



Measurement and Prediction of Molar Volumes of Bivalent Metal Sulfates and Their Mixtures in Aqueous Solution

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Abstract

Densities of aqueous solutions of MnSO_4 , CoSO_4 , NiSO_4 and CuSO_4 have been measured by vibrating tube densimetry up to near-saturation concentrations over the temperature range $293.15 \leq T/\text{K} \leq 343.15$ at 5 K intervals and at 0.1 MPa pressure. Apparent molar volumes, V_ϕ , calculated from the densities revealed close similarities among all four electrolytes, with their V_ϕ values essentially differing by constant concentration-independent addends for each salt at each temperature. It was found that there is an almost linear relationship between $V_\phi(\text{MSO}_4, \text{aq})$ and the M–O bond length of the hydrated cations obtained from structural studies. This relationship can be used to predict values of $V_\phi(\text{MSO}_4, \text{aq})$ for other sulfate salts over wide ranges of concentration and temperature, providing that the requisite structural data are available. Measurements of selected ternary, quaternary and quinary mixtures of these electrolytes at constant total concentrations showed that their V_ϕ values almost always exhibit linear mixing (Young's rule) behavior at all temperatures investigated. This finding can be exploited to predict the volumetric properties of solutions containing complex mixtures of bivalent metal sulfates.

Keywords Manganese sulfate · Cobalt sulfate · Nickel sulfate · Copper sulfate · Density · Molar volume · Prediction

1 Introduction

Aqueous solutions of the sulfate salts of the bivalent first transition row metal ions have vast applications in agriculture [1], marine science [2], medicine [3], and so on. Arguably, however, their most important roles are those that each plays (to varying degree) in the hydrometallurgical extraction, separation, recovery and purification of their respective metals [4].

The volumetric properties of metal sulfate solutions are required industrially for process engineering purposes [5]. However, while these solutions have been reasonably well

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characterized at near-ambient temperatures, they have been surprisingly little-studied at the higher temperatures more relevant to most practical processes (Table 1). To give just one example, the electrolytic deposition of nickel from acidified $\text{NiSO}_4(\text{aq})$ solutions, the standard method for nickel electrorefining [6], is invariably conducted at temperatures around 333 K. Similar conditions apply with respect to the hydrometallurgical processing of the other first transition row metals.

This paper presents a detailed investigation of the densities of the aqueous solutions of MnSO_4 , CoSO_4 , NiSO_4 and CuSO_4 over the temperature range $293.15 \leq T/\text{K} \leq 343.15$ and up to near-saturation concentrations. Iron(II) sulfate was omitted from this study because of the difficulty of maintaining constant its oxidation state and chemical speciation in near-neutral solutions [7, 8]. Measurements of $\text{ZnSO}_4(\text{aq})$ were unnecessary as they have been reported elsewhere under the present conditions [9].

In addition to measurements of the binary metal(II) sulfate solutions (containing just one solute + the solvent), data have also been obtained for representative ternary (two solutes + the solvent), quaternary (three solutes + the solvent) and one quinary (four solutes + the solvent) solutions. These data are of particular practical interest as industrial process

Table 1 Selected literature publications on the volumetric behavior of $\text{MnSO}_4(\text{aq})$, $\text{CoSO}_4(\text{aq})$, $\text{NiSO}_4(\text{aq})$ and $\text{CuSO}_4(\text{aq})$

Author(s)	Year	Method ^a	$m/\text{mol}\cdot\text{kg}^{-1}$	T^b/K
$\text{MnSO}_4(\text{aq})$				
Herz [11]	1914	pyc ^c	0.4–3.4	298
Lo Surdo and Millero [12]	1980	vtd	0.06–1.0	298
Przepiera and Zielenkiewicz [13]	2000	vtd	1.6–3.5	298–318
$\text{CoSO}_4(\text{aq})$				
Lo Surdo and Millero [12]	1980	vtd	0.05–0.9	298
Akilan et al. [14]	2020	vtd	0.01–1.2	298
$\text{NiSO}_4(\text{aq})$				
Phillips [15]	1972	pyc	0.4–3.5	293–333
Isono [16]	1980	pyc ^c	0.05–2.0	288–328
Lo Surdo and Millero [12]	1980	vtd	0.06–0.9	298
Akilan et al. [14]	2020	vtd	0.01–1.5	298
$\text{CuSO}_4(\text{aq})$				
Herz [11]	1914	pyc ^c	0.3–1.1	298
Pearce and Pumphlin [17]	1937	pyc	0.1–1.4	298
Suryanarayana and Alamelu [18]	1959	–	0.1–2.3	303–333
Lo Surdo and Millero [12]	1980	mfd	0.002–0.55	298
Puchalska et al. [19]	1993	vtd	0.01–1.3	288–328
Ernst et al. [20]	1999	pyc	0.13–1.1	288–313
Hervello and Sanchez [21]	2007	vtd	0.13–1.2	283–298
Zhuo et al. [22]	2008	vtd	0.05–0.5	298
Akilan et al. [14]	2020	vtd	0.01–1.1	298

Experimental pressure is usually not stated but is assumed to be 0.1 MPa throughout

^avtd vibrating tube densimetry, mfd magnetic float densimetry, pyc pycnometry

^bRounded values

^cPresumed; method not stated

solutions almost invariably contain mixtures of solutes. Such data can also be used as a stern test of a simple linear mixing model (Young's rule) [10] which, if proven to be applicable, can be used to *predict* with good accuracy the volumetric properties of mixtures over wide ranges of conditions. Confirmation of the applicability of Young's rule for any given system represents a major improvement over the purely empirical models that are nowadays routinely employed in the computer packages used for process design and optimization. Conformance to Young's rule also minimizes the need for economically prohibitive experimental efforts that are required to define the multi-dimensional property spaces of real systems.

2 Experimental Section

2.1 Reagents

Sources and purities of the reagents used are given in Table 2. All salts were commercial materials recrystallized once from slightly acidified aqueous solutions. Concentrated stock solutions were prepared by dissolving the purified solid metal(II) sulfate hydrate in ultra-pure water (Ibis Technology, Australia; resistivity >18 M Ω -cm) and acidifying with sulfuric acid to pH \approx 4 to minimize cation hydrolysis. These solutions were allowed to stand for at least 12 h, filtered (Millipore 0.5 μ m) and, standardized (\pm 0.2%) by titration with a commercial concentrated volumetric standard containing ethylenediaminetetraacetate (EDTA), using either Eriochrome Black T or murexide indicator [23]. Occasional cross-checks were made by evaporative gravimetry, which involved sub-boiling evaporation at \sim 340 K to superficial dryness followed by heating to constant mass at about 570 K. Such assays had a typical reproducibility of \pm 0.05% and agreed with the titrimetric results to within 0.2%. Working solutions were prepared by mass dilution of the stock solutions with ultra-pure water. Mixed electrolyte solutions, covering all the ternary, quaternary and one quinary solution, were prepared by mass from \sim 1.0 mol \cdot kg $^{-1}$ sample solutions, so as to obtain approximately constant stoichiometric molalities of the various metal ions present. Buoyancy corrections were applied throughout.

2.2 Density Determinations

Densities were determined with an Anton Paar (Graz, Austria) DMA 5000 M glass vibrating-tube densimeter (vtd). The calibration of this instrument with water and air, and the measurement protocol have been described in detail elsewhere [24]. Measurements were

Table 2 Sample sources and purities

Chemical name	CASRN	Source	Mass fraction purity ^a
Manganese(II) sulfate monohydrate	10034-96-5	Chem-supply	\geq 0.985
Cobalt(II) sulfate heptahydrate	10026-24-1	Chem-supply	\geq 0.99
Nickel(II) sulfate hexahydrate	10101-97-0	Fluka	\geq 0.99
Copper(II) sulfate pentahydrate	7758-99-8	Chem-supply	\geq 0.98

^aManufacturers' stated purity; the major "impurity" in all cases was water

performed isoplethically over the temperature range $293.15 \leq T/\text{K} \leq 343.15$ at 5 K intervals. The temperature of the solutions in the densimeter tube was controlled to ± 0.002 K using the in-built thermostat of the vtd. The experimental pressure of (102 ± 2) kPa was obtained from the in-built sensor of the densimeter. Reproducibility of the measured densities was generally within $\pm 10 \mu\text{g}\cdot\text{cm}^{-3}$.

3 Results and Discussion

3.1 Densities and Apparent Molar Volumes

The experimental density differences between the sample solutions and pure water $\Delta\rho$ were converted to apparent molar volumes V_ϕ with the usual equation

$$V_\phi = \frac{M}{\Delta\rho + \rho_w} - \frac{\Delta\rho}{m\rho_w(\Delta\rho + \rho_w)} \quad (1)$$

where ρ_w is the density of pure water at the measurement conditions, which was calculated from the IAPWS-95 EOS [25]. In Eq. 1, m is the molality ($\text{mol}\cdot\text{kg}^{-1}$) and M is the molar mass of the anhydrous solute. The latter were calculated using the current IUPAC atomic masses [26] and had values (in $\text{g}\cdot\text{mol}^{-1}$) of 150.99 (MnSO_4), 154.99 (CoSO_4), 154.75 (NiSO_4) and 159.60 (CuSO_4). Each of these molar masses has an uncertainty of approximately $\pm 0.02 \text{ g}\cdot\text{mol}^{-1}$ mostly ascribable to sulfur.

The values of $\Delta\rho$ and V_ϕ at molalities m , temperatures T and pressure $p = 0.1$ MPa for the binary $\text{MSO}_4(\text{aq})$ solutions are given in Tables 3, 4, 5 and 6. These results are compared graphically in Figs. 1, 2, 3 and 4 with selected literature data (Table 1) and are discussed in the following sub-sections.

