

Volumes and Heat Capacities of Cobalt(II), Nickel(II) and Copper(II) Sulfate in Aqueous Solution

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ABSTRACT: Densities and isobaric volumetric heat capacities of aqueous solutions of the sulfate salts of cobalt(II), nickel(II) and copper(II) have been measured at 298.15 K and 0.1 MPa using vibrating tube densimetry and Picker flow calorimetry, respectively, at concentrations in the range $0.01 \lesssim m/\text{mol}\cdot\text{kg}^{-1} \lesssim 1.5$. These data were used to derive the corresponding apparent molar volumes, V_ϕ , and apparent molar isobaric heat capacities, $C_{p\phi}$. Where comparisons were possible the present V_ϕ results were in good agreement with literature data. No $C_{p\phi}$ data appear to have been reported previously for any of these salts. The variations of V_ϕ and $C_{p\phi}$ with concentration were well correlated using the Pitzer formalism combined with values of V° and C_p° estimated from literature data. Both V_ϕ and $C_{p\phi}$ for all three salts show remarkable similarities and can be shown to lie on a common line by applying fixed addends over almost the whole concentration range studied.

1. INTRODUCTION

Sulfate-based hydrometallurgy is widely employed for the extraction and purification of many economically-critical metals.¹ For example, about 70 % of the world's nickel resources occur in heavily oxidized nickel laterite ores, which are invariably digested with aqueous solutions of sulfuric acid.² As laterite ores typically contain significant amounts of the more-valuable cobalt, the solution properties of both these metal sulfates are of special interest. Likewise, copper(II) sulfate solutions form key stages in the extraction, purification and subsequent use (eg, in electroplating) of copper.³ Solutions containing all three of these (and other) salts are also important in the treatment of acid mine drainage from old and existing mine sites.⁴

In addition to their vast range of applications, divalent metal sulfate solutions have attracted considerable scientific interest as archetypal higher-charged symmetrical electrolytes.^{5,6} Such solutions have been widely used to test the application of theories of activity coefficients, electrical conductance and the self-association of electrolyte solutions.

Numerous publications have described various aspects of the physicochemical properties of solutions of cobalt, nickel and copper sulfate solutions.⁷ However, there have been few modern studies of their volumetric properties and virtually no data (old or recent) are available for their heat capacities. This is unfortunate because both volumetric and heat capacity data are essential for the reliable modelling of mass and heat transfer processes required for chemical engineering purposes⁸ and for environmental activities.⁴

This paper reports volumes and heat capacities obtained, respectively, by vibrating-tube densimetry and flow calorimetry, of aqueous solutions of the industrially-important cobalt(II), nickel(II) and copper(II) sulfates up to high concentrations at 298.15 K.

2. EXPERIMENTAL SECTION

2.1 Materials. The sources and purities of the three metal sulfates are summarized in Table 1. Briefly, $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ were recrystallized twice from aqueous solution; commercial $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ was used as received. Stock solutions prepared from these solids were adjusted to $\text{pH} = 4.0 \pm 0.5$, by the addition of trivial amounts of sulfuric acid, to restrict both cation hydrolysis¹¹ and protonation of the anion.¹² These solutions were then filtered (Millipore, USA, $0.45 \mu\text{m}$) and assayed ($\pm 0.2 \%$) by complexometric titration against EDTA (BDH, UK, Concentrated Volumetric Standard).¹³ More dilute solutions were prepared by weight, without buoyancy corrections. The concentrations studied cover up to approximately (50, 60 and 80) % of the saturation concentrations at 298 K for the (Co, Ni and Cu) sulfates respectively. Solutions of sodium chloride (used for calibration purposes) were prepared individually by weight from NaCl(s) that had been dried overnight at 450 K under vacuum. All solutions were prepared using freshly degassed high purity water (Millipore Milli-Q system).

Table 1. Sample Sources and Purities

chemical name	CASRN	source	initial mass		final mass		analysis method
			fraction purity	purification method	fraction purity		
cobalt sulfate heptahydrate	10026-24-1	Sigma	≥ 0.99	recrystallisation from water	0.998		complexometric titration
nickel sulfate hexahydrate	10101-97-0			recrystallisation from water			
copper sulfate pentahydrate	7758-99-8	Aldrich	$\geq 0.9999^a$	none	0.998		complexometric titration
sodium chloride	7440-23-5	Biolab	≥ 0.98	none	-	-	-
EDTA, disodium salt	6381-92-6	APS	≥ 0.999	none	-	-	-
		BDH	$\geq 0.998^b$	none	-	-	-

^aOn a metals basis only. ^bCommercial Concentrated Volumetric Standard solution.

