and Eckert [18]
	298.15	35.68	Lindstrom and Wirth [20][b]
	298.15	35.2	Larson et al. [21]
	298.15	36.3 ± 0.25	Larson et al. [21][c]
	298.15	36.82 ± 0.14	Hovey and Hepler [22]
	313.15	38.22 ± 0.11	Hovey and Hepler [22]
	328.15	39.06 ± 0.13	Hovey and Hepler [22]
$\Delta_r V°$	298.15	20.0 ± 1.0	Rohwer et al. [35]
	298.15	20.2 ± 1.0	Klotz and Eckert [18]
	298.15	21.6 ± 1.0	Lindstrom and Wirth [20]
	298.15	19 ± 1.0	Bilal and Müller [32][d]
	323.15	21.4 ± 0.6	Bilal and Müller [32][d]
	348.15	25.3 ± 0.6	Bilal and Müller [32][d]
	373.15	31.1 ± 0.7	Bilal and Müller [32][d]

[a]Assuming $V°(H^+) \equiv 0$ cm^3 mol^{-1} at all T. [b]Value also recommended by Millero [36]. [c]Recalculated by Hovey and Hepler [22]. [d]Extrapolated value.

employs the Pitzer variant of the DHLL for a mixture [33]. Method (3) is based on Young's rule [34] with the end member V_ϕ values calculated from the DHLL. Method (4) also uses Young's rule but with the end member V_ϕ values calculated from the Pitzer variant of the DHLL. The speciation necessary for all of these calculations was modelled using the log $K_a°$ values of Dickson et al. (Eq. 6) [31], which are regarded as reliable [7], and the Pitzer variant of the DHLL for activity coefficients [33].

With respect to Methods (1) and (2), the pressure derivative of the LL expression for the excess Gibbs energy of the considered mixture yields the following equation for $V_\phi(H_2SO_4,aq)$:

$$V_\phi = (1 - \alpha)V_1° + \alpha V_2° + A_V(1 + 2\alpha)f(I) \qquad (3)$$

where α is the degree of dissociation of HSO_4^- (aq), A_V is the DH slope for volumes [37] and $f(I)$ represents the chosen ionic strength dependence: $I^{1/2}$ for the DHLL and $\ln(1 + bI^{1/2})/b$ for its Pitzer variant, with b = 1.2 (kg·mol^{-1})$^{1/2}$. The ionic strength of the solution is $(1 + 2\alpha)m$.

With regards to Methods (3) and (4) Young's rule for estimating $V_\phi(H_2SO_4,aq)$ can be written:

$$V_\phi = (1 - \alpha)V_{\phi,A} + \alpha V_{\phi,B} \qquad (4)$$

where and $V_{\phi,A}$ and $V_{\phi,B}$ are the apparent molar volumes of the hypothetical end-members: (A) H^+(aq) + HSO_4^-(aq) and (B) $2H^+$(aq) + SO_4^{2-}(aq) at the same (total) molality m. The $V_{\phi,i}$ values are calculated as

$$V_{\phi,i} = V_i° + A_V \frac{I}{m}f(I) \qquad (5)$$

The ionic strengths of the end-member solutions are m for (A) and $3m$ for (B).

The present experimental V_ϕ values were used to obtain $V_1°$ at each T using the four different calculation methods outlined above. Because the present treatments assume the absence of higher order interaction terms, only data at $m \leq 0.1$ mol·kg^{-1} were included in the fits. Conventional values of $V_2°$ are given in Table 5 and were estimated by assuming ionic additivity (M = Li or Na: $V_2°$ = $V°(M_2SO_4,aq) - 2 V°(M^+,aq)$) using relevant literature data for Li_2SO_4 [38] and Na_2SO_4 [39,40] and conventional values of $V°(M^+,aq)$ based on those of Marcus [41]. All fits were done with the PyMC3 Bayesian statistics package for Python [42]. The combined uncertainties $u_c(V_\phi)$ (Table 3) were included in the regression.