$\text{MnSO}_4(\text{aq})$. Compared with the other bivalent metal sulfate solutions investigated here (see below), few studies have been reported for $\text{MnSO}_4(\text{aq})$, even at 298.15 K (Fig. 1, Table 1). The present results are slightly higher (by $\sim 1 \text{ cm}^3\cdot\text{mol}^{-1}$) than the literature values [11–13] but show the same trend with respect to concentration (Fig. 1a) and are consistent with the infinite dilution volume V° , calculated from the $V^\circ(\text{ion})$ values tabulated by Marcus [27]. At other temperatures, only the results of Przepiera and Zielenkiewicz [13] are available for comparison. Their values at $T = 318.15$ K (the highest temperature reported) are again lower than the present results by about $1 \text{ cm}^3\cdot\text{mol}^{-1}$ (Fig. 1b).

$\text{CoSO}_4(\text{aq})$. Independent studies of the volumetric properties of $\text{CoSO}_4(\text{aq})$ at $T = 298.15$ K [12, 14] are in unusually good agreement with the present results (Fig. 2). However, in marked contrast, no reliable V_ϕ values appear to be available for $\text{CoSO}_4(\text{aq})$ solutions at other temperatures.

$\text{NiSO}_4(\text{aq})$. The volumetric properties of $\text{NiSO}_4(\text{aq})$ have been studied over wide of ranges of concentration and temperature. At $T = 298.15$ K (Fig. 3a), the present results and the literature data fit within a span of $\sim \pm 0.5 \text{ cm}^3\cdot\text{mol}^{-1}$. At higher temperatures (Fig. 3b), the pycnometric results of Phillips [15] and Isono [16] show similar agreement with the present data.

$\text{CuSO}_4(\text{aq})$. The volumetric properties of $\text{CuSO}_4(\text{aq})$ at 298.15 K have been studied extensively over a wide concentration range (Fig. 4a). With the exception of the results of Puchalska et al. [19] (hexagons) at $m \geq 0.2 \text{ mol}\cdot\text{kg}^{-1}$, and the obvious outliers from the historic study by Herz [11] (triangles down), the various independent V_ϕ values are in reasonable agreement with each other and with the present results at this temperature. Thus,

Table 3 Experimental density differences $\Delta\rho$ and apparent molar volumes V_ϕ for aqueous solutions of MnSO_4 at Molalities m , Temperatures T and Pressure = 0.1 MPa

$m/\text{mol}\cdot\text{kg}^{-1}$	$\Delta\rho/\text{kg}\cdot\text{m}^{-3}$	$V_\phi/\text{cm}^3\cdot\text{mol}^{-1}$	$\Delta\rho/\text{kg}\cdot\text{m}^{-3}$	$V_\phi/\text{cm}^3\cdot\text{mol}^{-1}$
	$T = 293.15 \text{ K}, \rho_w = 998.207 \text{ kg}\cdot\text{m}^{-3}$		$T = 298.15 \text{ K}, \rho_w = 997.047 \text{ kg}\cdot\text{m}^{-3}$	
0.01019	1.541	- 0.44(55)	1.532	0.25(57)
0.02006	3.005	0.91(31)	2.991	1.43(32)
0.04008	5.954	2.17(20)	5.926	2.71(20)
0.05999	8.866	2.92(17)	8.814	3.62(17)
0.09993	14.669	3.89(16)	14.589	4.52(16)
0.2000	29.009	5.52(16)	28.857	6.11(16)
0.3997	57.014	7.68(15)	56.732	8.21(15)
0.6000	84.429	9.27(14)	84.030	9.74(14)
0.7996	111.174	10.55(14)	110.669	11.00(13)
0.9991	137.484	11.58(13)	136.878	11.99(13)
1.499	201.008	13.91(12)	200.210	14.25(12)
1.998	261.226	15.92(11)	260.302	16.20(11)
2.499	318.620	17.68(10)	317.626	17.90(10)
2.999	372.805	19.31(9)	371.799	19.48(9)
3.498	424.091	20.77(9)	423.103	20.90(9)
3.959	468.780	22.07(8)	467.822	22.18(8)
	$T = 303.15 \text{ K}, \rho_w = 995.649 \text{ kg}\cdot\text{m}^{-3}$		$T = 308.15 \text{ K}, \rho_w = 994.033 \text{ kg}\cdot\text{m}^{-3}$	
0.01019	1.524	0.78(60)	1.521	0.93(62)
0.02006	2.977	1.92(33)	2.966	2.23(34)
0.04008	5.898	3.21(21)	5.874	3.57(21)
0.05999	8.772	4.12(18)	8.741	4.40(18)
0.09993	14.522	4.99(16)	14.468	5.30(16)
0.2000	28.726	6.56(16)	28.617	6.88(16)
0.3997	56.487	8.61(15)	56.278	8.91(15)
0.6000	83.683	10.12(14)	83.381	10.39(14)
0.7996	110.227	11.34(13)	109.842	11.60(13)
0.9991	136.352	12.31(13)	135.896	12.54(13)
1.499	199.516	14.51(12)	198.915	14.69(12)
1.998	259.500	16.40(11)	258.803	16.54(11)
2.499	316.769	18.06(10)	316.030	18.16(10)
2.999	370.929	19.60(9)	370.189	19.67(9)
3.498	422.260	20.99(9)	421.543	21.03(9)
3.959	467.011	22.24(8)	466.331	22.26(8)
	$T = 313.15 \text{ K}, \rho_w = 992.216 \text{ kg}\cdot\text{m}^{-3}$		$T = 318.15 \text{ K}, \rho_w = 990.212 \text{ kg}\cdot\text{m}^{-3}$	
0.01019	1.516	1.10(64)	1.508	1.65(67)
0.02006	2.958	2.39(35)	2.950	2.48(36)
0.04008	5.851	3.89(22)	5.838	3.93(22)
0.05999	8.711	4.65(18)	8.692	4.68(18)
0.09993	14.418	5.55(17)	14.380	5.65(17)
0.2000	28.520	7.11(16)	28.440	7.24(16)
0.3997	56.090	9.13(15)	55.938	9.25(15)
0.6000	83.116	10.59(14)	82.888	10.70(14)
0.7996	109.506	11.77(13)	109.212	11.88(14)

Table 3 (continued)

$m/\text{mol}\cdot\text{kg}^{-1}$	$\Delta\rho/\text{kg}\cdot\text{m}^{-3}$	$V_\phi/\text{cm}^3\cdot\text{mol}^{-1}$	$\Delta\rho/\text{kg}\cdot\text{m}^{-3}$	$V_\phi/\text{cm}^3\cdot\text{mol}^{-1}$
0.9991	135.495	12.70(13)	135.150	12.79(13)
1.499	198.391	14.81(12)	197.932	14.87(12)
1.998	258.202	16.63(11)	257.673	16.66(11)
2.499	315.396	18.21(10)	314.840	18.22(10)
2.999	369.553	19.69(9)	368.999	19.68(9)
3.498	420.937	21.03(9)	420.412	21.00(9)
3.959	465.761	22.24(8)		
$T = 323.15 \text{ K}, \rho_w = 988.034 \text{ kg}\cdot\text{m}^{-3}$			$T = 328.15 \text{ K}, \rho_w = 985.693 \text{ kg}\cdot\text{m}^{-3}$	
0.01019	1.504	1.62(69)	1.506	1.11(72)
0.02006	2.942	2.56(37)	2.936	2.52(39)
0.04008	5.825	3.94(23)	5.817	3.80(23)
0.05999	8.669	4.76(19)	8.654	4.67(19)
0.09993	14.345	5.69(17)	14.316	5.66(17)
0.2000	28.371	7.29(16)	28.311	7.27(16)
0.3997	55.799	9.30(15)	55.682	9.29(15)
0.6000	82.686	10.76(14)	82.514	10.75(14)
0.7996	108.957	11.92(14)	108.734	11.91(14)
0.9991	134.849	12.82(13)	134.579	12.81(13)
1.499	197.535	14.88(12)	197.183	14.85(12)
1.998	257.217	16.65(11)	256.821	16.60(11)
2.499	314.366	18.19(10)	313.957	18.12(10)
2.999	368.542	19.63(9)	368.144	19.55(9)
3.498	419.988	20.94(9)	419.626	20.85(9)
$T = 333.15 \text{ K}, \rho_w = 983.195 \text{ kg}\cdot\text{m}^{-3}$			$T = 338.15 \text{ K}, \rho_w = 980.550 \text{ kg}\cdot\text{m}^{-3}$	
0.01019	1.502	1.18(74)	1.502	0.67(77)
0.02006	2.929	2.47(40)	2.927	2.18(41)
0.04008	5.803	3.79(24)	5.796	3.58(24)
0.05999	8.640	4.55(19)	8.632	4.30(20)
0.09993	14.293	5.54(17)	14.273	5.36(17)
0.2000	28.259	7.19(16)	28.215	7.04(16)
0.3997	55.576	9.23(15)	55.487	9.10(15)
0.6000	82.358	10.69(14)	82.224	10.58(14)
0.7996	108.537	11.85(14)	108.366	11.74(14)
0.9991	134.346	12.74(13)	134.140	12.63(13)
1.499	196.876	14.78(12)	196.606	14.66(12)
1.998	256.476	16.51(11)	256.177	16.39(11)
2.499	313.602	18.03(10)	313.298	17.90(10)
2.999	367.810	19.45(9)	367.529	19.31(9)
3.498	419.327	20.73(9)		
$T = 343.15 \text{ K}, \rho_w = 977.764 \text{ kg}\cdot\text{m}^{-3}$				
0.01019	1.503	0.19(79)		
0.02006	2.925	1.85(42)		
0.04008	5.788	3.37(25)		
0.05999	8.619	4.11(20)		

Table 3 (continued)

$m/\text{mol}\cdot\text{kg}^{-1}$	$\Delta\rho/\text{kg}\cdot\text{m}^{-3}$	$V_\phi/\text{cm}^3\cdot\text{mol}^{-1}$	$\Delta\rho/\text{kg}\cdot\text{m}^{-3}$	$V_\phi/\text{cm}^3\cdot\text{mol}^{-1}$
0.09993	14.248	5.22(17)		
0.2000	28.172	6.87(16)		
0.3997	55.403	8.94(15)		
0.6000	82.105	10.42(14)		
0.7996	108.212	11.59(14)		
0.9991	133.957	12.48(13)		
1.499	196.369	14.51(12)		
1.998	255.913	16.24(11)		
2.499	313.038	17.74(10)		
2.999	367.289	19.15(9)		

Standard uncertainties are $u_i(m) = 0.001$, $u(T) = 0.02$ K, $u_i(\rho) = 0.01$, $u(\Delta\rho) = 0.0005\cdot\Delta\rho$ or 0.005 $\text{kg}\cdot\text{m}^{-3}$, whichever is larger. Numbers in brackets are the uncertainty in last shown digit of V_ϕ .

almost all the reported V_ϕ results lie within a span of ~ 1 $\text{cm}^3\cdot\text{mol}^{-1}$ over the whole concentration range, with the present values lying comfortably within the spread of the literature data (Fig. 4a).

In contrast to the other systems studied here, numerous V_ϕ values have been reported in the literature for $\text{CuSO}_4(\text{aq})$ at temperatures over the range $283.15 \leq T/\text{K} \leq 333.15$ (Fig. 4). The spread in the literature data and their relation to the present values mimic those at 298.15 K (Fig. 4a). Similar results were obtained at other temperatures (data not shown).

3.2 Comparison of Bivalent Metal Sulfate Solutions

Comparison of the data obtained for the present electrolytes with those of other bivalent metal sulfates (MgSO_4 , FeSO_4 , ZnSO_4 and CdSO_4) provides a clear-cut example of the well-known chemical similarities of the aqueous solutions of these salts (Fig. 5). Like the more-limited range of bivalent metal sulfates studied previously (see Fig. 5 in Ref. [14]) the V_ϕ values of the present salts differ (in essence) only by fixed, almost concentration-independent addends. Inclusion of these addends confirms that, as found previously [14], all $V_\phi(\text{MSO}_4, \text{aq})$ can be made to lie on a single common line, from infinite dilution to near-saturation concentrations, at temperatures up to at least 343.15 K (the maximum temperature investigated here).

3.3 Prediction of Apparent Molar Volumes of $\text{MSO}_4(\text{aq})$ Solutions

A plot of $V_\phi(\text{MSO}_4, \text{aq})$ against $r_{\text{M-O}}$, the metal-oxygen bond length in the *hydrated* bivalent first-row transition metal ions, obtained from structural studies, produces an almost-straight line (Fig. 6a). This strongly suggests that the observed differences in $V_\phi(\text{MSO}_4, \text{aq})$ in Fig. 5 are largely determined by the size (volume) of the hydrated cations. Furthermore, because $r_{\text{M-O}}$ does not vary much with temperature over the present range of interest, the relationship in Fig. 6a persists up to at least $T = 343.15$ K with an essentially unchanged slope (Fig. 6b). An interesting exception to this systematic behavior is found for CuSO_4

Table 4 Experimental density differences $\Delta\rho$ and apparent molar volumes V_ϕ for aqueous solutions of CoSO_4 at Molalities m , Temperatures T and Pressure = 0.1 MPa

$m / \text{mol}\cdot\text{kg}^{-1}$	$\Delta\rho / \text{kg}\cdot\text{m}^{-3}$	$V_\phi / \text{cm}^3\cdot\text{mol}^{-1}$	$\Delta\rho / \text{kg}\cdot\text{m}^{-3}$	$V_\phi / \text{cm}^3\cdot\text{mol}^{-1}$
	$T = 293.15 \text{ K}, \rho_w = 998.207 \text{ kg}\cdot\text{m}^{-3}$		$T = 298.15 \text{ K}, \rho_w = 997.047 \text{ kg}\cdot\text{m}^{-3}$	
0.01059	1.734	- 9.06(54)	1.721	- 8.00(56)
0.02051	3.331	- 7.66(31)	3.314	- 7.06(32)
0.04093	6.603	- 6.57(21)	6.570	- 5.97(21)
0.06044	9.696	- 5.67(18)	9.644	- 5.00(18)
0.09983	15.919	- 4.68(18)	15.835	- 4.04(18)
0.2003	31.588	- 2.89(17)	31.430	- 2.30(17)
0.4002	62.150	- 0.54(16)	61.860	- 0.03(16)
0.6002	92.161	1.07(15)	91.739	1.56(15)
0.8001	121.608	2.44(15)	121.063	2.90(15)
1.000	150.597	3.62(14)	149.958	4.03(14)
1.500	220.841	6.13(13)	219.998	6.47(13)
1.914	276.751	7.97(12)	275.800	8.24(12)
	$T = 303.15 \text{ K}, \rho_w = 995.649 \text{ kg}\cdot\text{m}^{-3}$		$T = 308.15 \text{ K}, \rho_w = 994.033 \text{ kg}\cdot\text{m}^{-3}$	
0.01059	1.709	- 7.10(58)	1.703	- 6.76(60)
0.02051	3.299	- 6.56(33)	3.290	- 6.39(34)
0.04093	6.541	- 5.50(21)	6.514	- 5.10(22)
0.06044	9.602	- 4.54(19)	9.566	- 4.21(19)
0.09983	15.766	- 3.58(18)	15.703	- 3.21(18)
0.2003	31.294	- 1.85(17)	31.176	- 1.53(17)
0.4002	61.602	0.38(16)	61.377	0.68(16)
0.6002	91.366	1.94(15)	91.045	2.21(15)
0.8001	120.596	3.24(15)	120.193	3.48(15)
1.000	149.405	4.34(14)	148.926	4.56(14)
1.500	219.265	6.71(13)	218.630	6.88(13)
1.914	274.966	8.44(12)	274.239	8.57(12)
	$T = 313.15 \text{ K}, \rho_w = 992.216 \text{ kg}\cdot\text{m}^{-3}$		$T = 318.15 \text{ K}, \rho_w = 990.212 \text{ kg}\cdot\text{m}^{-3}$	
0.01059	1.700	- 6.78(62)	1.694	- 6.55(65)
0.02051	3.279	- 6.16(35)	3.265	- 5.80(36)
0.04093	6.494	- 4.91(22)	6.475	- 4.78(23)
0.06044	9.537	- 4.02(19)	9.510	- 3.90(19)
0.09983	15.652	- 2.99(18)	15.608	- 2.87(18)
0.2003	31.069	- 1.28(17)	30.980	- 1.16(17)
0.4002	61.181	0.88(16)	61.010	0.99(16)
0.6002	90.766	2.39(15)	90.528	2.48(15)
0.8001	119.842	3.63(15)	119.542	3.70(15)
1.000	148.508	4.69(14)	148.141	4.76(14)
1.500	218.080	6.98(13)	217.601	7.01(13)
1.914	273.611	8.64(12)	273.074	8.65(12)
	$T = 323.15 \text{ K}, \rho_w = 988.034 \text{ kg}\cdot\text{m}^{-3}$		$T = 328.15 \text{ K}, \rho_w = 985.693 \text{ kg}\cdot\text{m}^{-3}$	
0.01059	1.690	- 6.54(67)	1.694	- 7.33(70)
0.02051	3.261	- 5.97(37)	3.254	- 6.02(38)
0.04093	6.459	- 4.74(23)	6.447	- 4.84(24)

Table 4 (continued)

$m / \text{mol} \cdot \text{kg}^{-1}$	$\Delta\rho / \text{kg} \cdot \text{m}^{-3}$	$V_\phi / \text{cm}^3 \cdot \text{mol}^{-1}$	$\Delta\rho / \text{kg} \cdot \text{m}^{-3}$	$V_\phi / \text{cm}^3 \cdot \text{mol}^{-1}$
0.06044	9.492	− 3.96(20)	9.470	− 3.98(20)
0.09983	15.569	− 2.83(18)	15.540	− 2.92(18)
0.2003	30.905	− 1.13(17)	30.845	− 1.19(17)
0.4002	60.864	1.02(16)	60.736	0.99(16)
0.6002	90.319	2.50(15)	90.129	2.47(15)
0.8001	119.281	3.71(15)	119.046	3.66(15)
1.000	147.824	4.77(14)	147.544	4.71(14)
1.500	217.187	6.99(13)	216.824	6.92(13)
1.914	272.612	8.61(12)	272.210	8.53(12)
	$T = 333.15 \text{ K}, \rho_w = 983.195 \text{ kg} \cdot \text{m}^{-3}$		$T = 338.15 \text{ K}, \rho_w = 980.550 \text{ kg} \cdot \text{m}^{-3}$	
0.01059	1.693	− 7.72(72)	1.692	− 8.13(74)
0.02051	3.247	− 6.10(40)	3.245	− 6.46(41)
0.04093	6.433	− 4.91(24)	6.427	− 5.21(25)
0.06044	9.448	− 4.02(20)	9.438	− 4.30(20)
0.09983	15.512	− 3.04(18)	15.490	− 3.25(19)
0.2003	30.790	− 1.31(17)	30.742	− 1.49(17)
0.4002	60.626	0.88(16)	60.529	0.72(16)
0.6002	89.968	2.37(15)	89.825	2.21(15)
0.8001	118.842	3.56(15)	118.660	3.41(15)
1.000	147.297	4.61(14)	147.080	4.46(14)
1.500	216.509	6.80(13)	216.235	6.65(13)
1.914	271.863	8.40(12)	271.566	8.24(12)
	$T = 343.15 \text{ K}, \rho_w = 977.764 \text{ kg} \cdot \text{m}^{-3}$			
0.01059	1.691	− 8.48(77)		
0.02051	3.240	− 6.69(42)		
0.04093	6.418	− 5.46(25)		
0.06044	9.425	− 4.54(21)		
0.09983	15.470	− 3.51(19)		
0.2003	30.699	− 1.72(17)		
0.4002	60.443	0.51(16)		
0.6002	89.698	2.02(16)		
0.8001	118.500	3.21(15)		
1.000	146.890	4.26(14)		
1.500	215.998	6.45(13)		
1.914	271.313	8.04(12)		

Standard uncertainties are $u_r(m) = 0.001$, $u(T) = 0.02 \text{ K}$, $u_r(p) = 0.01$, $u(\Delta\rho) = 0.0005 \cdot \Delta\rho$ or $0.005 \text{ kg} \cdot \text{m}^{-3}$, whichever is larger. Numbers in brackets are the uncertainty in last shown digit of V_ϕ .