The four methods of calculation show systematic differences that decrease with increasing temperature (Fig. 3). These differences arise from the slightly different limiting law behaviour of
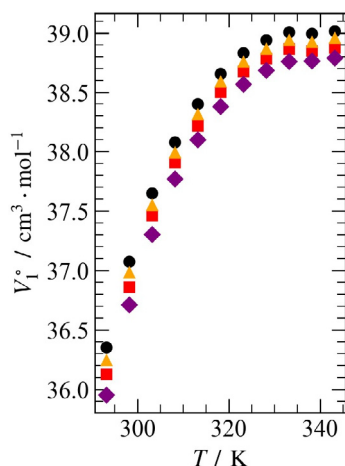
straightforward. Two general methods have been used to obtain these parameters: indirect estimation from volumetric data (densimetry or dilatometry) or directly from the pressure dependence of log $K_a°$ [32]. Reported values are summarized in Table 4, noting that all single-ion volumes discussed here are "conventional" values, based on the assumption that $V°(H^+,aq) \equiv 0$ at all temperatures.

The data in Table 4 indicate that the reported $V_1°$ values have a spread of 1.7 cm^3·mol^{-1} at 298.15 K. This rather large uncertainty mostly arises from systematic differences in the methods and assumptions used to derive $V_1°$ from the observed V_ϕ. Four calculation methods are presented here. Method (1) uses the Debye-Hückel (DH) limiting law (LL) for a mixture. Method (2)

Fig. 3. Effects of the different calculation methods on $V_1^\circ(HSO_4^-, aq)$: red squares, Method (1); black dots, Method (2); purple diamonds, Method(3); orange triangles, Method (4). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Fig. 4. Sensitivity (in $cm^3 \cdot mol^{-1}$ per 0.01 log unit) of the calculated V_1° values to changes in $\log K_a^\circ$ as a function of temperature T.

the thermodynamically rigorous formulations (Methods (1) and (2)) and Young's rule (Methods (3) and (4)), and the difference between the DHLL and its Pitzer variant. Because the Pitzer variants produce lower V_ϕ estimates, they conversely lead to higher V_1° values. Likewise, as Young's rule leads to systematically higher V_ϕ than the thermodynamic approach, the calculated V_1° values are systematically lower.

Overall, the V_1° values obtained from these various approaches show a spread of ca. 0.4 $cm^3 \cdot mol^{-1}$ (Fig. 3). There are, however, two additional sources of uncertainty in V_1°: the values assumed for V_2° and for the protonation constant, $\log K_a^\circ$ (Eq. 1). These uncertainties were estimated by finite differences. Varying V_2° by ± 0.1 $cm^3 \cdot mol^{-1}$ resulted in an uncertainty in V_1° of ±(0.01–0.06) $cm^3 \cdot mol^{-1}$, decreasing in magnitude at higher T. Uncertainties stemming from $\log K_a^\circ$ are significantly larger, with values of ±(0.06–0.14) $cm^3 \cdot mol^{-1}$ corresponding to an uncertainty of ± 0.01 in $\log K_a^\circ$. In principle this uncertainty also decreases as T increases (Fig. 4), but is counteracted to some extent by the increasing uncertainty in $\log K_a^\circ$ at higher T (Fig 5.)

Recommended values for V_1°, calculated as the unweighted average of the results from the four calculation methods, are given in Table 5. The uncertainties in V_1° are combined values (u_c) estimated from the uncertainties in the calculation methods, as discussed above, and assuming $u(V_2^\circ) = 0.10$ $cm^3 \cdot mol^{-1}$ and $u(\log K_a^\circ) = 0.01$. Both of the latter limits are probably optimistic. The values of V_1° and $u_c(V_1^\circ)$ at 283.15 K were taken from Hovey and Hepler [22] (Table 4).

As would be expected (see above) the values of V_2° for SO_4^{2-} (Table 5) are similar to those of Marcus [41] but were derived using more recent data [38–40] and so are likely to be more reliable. At 298.15 K the present 'conventional' value of $V_1^\circ(36.9 ± 0.4)$ $cm^3 \cdot mol^{-1}$ (Table 5) agrees almost quantitatively with that of Hovey and Hepler (Table 4), obtained from their combined Pitzer and Young's rule analysis of their own sulfuric acid data [22]. It also compares well with the other literature values listed in Table 4 [11,18,20–22,36]. At 313.15 and 328.15 K, the only other temperatures where direct comparisons are possible, the present results (Table 5, Figure 5) for V_1° again agree within the error limits with those of Hovey and Hepler (Table 4).

With regard to $\Delta_r V^\circ$, the standard volume change for the protonation reaction, the present result at 298.15 K (Table 5) is slightly higher than previous estimates (Table 4), although probably within the true uncertainties. At higher temperatures, the agreement
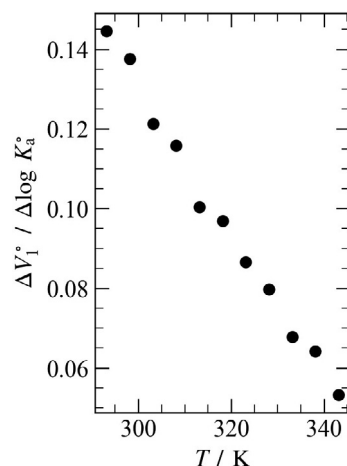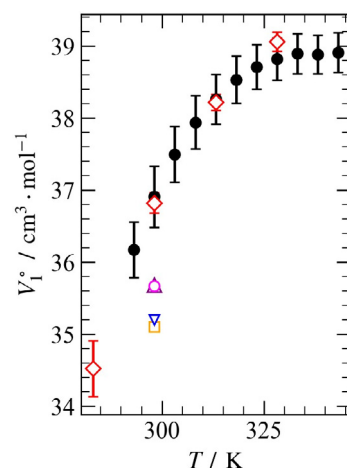

Fig. 5. $V_1^\circ(HSO_4^-)$ as a function of temperature T at 0.101 MPa pressure: black dots, average of present methods (Table 5); red diamonds [22]; blue downward triangle [21]; pink circle [36]; purple triangle [20]; orange square [18]. Error bars, where given, correspond to standard uncertainties. (For interpretation of the references to colour in this Figure legend, the reader is referred to the web version of this article.)

between the present results (Table 5) and those of Bilal and Müller [32] (Table 4), obtained from potentiometric measurements of the effects of pressure on K_a° are within the stated error limits.

3.4. Comparison with other acids

Given the evidence above that indicates that at moderate concentrations $H_2SO_4(aq)$ behaves essentially as a 1:1 electrolyte, it is interesting to compare its behaviour with common strong monoprotic acids. Fig. 6 plots $V^\circ(HX,aq)$ for various mineral acids (extracted from the JESS database [10,38,43,44]) as a function of temperature. Note however that for representational purposes the position of each curve on the y-axis is arbitrary, with fixed addends chosen so as to maintain the actual V° sequence HTf > HClO_4 > H_2SO_4 > HNO_3 > HCl, where HTf is trifluoromethanesulfonic acid. The shapes of the $V^\circ(T)$ curves for all five acids are broadly similar (Fig. 6) over the present temperature range. It is perhaps noteworthy that the volumetric behaviour of $H_2SO_4(aq)$ appears to be somewhat more like the very weakly associated $HNO_3(aq)$ and $HCl(aq)$, rather than the stronger $HClO_4(aq)$ and $HTf(aq)$. This may indicate the presence of traces of $H_2SO_4^0$ (aq).

Table 5
Literature values for $V_2°$ and present values for $V_1°$ and $\Delta_r V°$ for the protonation of the sulfate ion from 283.15 to 343.15 K at 0.101 MPa pressure.[a]

T/K	$V_2°(SO_4^{2-})^b$/cm^3·mol^{-1}	$V_1°(HSO_4^-)$/cm^3·mol^{-1}	$\Delta_r V°$/cm^3·mol^{-1}
283.15	–	34.52(39)^c	–
293.15	13.59	36.17(39)	22.58
298.15	14.15	36.90(41)	22.75
303.15	14.52	37.49(39)	22.97
308.15	14.73	37.93(37)	23.2
313.15	14.78	38.26(35)	23.48
318.15	14.72	38.52(32)	23.8
323.15	14.55	38.70(31)	24.15
328.15	14.29	38.82(30)	24.53
333.15	13.94	38.89(28)	24.95
338.15	13.51	38.88(27)	25.37
343.15	13.02	38.91(28)	25.89