(aq). Thus, while the value of $V_\phi(\text{CuSO}_4, \text{aq})$ conforms well with the other $\text{MSO}_4(\text{aq})$ at $T = 298.15 \text{ K}$ (Fig. 6a), it deviates significantly as the temperature is increased (Fig. 6b).

By inspecting the isopleths of the different $\text{MSO}_4(\text{aq})$ solutions at, say, $m = 1.0 \text{ mol} \cdot \text{kg}^{-1}$, it becomes apparent that temperature dependency of $V_\phi(\text{CuSO}_4, \text{aq})$ differs significantly from the other $V_\phi(\text{MSO}_4, \text{aq})$. Isopleths of $\text{MnSO}_4(\text{aq})$, $\text{CoSO}_4(\text{aq})$ and $\text{NiSO}_4(\text{aq})$,

Table 5 Experimental density differences $\Delta\rho$ and apparent molar volumes V_ϕ for aqueous solutions of NiSO_4 at Molalities m , Temperatures T and Pressure = 0.1 MPa

$m / \text{mol}\cdot\text{kg}^{-1}$	$\Delta\rho / \text{kg}\cdot\text{m}^{-3}$	$V_\phi / \text{cm}^3\cdot\text{mol}^{-1}$	$\Delta\rho / \text{kg}\cdot\text{m}^{-3}$	$V_\phi / \text{cm}^3\cdot\text{mol}^{-1}$
	$T = 293.15 \text{ K}, \rho_w = 998.207 \text{ kg}\cdot\text{m}^{-3}$		$T = 298.15 \text{ K}, \rho_w = 997.047 \text{ kg}\cdot\text{m}^{-3}$	
0.007333	1.230	- 13.22(76)	1.224	- 12.65(79)
0.01451	2.406	- 11.32(41)	2.390	- 10.45(42)
0.02904	4.778	- 10.05(25)	4.743	- 9.07(25)
0.04443	7.276	- 9.25(20)	7.238	- 8.60(21)
0.07233	11.770	- 8.18(18)	11.703	- 7.46(18)
0.1440	23.226	- 6.64(18)	23.112	- 6.06(18)
0.2855	45.461	- 4.56(17)	45.238	- 4.00(17)
0.4246	67.029	- 3.17(16)	66.704	- 2.63(16)
0.5618	88.007	- 2.00(16)	87.598	- 1.50(16)
0.6961	108.335	- 1.04(15)	107.848	- 0.57(15)
0.9914	152.185	0.85(14)	151.530	1.27(14)
1.487	223.473	3.42(13)	222.609	3.76(13)
1.982	291.634	5.68(12)	290.615	5.95(12)
2.353	340.787	7.21(11)	339.701	7.45(11)
	$T = 303.15 \text{ K}, \rho_w = 995.649 \text{ kg}\cdot\text{m}^{-3}$		$T = 308.15 \text{ K}, \rho_w = 994.033 \text{ kg}\cdot\text{m}^{-3}$	
0.007333	1.218	- 12.18(82)	1.212	- 11.61(85)
0.01451	2.378	- 9.88(44)	2.372	- 9.70(45)
0.02904	4.717	- 8.41(26)	4.701	- 8.14(27)
0.04443	7.204	- 8.08(21)	7.175	- 7.71(21)
0.07233	11.649	- 6.96(18)	11.604	- 6.61(19)
0.1440	23.009	- 5.58(18)	22.916	- 5.21(18)
0.2855	45.046	- 3.57(17)	44.872	- 3.23(17)
0.4246	66.424	- 2.22(16)	66.188	- 1.93(16)
0.5618	87.241	- 1.12(16)	86.934	- 0.85(16)
0.6961	107.418	- 0.21(15)	107.048	0.05(15)
0.9914	150.963	1.58(14)	150.467	1.81(14)
1.487	221.851	4.01(13)	221.196	4.18(13)
1.982	289.728	6.15(12)	288.963	6.28(12)
2.353	338.756	7.61(11)	337.947	7.71(11)
	$T = 313.15 \text{ K}, \rho_w = 992.216 \text{ kg}\cdot\text{m}^{-3}$		$T = 318.15 \text{ K}, \rho_w = 990.212 \text{ kg}\cdot\text{m}^{-3}$	
0.007333	1.212	- 11.83(89)	1.206	- 11.43(92)
0.01451	2.366	- 9.63(47)	2.357	- 9.38(49)
0.02904	4.691	- 8.10(27)	4.679	- 8.03(28)
0.04443	7.151	- 7.45(22)	7.135	- 7.44(22)
0.07233	11.574	- 6.50(19)	11.544	- 6.42(19)
0.1440	22.842	- 5.00(18)	22.776	- 4.87(18)
0.2855	44.724	- 3.01(17)	44.596	- 2.89(17)
0.4246	65.976	- 1.73(16)	65.798	- 1.64(16)
0.5618	86.671	- 0.67(16)	86.443	- 0.59(16)
0.6961	106.721	0.22(15)	106.442	0.31(15)
0.9914	150.033	1.95(14)	149.664	2.02(14)
1.487	220.626	4.29(13)	220.128	4.32(13)

Table 5 (continued)

$m / \text{mol}\cdot\text{kg}^{-1}$	$\Delta\rho / \text{kg}\cdot\text{m}^{-3}$	$V_\phi / \text{cm}^3\cdot\text{mol}^{-1}$	$\Delta\rho / \text{kg}\cdot\text{m}^{-3}$	$V_\phi / \text{cm}^3\cdot\text{mol}^{-1}$
1.982	288.303	6.35(12)	287.728	6.36(12)
2.353	337.251	7.75(11)	336.652	7.73(11)
	$T = 323.15 \text{ K}, \rho_w = 988.034 \text{ kg}\cdot\text{m}^{-3}$		$T = 328.15 \text{ K}, \rho_w = 985.693 \text{ kg}\cdot\text{m}^{-3}$	
0.007333	1.202	- 11.27(96)	1.199	- 11.24(99)
0.01451	2.352	- 9.36(50)	2.348	- 9.52(52)
0.02904	4.672	- 8.16(29)	4.666	- 8.36(30)
0.04443	7.117	- 7.41(22)	7.101	- 7.45(23)
0.07233	11.511	- 6.33(19)	11.488	- 6.40(19)
0.1440	22.719	- 4.83(18)	22.669	- 4.87(18)
0.2855	44.494	- 2.88(17)	44.398	- 2.92(17)
0.4246	65.640	- 1.61(16)	65.501	- 1.65(16)
0.5618	86.230	- 0.55(16)	86.050	- 0.59(16)
0.6961	106.190	0.33(15)	105.975	0.28(15)
0.9914	149.339	2.02(14)	149.051	1.96(14)
1.487	219.694	4.30(13)	219.313	4.24(13)
1.982	287.232	6.32(12)	286.806	6.23(12)
2.353	336.142	7.68(11)	335.704	7.57(11)
	$T = 333.15 \text{ K}, \rho_w = 983.195 \text{ kg}\cdot\text{m}^{-3}$		$T = 338.15 \text{ K}, \rho_w = 980.550 \text{ kg}\cdot\text{m}^{-3}$	
0.007333	1.199	- 11.70(103)	1.197	- 11.94(106)
0.01451	2.344	- 9.68(54)	2.342	- 10.02(55)
0.02904	4.656	- 8.45(30)	4.653	- 8.81(31)
0.04443	7.089	- 7.60(23)	7.078	- 7.80(24)
0.07233	11.470	- 6.57(20)	11.455	- 6.82(20)
0.1440	22.624	- 4.97(18)	22.591	- 5.18(18)
0.2855	44.312	- 3.02(17)	44.241	- 3.20(17)
0.4246	65.381	- 1.76(16)	65.273	- 1.92(16)
0.5618	85.892	- 0.70(16)	85.752	- 0.85(16)
0.6961	105.784	0.18(15)	105.619	0.02(15)
0.9914	148.799	1.85(14)	148.579	1.69(14)
1.487	218.983	4.12(13)	218.701	3.95(13)
1.982	286.443	6.09(12)	286.133	5.92(12)
2.353	335.336	7.43(11)	335.026	7.25(11)
	$T = 343.15 \text{ K}, \rho_w = 977.764 \text{ kg}\cdot\text{m}^{-3}$			
0.007333	1.195	- 12.17(110)		
0.01451	2.341	- 10.48(57)		
0.02904	4.649	- 9.17(32)		
0.04443	7.075	- 8.22(24)		
0.07233	11.439	- 7.07(20)		
0.1440	22.560	- 5.43(18)		
0.2855	44.181	- 3.44(17)		
0.4246	65.181	- 2.14(16)		
0.5618	85.631	- 1.06(16)		
0.6961	105.474	- 0.19(15)		
0.9914	148.386	1.49(14)		

Table 5 (continued)

$m / \text{mol}\cdot\text{kg}^{-1}$	$\Delta\rho / \text{kg}\cdot\text{m}^{-3}$	$V_\phi / \text{cm}^3\cdot\text{mol}^{-1}$	$\Delta\rho / \text{kg}\cdot\text{m}^{-3}$	$V_\phi / \text{cm}^3\cdot\text{mol}^{-1}$
1.487	218.454	3.75(13)		
1.982	285.869	5.71(12)		
2.353	334.769	7.04(11)		

Standard uncertainties are $u_r(m) = 0.001$, $u(T) = 0.02$ K, $u_r(p) = 0.01$, $u(\Delta\rho) = 0.0005\cdot\Delta\rho$ or 0.005 $\text{kg}\cdot\text{m}^{-3}$, whichever is larger. Numbers in brackets are the uncertainty in last shown digit of V_ϕ .

show the expected behavior, i.e., a weak maximum at $T \approx 323$ K, similar to $\text{ZnSO}_4(\text{aq})$ and $\text{MgSO}_4(\text{aq})$. For $\text{CuSO}_4(\text{aq})$, the maximum, however, lies at or just outside the upper temperature limit of the present study, $T = 343$ K. This may be partly due to the Jahn–Teller effect [8, 31], causing a distortion of the otherwise octahedral coordination sphere possessed by the Cu^{2+} ions. In this context, it is noteworthy that $\text{CuSO}_4(\text{aq})$ solutions show a marked increase in the concentration of contact ion-pairs with increasing temperature [32]. Such a change is likely to lead to an increase in V_ϕ .

The simple relationship evident from Fig. 6 creates the possibility of *predicting* values of $V_\phi(\text{MSO}_4, \text{aq})$ over wide ranges of m and T , providing the appropriate structural information (i.e., $r_{\text{M-O}}$) exists. Such data are available, in both solid and solution states, for many compounds from X-ray and neutron scattering experiments and related techniques such as EXAFS. This pathway for estimating V_ϕ values is potentially valuable for electrolytes that are difficult (or even impossible) to study experimentally. Some of these are now considered in the following paragraphs.

$V_\phi(\text{FeSO}_4, \text{aq})$. As noted in the Introduction above, $\text{FeSO}_4(\text{aq})$ was not included in the present study due to its tendency to oxidize and hydrolyze in near-neutral aqueous solutions [7, 8]. This is unfortunate because the volumetric data for such solutions are of considerable interest industrially.

Taking $r_{\text{Fe-O}} = 0.212$ nm from the solution-XRD data of Ohtaki et al. [33] and using the relationship between V_ϕ and $r_{\text{M-O}}$ (Fig. 6) enabled calculation of $V_\phi(\text{FeSO}_4, \text{aq})$ at $T = 298.15$ K as a function of concentration (Fig 7). The values so obtained are in good agreement with the experimental (vtd) data of Königsberger et al. [30], being lower on average by ~ 0.6 $\text{cm}^3\cdot\text{mol}^{-1}$. The experimental uncertainties in the results of Königsberger et al. are unknown but are likely to be significant given that FeSO_4 is a reactive 2:2 electrolyte. Accordingly, some confidence can be placed in the values predicted for $V_\phi(\text{FeSO}_4, \text{aq})$ using this approach at other m and T (Table S1, Supporting Information) where no experimental volumetric data are available. Such estimates represent a significant improvement on the existing database and are sufficiently accurate for most industrial applications.

On the other hand, it needs to be noted that the predicted values of $V_\phi(\text{FeSO}_4, \text{aq})$ are very sensitive to the value chosen for $r_{\text{Fe-O}}$. For example, adopting $r_{\text{Fe-O}} = 0.213$ nm (the unfilled square in Fig. 6), determined from a single-crystal XRD study [34] increases $V_\phi(\text{FeSO}_4, \text{aq})$ by ~ 0.6 $\text{cm}^3\cdot\text{mol}^{-1}$. While this change brings the calculated values into near-quantitative agreement with the experimental volumes [30], it is almost certainly fortuitous. Nevertheless, this tiny change (of just 1 pm!) also makes $r_{\text{Fe-O}}$ more

Table 6 Experimental density differences $\Delta\rho$ and apparent molar volumes V_ϕ for aqueous solutions of CuSO_4 at Molalities m , Temperatures T and Pressure = 0.1 MPa

$m / \text{mol}\cdot\text{kg}^{-1}$	$\Delta\rho / \text{kg}\cdot\text{m}^{-3}$	$V_\phi / \text{cm}^3\cdot\text{mol}^{-1}$	$\Delta\rho / \text{kg}\cdot\text{m}^{-3}$	$V_\phi / \text{cm}^3\cdot\text{mol}^{-1}$
	$T = 293.15 \text{ K}, \rho_w = 998.207 \text{ kg}\cdot\text{m}^{-3}$		$T = 298.15 \text{ K}, \rho_w = 997.047 \text{ kg}\cdot\text{m}^{-3}$	
0.01007	1.680	- 7.58(56)	1.665	- 6.31(59)
0.02004	3.321	- 6.38(32)	3.299	- 5.46(33)
0.04018	6.608	- 5.11(21)	6.565	- 4.24(21)
0.06002	9.826	- 4.35(19)	9.757	- 3.40(19)
0.1000	16.252	- 3.13(18)	16.149	- 2.31(18)
0.1999	32.125	- 1.35(17)	31.934	- 0.60(17)
0.3998	63.296	0.94(16)	62.913	1.67(16)
0.5997	93.907	2.50(16)	93.360	3.18(16)
0.7996	123.947	3.86(15)	123.247	4.49(15)
0.9996	153.524	4.98(14)	152.674	5.58(14)
1.284	194.696	6.42(13)	193.663	6.96(13)
	$T = 303.15 \text{ K}, \rho_w = 995.649 \text{ kg}\cdot\text{m}^{-3}$		$T = 308.15 \text{ K}, \rho_w = 994.033 \text{ kg}\cdot\text{m}^{-3}$	
0.01007	1.657	- 5.75(61)	1.649	- 5.28(63)
0.02004	3.284	- 4.94(34)	3.273	- 4.67(35)
0.04018	6.530	- 3.60(22)	6.497	- 3.05(22)
0.06002	9.702	- 2.72(19)	9.654	- 2.19(19)
0.1000	16.059	- 1.64(18)	15.976	- 1.08(18)
0.1999	31.756	0.05(17)	31.592	0.60(17)
0.3998	62.571	2.28(16)	62.260	2.78(16)
0.5997	92.862	3.75(15)	92.409	4.22(15)
0.7996	122.610	5.01(15)	122.027	5.46(15)
0.9996	151.902	6.08(14)	151.195	6.50(14)
1.284	192.714	7.42(13)	191.841	7.81(13)
	$T = 313.15 \text{ K}, \rho_w = 992.216 \text{ kg}\cdot\text{m}^{-3}$		$T = 318.15 \text{ K}, \rho_w = 990.212 \text{ kg}\cdot\text{m}^{-3}$	
0.01007	1.641	- 4.78(66)	1.638	- 4.72(68)
0.02004	3.257	- 4.17(36)	3.244	- 3.85(37)
0.04018	6.463	- 2.50(23)	6.437	- 2.18(23)
0.06002	9.612	- 1.78(19)	9.571	- 1.42(19)
0.1000	15.902	- 0.63(18)	15.832	- 0.25(18)
0.1999	31.440	1.06(17)	31.302	1.43(17)
0.3998	61.968	3.21(16)	61.703	3.56(16)
0.5997	91.989	4.62(15)	91.594	4.96(15)
0.7996	121.485	5.83(15)	120.972	6.15(15)
0.9996	150.532	6.85(14)	149.911	7.15(14)
1.284	191.024	8.13(13)	190.258	8.40(13)
	$T = 323.15 \text{ K}, \rho_w = 988.034 \text{ kg}\cdot\text{m}^{-3}$		$T = 328.15 \text{ K}, \rho_w = 985.693 \text{ kg}\cdot\text{m}^{-3}$	
0.01007	1.634	- 4.74(71)	1.627	- 4.49(73)
0.02004	3.229	- 3.46(38)	3.216	- 3.19(39)
0.04018	6.408	- 1.81(24)	6.392	- 1.79(24)
0.06002	9.536	- 1.19(20)	9.502	- 1.00(20)
0.1000	15.765	0.07(18)	15.701	0.34(18)
0.1999	31.168	1.76(17)	31.040	2.04(17)

Table 6 (continued)

$m / \text{mol}\cdot\text{kg}^{-1}$	$\Delta\rho / \text{kg}\cdot\text{m}^{-3}$	$V_\phi / \text{cm}^3\cdot\text{mol}^{-1}$	$\Delta\rho / \text{kg}\cdot\text{m}^{-3}$	$V_\phi / \text{cm}^3\cdot\text{mol}^{-1}$
0.3998	61.455	3.83(16)	61.205	4.10(16)
0.5997	91.223	5.23(15)	90.861	5.48(15)
0.7996	120.491	6.41(15)	120.021	6.64(15)
0.9996	149.324	7.39(14)	148.756	7.60(14)
1.284	189.534	8.63(13)	188.835	8.82(13)
	$T = 333.15 \text{ K}, \rho_w = 983.195 \text{ kg}\cdot\text{m}^{-3}$		$T = 338.15 \text{ K}, \rho_w = 980.550 \text{ kg}\cdot\text{m}^{-3}$	
0.01007	1.625	-4.72(76)	1.619	-4.56(78)
0.02004	3.204	-3.00(40)	3.194	-2.94(42)
0.04018	6.367	-1.57(25)	6.342	-1.37(25)
0.06002	9.466	-0.80(20)	9.432	-0.65(21)
0.1000	15.640	0.56(18)	15.582	0.72(19)
0.1999	30.916	2.27(17)	30.798	2.45(17)
0.3998	60.971	4.30(16)	60.739	4.48(16)
0.5997	90.516	5.67(16)	90.179	5.84(16)
0.7996	119.570	6.82(15)	119.132	6.98(15)
0.9996	148.211	7.78(14)	147.684	7.91(14)
1.284	188.169	8.97(13)	187.521	9.09(13)
	$T = 343.15 \text{ K}, \rho_w = 977.764 \text{ kg}\cdot\text{m}^{-3}$			
0.01007	1.615	-4.53(81)		
0.02004	3.182	-2.80(43)		
0.04018	6.321	-1.30(26)		
0.06002	9.398	-0.53(21)		
0.1000	15.525	0.86(19)		
0.1999	30.683	2.60(17)		
0.3998	60.516	4.62(16)		
0.5997	89.851	5.97(16)		
0.7996	118.706	7.10(15)		
0.9996	147.167	8.03(14)		
1.284	186.887	9.19(13)		

Standard uncertainties are $u_i(m) = 0.001$, $u(T) = 0.02 \text{ K}$, $u_i(p) = 0.01$, $u(\Delta\rho) = 0.0005\Delta\rho$ or $0.005 \text{ kg}\cdot\text{m}^{-3}$, whichever is larger. Numbers in brackets are the uncertainty in last shown digit of V_ϕ .

consistent with the $r_{\text{M-O}}$ values of the other first-row transition metal ions (Fig. 6a), although this is again probably fortuitous.