[a]Numbers in brackets are the combined standard uncertainties $u_c(V_1°)$. All $V°$(ion) values are based on $V°(H^+,aq) \equiv 0$ at all T. [b]Derived from literature data as described in the text. [c]From Hovey and Hepler [22].
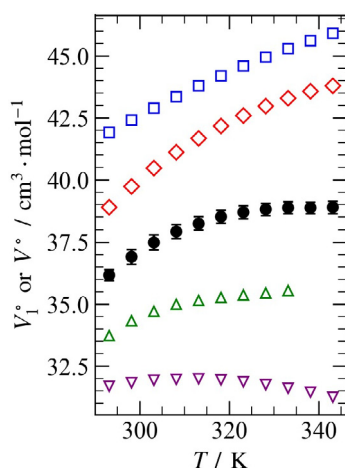

Fig. 6. Comparison of $V_1°(HSO_4^-,aq)$ and $V°(HX,aq)$ for various mineral acids: black dots, present results; blue squares, HTf (trifluoromethanesulfonic acid) [38,43,44] (−32.5 cm^3· mol^{-1}); red diamonds, HClO$_4$ [10] (-4 cm^3· mol^{-1}), green triangles, HNO$_3$ [10] (+5 cm^3· mol^{-1}); purple downward triangles, HCl [10] (+14 cm^3· mol^{-1}). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

4. Conclusions

Densities of aqueous solutions of sulfuric acid determined by vibrating tube densimetry have been used to calculate apparent molar volumes $V_\phi(H_2SO_4,aq)$ at temperatures in the range $293.15 \leq T/K \leq 343.15$ and concentrations $0.01 \leq m/mol·kg^{-1} \leq 3.0$. Consistent with earlier studies, the present V_ϕ values show an unusually large decrease at low solute concentrations. This is consistent with a change in chemical speciation of the sulfuric acid from a mainly 1:1 electrolyte ($H^+(aq) + HSO_4^-(aq)$) to a predominantly 1:2 electrolyte ($2H^+ + SO_4^{2-}(aq)$). Analysis of these data using combinations of different limiting laws and mixing equations, along with relevant literature data, enabled estimation of the standard state volume of $HSO_4^-(aq)$ and volume change for the first protonation reaction of the sulfate ion ($H^+(aq) + SO_4^{2-}(aq)$) as functions of temperature.

CRediT authorship contribution statement

Tuomas Vielma: Investigation, Writing - original draft, Funding acquisition. **Lubomir Hnedkovsky:** Methodology, Writing - review

& editing. **Glenn Hefter:** Supervision, Resources, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jct.2021.106408.