$V_\phi(\text{VSO}_4, \text{aq})$. While the volumetric database for $\text{FeSO}_4(\text{aq})$ is limited, that for $\text{VSO}_4(\text{aq})$ is non-existent [35]. This is not surprising because $\text{V}^{2+}(\text{aq})$ is highly reactive [8]. It follows that measurements of the volumetric properties of $\text{VSO}_4(\text{aq})$ would require a disproportionate (and possibly fruitless) experimental effort. However, combining the value of $r_{\text{V-O}} = 0.215 \text{ nm}$, from the single crystal XRD data of Montgomery et al. [34] with the correlation of Fig. 6 enables calculation of $V_\phi(\text{VSO}_4, \text{aq})$ over a wide range of m and T . A selection of these values is given in Table S2 in the Supporting Information.

Other M^{2+} sulfates. The present method for predicting $V_\phi(\text{MSO}_4, \text{aq})$ can be easily extended to other bivalent metal sulfates as long as suitable structural data are available

to fix the value of r_{M-O} . Fortunately, the popularity and quality of structural investigations has created an extensive and reliable database of inorganic compounds suited to this purpose (see Persson [36]), including some species that are too reactive to persist in solution but which can be stabilized in the solid state.

It must be noted in passing that the correlation in Fig. 6 does not include bivalent main group sulfates, even though their plots of $V_\phi(m)$ follow the pattern of the transition metals (Fig. 5). Since most of these are only sparingly soluble this is not of major consequence.

3.4 Mixtures of Bivalent Metal Sulfate Solutions

The volumetric properties of binary metal sulfate solutions are, as noted in the Introduction, important physicochemical quantities in their own right. However, in most industrial situations working solutions typically contain (often many) more than one solute. It is therefore of interest to investigate the behavior of mixtures of metal sulfate solutions. Because of the ‘dimensional explosion’ that is inevitable when trying to characterize the properties of complex mixtures, the present density measurements were restricted to one quinary, four quaternary and six ternary mixtures. Each system was investigated at a single composition corresponding to approximately equal concentrations of each constituent metal ion. Apart from limiting the experimental effort, this choice was made because departures from ideal mixing (see below) are typically maximal at, or close to, such composition ratios [10].

The experimental density differences, $\Delta\rho$, and the mean apparent molar volumes $V_{\phi,\text{mix}}$ calculated from them for various mixtures are listed in Table 7. The $V_{\phi,\text{mix}}$ values were obtained by substituting molality m in Eq. 1 by the total molality $m_T = \sum_i m_i$ (where m_i is the molality of the salt i in the solution), and by replacing the molar mass M with the mean molar mass $\bar{M} = \sum_i m_i M_i / m_T$ where M_i is the molar mass of the anhydrous salt i . A useful way of examining such data is to compare them with those calculated using Young’s rule [10]. This rule can be expressed as:

$$V_{\phi,\text{YR}} = \sum_i m_i V_{\phi,i} / m_T \quad (2)$$

which corresponds to ideal (linear) mixing behavior. Note that Young’s rule requires no adjustable parameters and no experimental information beyond $V_{\phi,i}$, the apparent molar volumes of the neat binary solutions for each solute at m_T .

The departures of the present data from Young’s rule, $\Delta V_{\phi,\text{mix}}^* = V_{\phi,\text{mix}} - V_{\phi,\text{YR}}$ are listed in Table 7. The overall situation for the various mixtures is plotted in Fig. 8, with the position of the bars on the x -axis indicating the magnitude of the departure from ideal mixing while the length of the bar corresponds to the effect of temperature on $\Delta V_{\phi,\text{mix}}^*$. In general, $\Delta V_{\phi,\text{mix}}^*$ increases with increasing T (Fig. 9a) but more importantly, with values ranging from ca. -0.1 to $+0.2 \text{ cm}^3 \cdot \text{mol}^{-1}$, all lie within the estimated experimental uncertainties (Table 7, Fig. 9b). It is interesting to note that the systems showing the largest departures (Figs. 8, 9) always involve Cu^{2+} . The small magnitude of $\Delta V_{\phi,\text{mix}}^*$ (Fig. 10) is particularly pleasing for the more complex (i.e., quaternary and quinary) mixtures.

On the basis of the present equimolar measurements (Table 7, Figs. 8, 9 and 10), it is reasonable to conclude that Young’s rule holds for the present systems at all concentration ratios, at least up to $m_T = 1.0 \text{ mol} \cdot \text{kg}^{-1}$ and $T = 343.15 \text{ K}$, and probably well beyond.

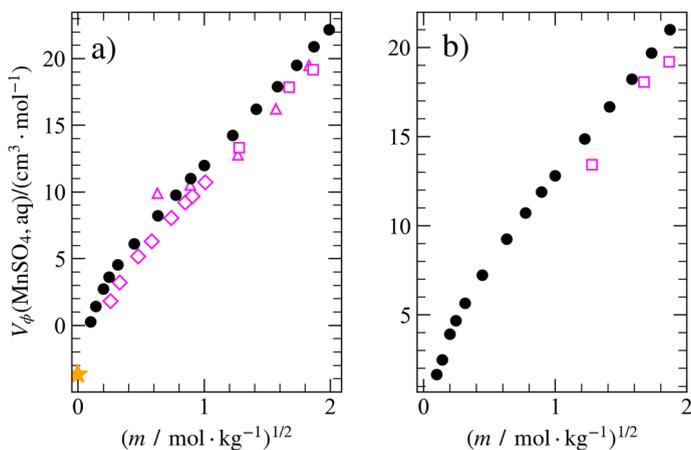
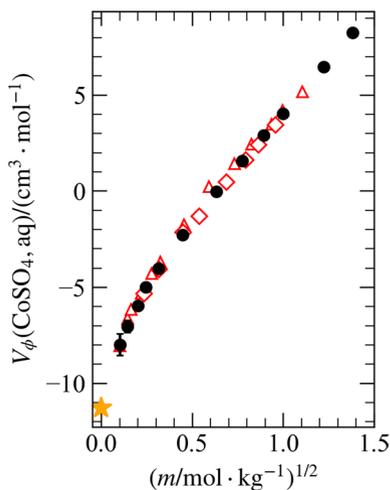


Fig. 1 Comparison at: **a** $T = 298.15 \text{ K}$ and **b** $T = 318.15 \text{ K}$ of present (black dots) and literature (other symbols [11–13]) values of apparent molar volumes $V_\phi(\text{MnSO}_4, \text{aq})$ at $p = 0.1 \text{ MPa}$. Orange star: V° calculated from the ionic volumes tabulated by Marcus [27] (Color figure online)

Fig. 2 Comparison of present (black dots) and literature (other symbols [12, 14]) values of apparent molar volumes V_ϕ for $\text{CoSO}_4(\text{aq})$ at $T = 298.15 \text{ K}$ and $p = 0.1 \text{ MPa}$. Orange star: V° calculated from the ionic volumes tabulated by Marcus [27] (Color figure online)



Similar observations have been made by Chen [37] for ternary $\text{CoSO}_4(\text{aq}) + \text{NiSO}_4(\text{aq})$ mixtures at $T = 298.15 \text{ K}$.

The applicability of Young's rule to these mixtures makes possible the estimation, with some confidence, of the volumetric properties of solutions of even more complex composition, without any experimental data beyond that of the component binary solutions. This approach represents a significant advance over the computational packages currently used for process engineering that either rely on empirical corrections or ignore such effects altogether.

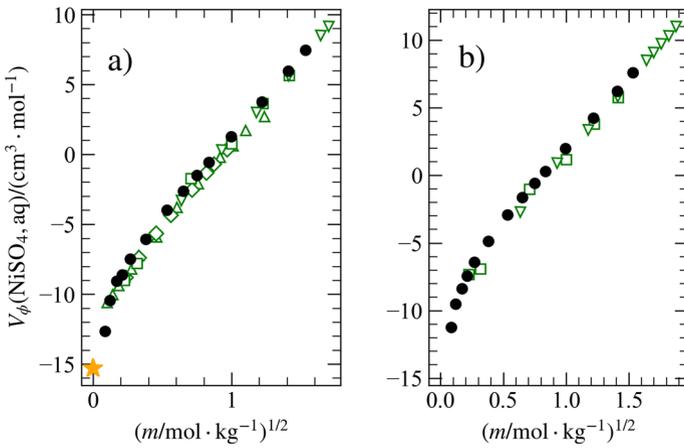


Fig. 3 Comparison at: **a** $T = 298.15 \text{ K}$ and **b** $T = 328.15 \text{ K}$ of present (black dots) and literature (other symbols [12, 14–16]) values of apparent molar volumes $V_{\phi}(\text{NiSO}_4, \text{aq})$ at $p = 0.1 \text{ MPa}$. Orange star: V° calculated from the ionic volumes tabulated by Marcus [27] (Color figure online)

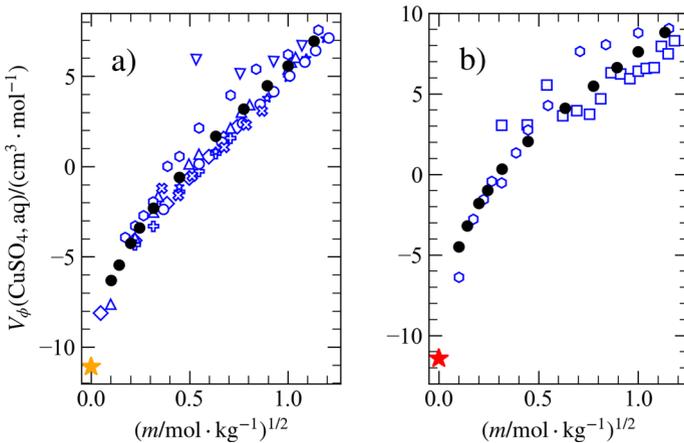


Fig. 4 Comparison at: **a** $T = 298.15 \text{ K}$ and **b** $T = 328.15 \text{ K}$ of present (black dots) and literature (other symbols [11, 12, 14, 17–22]) values of apparent molar volumes $V_{\phi}(\text{CuSO}_4, \text{aq})$ at $p = 0.1 \text{ MPa}$. Orange star: V° calculated from the ionic volumes tabulated by Marcus [27] Red star: using unpublished $V^{\circ}(\text{Cu}^{2+}, \text{aq})$ value [28] (Color figure online)