References

[1] H. Müller, Sulfuric acid and sulfur trioxide, in: F. Ullmann, W. Gerhartz (Eds.), Ullmann's Encyclopedia of Industrial Chemistry, Wiley-VCH, Weinheim, Germany, 2000.
[2] F.K. Crundwell, M.S. Moats, V. Ramachandran, T.G. Robinson, W.G. Davenport, Extractive Metallurgy of Nickel, Cobalt and Platinum-Group Metals, Elsevier, Oxford, UK, 2011.
[3] R.J. Sinclair, The Extractive Metallurgy of Zinc, AUSSIM, Carlton, Australia, 2005.
[4] J.A. Jacobs, J.H. Lehr, S.M. Testa, Acid Mine Drainage, Rock Drainage, and Acid Sulfate Soils: Causes, Assessment, Prediction, Prevention, and Remediation, Wiley-Blackwell, Hoboken, USA, 2014.
[5] M. Sipila, T. Berndt, T. Petaja, D. Brus, J. Vanhanen, F. Stratmann, J. Patokoski, R. L. Mauldin, A.-P. Hyvarinen, H. Lihavainen, M. Kulmala, The role of sulfuric acid in atmospheric nucleation, Science 327 (5970) (2010) 1243–1246.
[6] N. N. Greenwood, A. Earnshaw, Chemistry of the Elements, Chap. 15, 2nd Edition, Butterworth-Heinemann, Oxford, 1997.
[7] G. Hefter, C. Gumiński, Remarks on the evaluation of thermodynamic data for sulfate ion protonation, J. Solution Chem. 48 (11-12) (2019) 1657–1670.
[8] A.V. Bandura, S.N. Lvov, The ionization constant of water over wide ranges of temperature and density, J. Phys. Chem. Ref. Data 35 (1) (2006) 15–30.
[9] P.L. Brown, C. Eckberg, Hydrolysis of Metal Ions, Wiley-VCH, Weinheim, Germany, 2016.
[10] P.M. May, D. Rowland, E. Königsberger, G. Hefter, JESS, a joint expert speciation system - IV: A large database of aqueous solution physicochemical properties with an automatic means of achieving thermodynamic consistency, Talanta 81 (2010) 142–148.
[11] E.W. Washburn (Ed.), International Critical Tables of Numerical Data, Physics, Chemistry and Technology, McGraw-Hill, New York, 1926.
[12] O. Söhnel, P. Novotny, Densities of Aqueous Solutions of Inorganic Substances, Elsevier, New York, 1985.
[13] G.G. Aseyev, I.D. Zaytsev, Volumetric Properties of Electrolyte Solutions; Estimation Methods and Experimental Data, Begell House, New York, USA, 1996.
[14] P.M. May, D. Rowland, Thermodynamic modeling of aqueous electrolyte systems: Current status, J. Chem. Eng. Data 62 (9) (2017) 2481–2495.
[15] A.-P. Hyvärinen, H. Lihavainen, K. Hautio, T. Raatikainen, Y. Viisanen, A. Laaksonen, Surface tensions and densities of sulfuric acid + dimethylamine + water solutions, J. Chem. Eng. Data 49 (4) (2004) 917–922.
[16] B.K. Joshi, N.D. Kandpal, Volumetric and transport properties of aqueous sulphuric acid, Phys. Chem. Liq. 45 (4) (2007) 463–470.
[17] L. Oca, J.M. Campillo-Robles, M.M. Bou-Ali, Review and analysis of thermophysical properties of a sulfuric acid water electrolyte, J. Chem. Eng. Data 63 (9) (2018) 3572–3583.
[18] I.M. Klotz, C.F. Eckert, The apparent molal volumes of aqueous solutions of sulfuric acid at 25°, J. Am. Chem. Soc. 64 (8) (1942) 1878–1880.
[19] P.L. Khare, Compressibility of dilute solutions of sulphuric acid, Trans. Faraday Soc. 58 (1961) 363–367.
[20] R.E. Lindstrom, H.E. Wirth, Estimation of the bisulfate ion dissociation in solutions of sulfuric acid and sodium bisulfate, J. Phys. Chem. 73 (1) (1969) 218–223.
[21] J.W. Larson, K.G. Zeeb, L.G. Hepler, Heat capacities and volumes of dissociation of phosphoric acid (1st, 2nd, and 3rd), bicarbonate ion, and bisulfate ion in aqueous solution, Can. J. Chem. 60 (16) (1982) 2141–2150.
[22] J.K. Hovey, L.G. Hepler, Thermodynamics of sulphuric acid: apparent and partial molar heat capacities and volumes of aqueous HSO$_4^-$ from 10–55 °C and calculation of the second dissociation constant to 350 °C, J. Chem. Soc. Faraday Trans. 86 (1990) 2831–2839.

[23] J.-H. Zhao, L.-C. Wang, H.-S. Xu, C.-Y. Song, F.-A. Wang, Densities and Viscosities of *p*-Aminophenol in Sulfuric Acid + Water at temperatures from (293.15 to 343.15) K, J. Chem. Eng. Data 51 (2) (2006) 660–664.

[24] X. Li, C. Jiang, Y. Qin, J. Liu, J. Yang, Q. Xu, C. Yan, Investigation of electrolytes of the vanadium redox flow battery (VII): Prediction of the viscosity of mixed electrolyte solution ($VOSO_4$ + H_2SO_4 + H_2O) based on Eyring's theory, J. Chem. Thermodyn. 134 (2019) 69–75.

[25] B. Hu, L. Hnedkovsky, W.u. Li, G. Hefter, Densities and molar volumes of aqueous solutions of $LiClO_4$ at temperatures from 293 K to 343 K, J. Chem. Eng. Data 61 (4) (2016) 1388–1394.

[26] J. Meija, T.B. Coplen, M. Berglund, W.A. Brand, P. De Bievre, M. Gröning, N.E. Holden, J. Irrgeher, R.D. Loss, T. Walczyk, T. Prohaska, Atomic weights of the elements 2013, Pure Appl. Chem. 88 (2016) 265–291.