These findings supplement earlier work, which has shown strong similarities among the osmotic and activity coefficients, heats of dilution and heat capacities of the bivalent first-row transition metal sulfate solutions. It is clear that the *differences* in the interactions of the metal cations with each other and with sulfate anions are almost

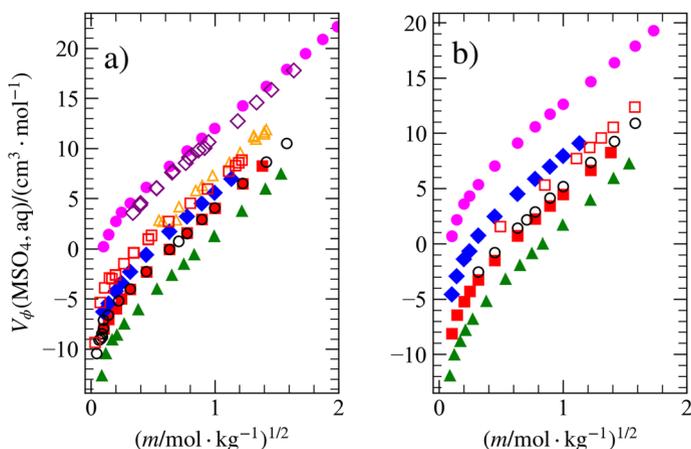


Fig. 5 Comparison at: **a** $T = 298.15$ K and **b** $T = 338.15$ K of apparent molar volumes $V_{\phi}(\text{MSO}_4, \text{aq})$ at $p = 0.1$ MPa. Filled symbols, this work: pink circles, $\text{MnSO}_4(\text{aq})$; red squares, CoSO_4 ; green triangles, $\text{NiSO}_4(\text{aq})$; blue diamonds, $\text{CuSO}_4(\text{aq})$. Unfilled symbols, literature: red squares, $\text{MgSO}_4(\text{aq})$ [29]; orange triangles, $\text{FeSO}_4(\text{aq})$ [30]; black circles, $\text{ZnSO}_4(\text{aq})$ [9]; purple diamonds, $\text{CdSO}_4(\text{aq})$ [12]. (Note: data at $T = 338.15$ K were used in order to include $\text{MgSO}_4(\text{aq})$) (Color figure online)

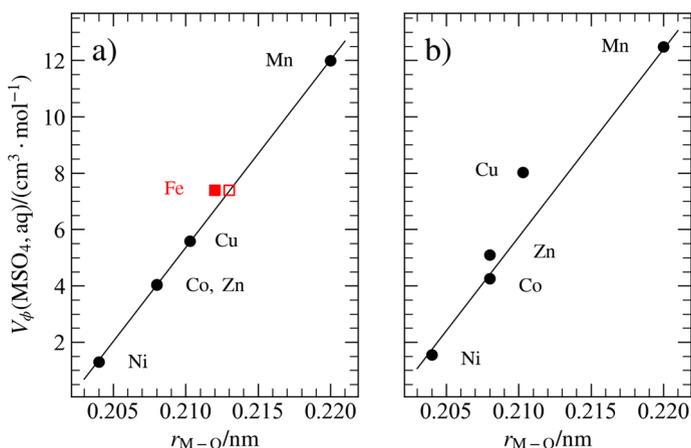
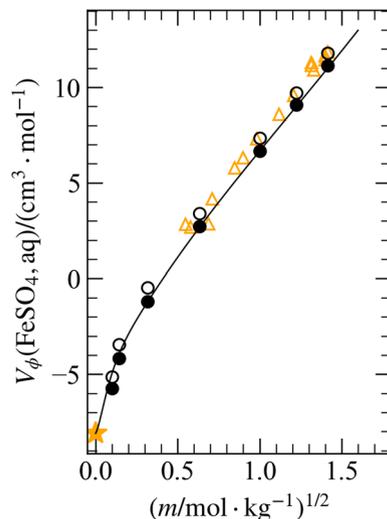


Fig. 6 Apparent molar volumes $V_{\phi}(\text{MSO}_4, \text{aq})$ at: **a** $T = 298.15$ K and **b** $T = 343.15$ K at concentration $m = 1.0$ $\text{mol} \cdot \text{kg}^{-1}$ at 0.1 MPa pressure as a function of $r_{\text{M-O}}$ in the hydrated cations. Values of $V_{\phi}(\text{MSO}_4, \text{aq})$: present results ($M = \text{Mn}, \text{Co}, \text{Ni}$ and Cu); literature values ($M = \text{Zn}$ [9] and Fe [30]). The unfilled square for Fe shows the effect of increasing $r_{\text{Fe-O}}$ from 0.212 nm to 0.213 nm (see text). The lines are best fits to the data (excluding Cu). Values of $r_{\text{M-O}}$ are taken to be independent of T

negligible. It is reasonable to assume that at least some of the other thermodynamic properties of these mixtures will also exhibit ideal mixing behavior. This is indeed the case for the heat capacity results reported by Chen [37] for $\text{CoSO}_4(\text{aq}) + \text{NiSO}_4$

Fig. 7 Comparison of literature values (triangles) [30] and present predictions (filled and unfilled circles) of $V_\phi(\text{FeSO}_4, \text{aq})$ at $T=298.15$ K and at 0.1 MPa pressure. The unfilled circles indicate the effect of an increase of 1 pm in $r_{\text{Fe-O}}$ (see text). Orange star: V° calculated from the ionic values tabulated by Marcus [27] The line is a visual guide only (Color figure online)



(aq) mixtures. Unfortunately, no other data appear to be available to further test this hypothesis.

4 Conclusions

The present density measurements greatly expand the database of the volumetric properties of aqueous solutions of bivalent metal sulfates. Comparison of the volumetric behavior of the various $\text{MSO}_4(\text{aq})$ solutions, as measured here and as reported in the literature, shows undeniable similarities. Moreover, a simple linear relationship is observed between the metal–oxygen bond length in the hydrated cations and the apparent molar volumes of the first-row transition metal sulfates in aqueous solution. The volumetric behavior of the experimentally difficult $\text{FeSO}_4(\text{aq})$ has been predicted by exploiting this relationship, with good agreement with literature data being obtained. Furthermore, it is shown that this approach can be used to calculate the volumetric properties of unmeasured bivalent metal sulfate solutions over wide ranges of temperature and concentration, providing the relevant structural information is available. Measurements of mixtures of various $\text{MSO}_4(\text{aq})$ show that their apparent molar volumes mostly follow linear (Young's rule) mixing behavior. This observation can be used to predict the volumetric behavior of complex mixtures of these electrolytes.

Table 7 Experimental density differences $\Delta\rho$ and apparent molar volumes $V_{\phi,\text{mix}}$ for aqueous mixtures of MnSO_4 , CoSO_4 , NiSO_4 and CuSO_4 at Molalities m_i , Temperatures T and Pressure = 0.1 MPa

T/K	$\Delta\rho/\text{kg}\cdot\text{m}^{-3}$	$V_{\phi,\text{mix}}/\text{cm}^3\cdot\text{mol}^{-1}$	$\Delta V_{\phi,\text{mix}}^*/\text{cm}^3\cdot\text{mol}^{-1}$	$\Delta\rho/\text{kg}\cdot\text{m}^{-3}$	$V_{\phi,\text{mix}}/\text{cm}^3\cdot\text{mol}^{-1}$	$\Delta V_{\phi,\text{mix}}^*/\text{cm}^3\cdot\text{mol}^{-1}$
	$m_{\text{Mn}^{2+}} = 0.516 \text{ mol}\cdot\text{kg}^{-1}$, $m_{\text{Co}^{2+}} = 0.484 \text{ mol}\cdot\text{kg}^{-1}$			$m_{\text{Mn}^{2+}} = 0.507 \text{ mol}\cdot\text{kg}^{-1}$, $m_{\text{Ni}^{2+}} = 0.488 \text{ mol}\cdot\text{kg}^{-1}$		
293.15	143.828	7.70	-0.04	144.714	6.29	-0.05
298.15	143.204	8.12	-0.04	144.081	6.71	-0.04
303.15	142.665	8.43	-0.04	143.535	7.02	-0.04
308.15	142.195	8.66	-0.03	143.061	7.25	-0.04
313.15	141.787	8.81	-0.03	142.648	7.40	-0.04
318.15	141.432	8.88	-0.05	142.290	7.48	-0.05
323.15	141.124	8.90	-0.04	141.976	7.50	-0.05
328.15	140.849	8.87	-0.04	141.700	7.46	-0.05
333.15	140.609	8.78	-0.04	141.457	7.37	-0.04
338.15	140.398	8.65	-0.04	141.246	7.24	-0.04
343.15	140.213	8.48	-0.04	141.058	7.06	-0.04
	$m_{\text{Mn}^{2+}} = 0.492 \text{ mol}\cdot\text{kg}^{-1}$, $m_{\text{Cu}^{2+}} = 0.507 \text{ mol}\cdot\text{kg}^{-1}$			$m_{\text{Co}^{2+}} = 0.506 \text{ mol}\cdot\text{kg}^{-1}$, $m_{\text{Ni}^{2+}} = 0.489 \text{ mol}\cdot\text{kg}^{-1}$		
293.15	145.412	8.40	0.19	151.329	2.30	0.04
298.15	144.687	8.90	0.20	150.677	2.72	0.06
303.15	144.039	9.31	0.19	150.116	3.04	0.06
308.15	143.454	9.64	0.20	149.631	3.25	0.06
313.15	142.919	9.90	0.21	149.207	3.39	0.06
318.15	142.434	10.10	0.18	148.830	3.47	0.06
323.15	141.983	10.24	0.18	148.506	3.47	0.07
328.15	141.561	10.34	0.20	148.221	3.42	0.06
333.15	141.163	10.41	0.20	147.974	3.31	0.06
338.15	140.786	10.43	0.20	147.756	3.16	0.06
343.15	140.427	10.42	0.21	147.566	2.96	0.05
	$m_{\text{Co}^{2+}} = 0.497 \text{ mol}\cdot\text{kg}^{-1}$, $m_{\text{Cu}^{2+}} = 0.503 \text{ mol}\cdot\text{kg}^{-1}$			$m_{\text{Ni}^{2+}} = 0.491 \text{ mol}\cdot\text{kg}^{-1}$, $m_{\text{Cu}^{2+}} = 0.504 \text{ mol}\cdot\text{kg}^{-1}$		
293.15	152.075	4.30	0.04	152.868	2.94	0.04
298.15	151.330	4.80	0.06	152.124	3.44	0.05
303.15	150.664	5.21	0.06	151.450	3.85	0.04
308.15	150.065	5.53	0.07	150.842	4.18	0.06
313.15	149.518	5.79	0.07	150.287	4.43	0.06
318.15	149.021	5.97	0.06	149.780	4.62	0.06
323.15	148.560	6.10	0.06	149.313	4.76	0.05
328.15	148.129	6.19	0.06	148.877	4.84	0.06
333.15	147.726	6.23	0.05	148.470	4.88	0.06
338.15	147.344	6.23	0.05	148.082	4.89	0.06
343.15	146.980	6.20	0.06	147.715	4.85	0.07
	$m_{\text{Mn}^{2+}} = 0.344 \text{ mol}\cdot\text{kg}^{-1}$, $m_{\text{Co}^{2+}} = 0.325 \text{ mol}\cdot\text{kg}^{-1}$, $m_{\text{Ni}^{2+}} = 0.328 \text{ mol}\cdot\text{kg}^{-1}$			$m_{\text{Mn}^{2+}} = 0.357 \text{ mol}\cdot\text{kg}^{-1}$, $m_{\text{Co}^{2+}} = 0.328 \text{ mol}\cdot\text{kg}^{-1}$, $m_{\text{Cu}^{2+}} = 0.318 \text{ mol}\cdot\text{kg}^{-1}$		
293.15	146.635	5.40	-0.06	146.902	6.82	-0.06

Table 7 (continued)

T/K	$\Delta\rho/\text{kg}\cdot\text{m}^{-3}$	$V_{\phi,\text{mix}}/\text{cm}^3\cdot\text{mol}^{-1}$	$\Delta V_{\phi,\text{mix}}^*/\text{cm}^3\cdot\text{mol}^{-1}$	$\Delta\rho/\text{kg}\cdot\text{m}^{-3}$	$V_{\phi,\text{mix}}/\text{cm}^3\cdot\text{mol}^{-1}$	$\Delta V_{\phi,\text{mix}}^*/\text{cm}^3\cdot\text{mol}^{-1}$
298.15	145.998	5.82	− 0.06	146.209	7.29	− 0.05
303.15	145.448	6.14	− 0.05	145.592	7.67	− 0.05
308.15	144.972	6.36	− 0.05	145.044	7.96	− 0.04
313.15	144.557	6.51	− 0.05	144.549	8.18	− 0.03
318.15	144.196	6.58	− 0.06	144.098	8.34	− 0.04
323.15	143.879	6.60	− 0.06	143.694	8.44	− 0.04
328.15	143.603	6.55	− 0.06	143.322	8.48	− 0.03
333.15	143.363	6.46	− 0.06	142.984	8.48	− 0.04
338.15	143.148	6.32	− 0.06	142.664	8.45	− 0.03
343.15	142.961	6.13	− 0.06	142.365	8.37	− 0.02
$m_{\text{Mn}^{2+}} = 0.333 \text{ mol}\cdot\text{kg}^{-1}$, $m_{\text{Ni}^{2+}} = 0.340 \text{ mol}\cdot\text{kg}^{-1}$, $m_{\text{Cu}^{2+}} = 0.323 \text{ mol}\cdot\text{kg}^{-1}$				$m_{\text{Co}^{2+}} = 0.353 \text{ mol}\cdot\text{kg}^{-1}$, $m_{\text{Ni}^{2+}} = 0.320 \text{ mol}\cdot\text{kg}^{-1}$, $m_{\text{Cu}^{2+}} = 0.324 \text{ mol}\cdot\text{kg}^{-1}$		
293.15	147.670	5.79	0.03	151.978	3.24	0.10
298.15	146.972	6.26	0.03	151.263	3.72	0.12
303.15	146.352	6.64	0.03	150.631	4.10	0.12
308.15	145.799	6.93	0.04	150.072	4.38	0.13
313.15	145.300	7.15	0.04	149.568	4.59	0.13
318.15	144.846	7.31	0.03	149.107	4.75	0.13
323.15	144.437	7.41	0.03	148.691	4.84	0.12
328.15	144.060	7.46	0.05	148.312	4.87	0.13
333.15	143.717	7.45	0.04	147.961	4.86	0.12
338.15	143.393	7.42	0.05	147.635	4.81	0.12
343.15	143.092	7.34	0.06	147.328	4.72	0.13
$m_{\text{Mn}^{2+}} = 0.228 \text{ mol}\cdot\text{kg}^{-1}$, $m_{\text{Co}^{2+}} = 0.255 \text{ mol}\cdot\text{kg}^{-1}$, $m_{\text{Ni}^{2+}} = 0.268 \text{ mol}\cdot\text{kg}^{-1}$, $m_{\text{Cu}^{2+}} = 0.246 \text{ mol}\cdot\text{kg}^{-1}$						
293.15	148.743	5.02	0.00			
298.15	148.057	5.48	0.01			
303.15	147.449	5.84	0.01			
308.15	146.914	6.11	0.02			
313.15	146.435	6.31	0.02			
318.15	146.000	6.45	0.01			
323.15	145.614	6.52	0.01			
328.15	145.260	6.55	0.02			
333.15	144.937	6.52	0.01			
338.15	144.640	6.46	0.02			
343.15	144.363	6.35	0.02			

^aStandard uncertainties are $u_r(m) = 0.002$, $u(T) = 0.02 \text{ K}$, $u_r(p) = 0.01$, $u_r(\Delta\rho) = 0.0005$, $u(V_{\phi,\text{mix}}) \approx 0.16 \text{ cm}^3\cdot\text{mol}^{-1}$

Fig. 8 Departures of $V_{\phi,\text{mix}}$ from Young's rule (Eq. 2) for equimolar mixtures of bivalent metal sulfate solutions at $m_T = 1.0 \text{ mol} \cdot \text{kg}^{-1}$ over the temperature range $293.15 \leq T/\text{K} \leq 343.15 \text{ K}$ and at 0.1 MPa pressure. The width of the horizontal bar represents the spread of $(V_{\phi,\text{mix}} - V_{\phi,\text{YR}})$ with T for each mixture

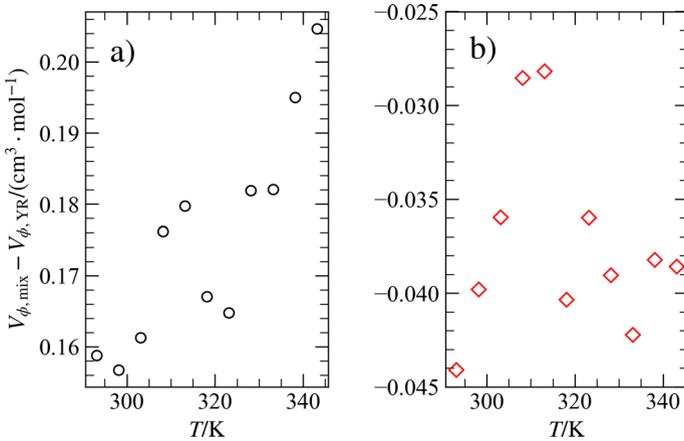
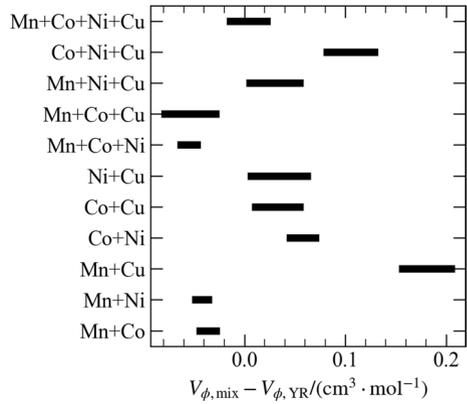
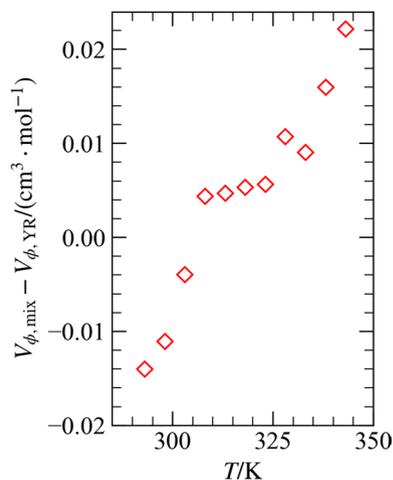


Fig. 9 Departures of $V_{\phi,\text{mix}}$ from Young's rule (Eq. 2) for: **a** $\text{CoSO}_4(\text{aq})+\text{CuSO}_4(\text{aq})$ and **b** $\text{CoSO}_4(\text{aq})+\text{MnSO}_4(\text{aq})$ equimolar mixtures at $m_T = 1.0 \text{ mol} \cdot \text{kg}^{-1}$ at temperatures $293.15 \leq T/\text{K} \leq 343.15$ and 0.1 MPa pressure

Fig. 10 Departures of $V_{\phi,\text{mix}}$ from Young's rule (Eq. 2) for an equimolar quinary mixture of $\text{MnSO}_4(\text{aq}) + \text{CoSO}_4(\text{aq}) + \text{NiSO}_4(\text{aq}) + \text{CuSO}_4(\text{aq})$ at $m_T = 1.0 \text{ mol} \cdot \text{kg}^{-1}$ at temperatures $293.15 \leq T/\text{K} \leq 343.15$ and 0.1 MPa pressure



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Declarations

Competing interests The authors declare no competing interests.

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