[27] W. Wagner, A. Pruß, I.A.P.W.S. The formulation 1995 for the thermodynamic properties of ordinary water substance for general and scientific use, J. Phys. Chem. Ref. Data 31 (2002) 387–535.

[28] 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.

[29] B.S. Krumgalz, R. Pogorelsky, K.S. Pitzer, Volumetric properties of single aqueous electrolytes from zero to saturation concentration at 298.15 K represented by Pitzer's ion-interaction equations, J. Phys. Chem. Ref. Data 25 (1996) 663–689.

[30] R.A. Robinson, R.H. Stokes, Electrolyte Solutions, 2nd Edition., Butterworths, London, 1970.

[31] A.G. Dickson, D.J. Wesolowski, D.A. Palmer, R.E. Mesmer, Dissociation constant of bisulfate ion in aqueous sodium chloride solutions to 250 °C, J. Phys. Chem. 94 (1990) 7978–7985.

[32] B.A. Bilal, E. Müller, Thermodynamics of HSO_4^- formation in aqueous solutions up to 473 K and 975 bar, Z. Naturforsch. A 48 (1993) 1073–1080.

[33] K.S. Pitzer, Ion interaction approach: theory and data correlation, in: K.S. Pitzer (Ed.), Activity Coefficients in Electrolyte Solutions, 2nd Edition., CRC Press, Boca Raton, USA, 1991, pp. 75–153.

[34] T.F. Young, M.B. Smith, Thermodynamic properties of mixtures of electrolytes in aqueous solutions, J. Phys. Chem. 58 (9) (1954) 716–724.

[35] E.F.C.H. Rohwer, J.A. Brink, J.J. Cruywagen, Dilatometric study of the protonation of sulphate, J. South. Afr. Chem. Inst. 28 (1975) 1–13.

[36] F.J. Millero, The partial molal volumes of electrolytes in aqueous solutions, in: R.A. Horne (Ed.), Water and Aqueous Solutions, Wiley, New York, 1974, pp. 519–595.

[37] D.P. Fernández, A.R.H. Goodwin, Eric W. Lemmon, J.M.H. Levelt Sengers, R.C. Williams, 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 26 (4) (1997) 1125–1166.

[38] B. Hu, L. Hnedkovsky, G. Hefter, Densities and apparent molar volumes of aqueous solutions of Li_2SO_4 and $LiCF_3SO_3$ at temperatures from 293 to 343 K, J. Chem. Eng. Data 61 (10) (2016) 3618–3626.

[39] M. Obšil, V. Majer, G. Hefter, V. Hynek, Densities and apparent molar volumes of Na_2SO_4 (aq) and K_2SO_4 (aq) at temperatures from 298 K to 573 K and at pressures up to 30 MPa, J. Chem. Eng. Data 42 (1) (1997) 137–142.

[40] S.L. Clegg, A.S. Wexler, Densities and apparent molar volumes of atmospherically important electrolyte solutions. 1. The solutes H_2SO_4, HNO_3, HCl, Na_2SO_4, $NaNO_3$, NaCl, $(NH_4)_2SO_4$, NH_4NO_3, and NH_4Cl from 0 to 50 °C, including extrapolations to very low temperature and to the pure liquid state, and $NaHSO_4$, NaOH, and NH_3 at 25 °C, J. Phys. Chem. A 115 (15) (2011) 3393–3460.

[41] Y. Marcus, The standard partial molar volumes of ions in solution. Part 4. Ionic volumes in water at 0–100 °C, J. Phys. Chem. B 113 (30) (2009) 10285–10291.

[42] J. Salvatier, T. V. Wiecki, C. Fonnesbeck, Probabilistic programming in Python using PyMC3, PeerJ Comput. Sci. 2 (2016) e55.

[43] C. Xiao, P. Tremaine, 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. 26 (3) (1997) 277–294.

[44] L. Hnedkovsky, G. Hefter, Densities and apparent molar volumes of aqueous solutions of sodium and potassium triflates to high concentrations at temperatures 293.15 K to 343.15 K, J. Chem. Eng. Data, manuscript No. je-2021-00009, accepted for publication (2021).

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