2.2 Instrumentation. Solution densities, ρ , were measured with a vibrating glass-tube densimeter (Anton Paar, Austria, Model DMA02D) fitted with an Anton Paar mPDS4000 data module. The temperature of the vibrating tube was controlled to 298.15 ± 0.01 K, with a NIST-traceable accuracy of 0.02 K, using a circulating thermostat (Haake, Germany, Model K20). The densimeter was calibrated with high purity water and dry air assuming literature densities^{9,10} of $0.997047 \text{ g}\cdot\text{cm}^{-3}$ and $1.1850 \text{ mg}\cdot\text{cm}^{-3}$ at 298.15 K and a pressure of 101 ± 1 kPa. Densities for $\text{CoSO}_4(\text{aq})$ and $\text{NiSO}_4(\text{aq})$ were reproducible to $\pm 10 \text{ }\mu\text{g}\cdot\text{cm}^{-3}$, and for $\text{CuSO}_4(\text{aq})$ to $\pm 15 \text{ }\mu\text{g}\cdot\text{cm}^{-3}$.

Isobaric volumetric heat capacities, σ_p , were measured with a Picker flow calorimeter (Sodev, Canada, Model CP-C) using a base power of 20 mW and a sensitivity of 3 mW, corresponding to an average measurement temperature of 298.15 ± 0.065 K. Temperatures outside the immediate measurement zone were controlled to ± 0.005 K using a Sodev circulator-thermostat Model CT-L. Liquids were introduced into the calorimeter via a four-way chromatography valve (Hamilton, USA, Model HVP). The flow rate was maintained at $\sim 0.6 \text{ cm}^3\cdot\text{min}^{-1}$ using a peristaltic pump (Gilson, USA, Minipuls 3). All measurements reported are ‘first leg’ values,¹⁵ corresponding to the displacement of water in the calorimeter by solution. Further details of the operation of the calorimeter are given elsewhere.^{14,15}

2.3 Calculations. Density differences, $\Delta\rho$, were obtained from the operational densimeter equation:

$$\Delta\rho = \rho - \rho_0 = k(\tau^2 - \tau_0^2) \quad (1)$$

where k is a calibration constant, τ is the oscillation period of the vibrating tube and the subscript $_0$ denotes a pure water quantity. Apparent molar volumes, V_ϕ , were calculated via the usual equation:

$$V_\phi = (M_s/\rho) - \{(\rho - \rho_0)/m\rho\rho_0\} \quad (2)$$

where M_s is the molar mass of the anhydrous solute (155.00, 154.75 and 159.61 $\text{g}\cdot\text{mol}^{-1}$ for CoSO_4 , NiSO_4 and CuSO_4 respectively) and m is its concentration (molality) in $\text{mol}\cdot\text{kg}^{-1}$.

Isobaric massic heat capacities, c_p , were calculated as $c_p = \sigma_p/\rho$ from the measured isobaric volumetric heat capacities and the present experimental densities. Isobaric apparent molar heat capacities, $C_{p\phi}$, were then obtained as:

$$C_{p\phi} = c_p M_s + \{(c_p - c_{p0})/m\} \quad (3)$$

where the isobaric massic heat capacity of pure water at 298.15 K and 101 kPa, $c_{p0} = 4.1813 \text{ J}\cdot\text{K}^{-1}\cdot\text{g}^{-1}$, was calculated from the IAPWS-95 equation of state.⁹

The operating protocols of both the densimeter and the calorimeter were verified by measurements on ca. eight NaCl(aq) solutions over the range $0.5 \lesssim m/\text{mol}\cdot\text{kg}^{-1} \lesssim 5$. The values of V_ϕ and $C_{p\phi}$ obtained agreed with those calculated using Archer's equation¹⁶ within the experimental uncertainties.

3. RESULTS AND DISCUSSION

The measured density differences, $\Delta\rho$, and relative isobaric volumetric heat capacity changes, $\Delta\sigma/\sigma$, for the aqueous solutions of the three metal sulfate salts are listed in Table 2. All reported values are the average of at least two independent measurements. Also shown in Table 2 are the corresponding apparent molar quantities, V_ϕ and $C_{p\phi}$, calculated via eqs 2 and 3 respectively, and their combined standard uncertainties u_c , which were estimated using the GUM convention.¹⁷ The values of V_ϕ and $C_{p\phi}$ so obtained varied smoothly over the investigated concentration ranges (Figures 1-4), with no evidence of the slight 'waviness' often observed in such plots for aqueous electrolyte solutions.¹⁸ For the convenience of potential users, equations that relate ρ and c_p to molality for each of the three sets of solutions are given in the Supplementary Information.

Table 2. Experimental Density ($\Delta\rho$) and Relative Isobaric Volumetric Heat Capacity ($\Delta\sigma/\sigma$) Differences Along with Apparent Molar Volumes (V_ϕ) and Isobaric Massic (c_p) and Apparent Molar ($C_{p\phi}$) Heat Capacities for CoSO₄(aq), NiSO₄(aq) and CuSO₄(aq) at 298.15 K and 0.101 MPa^a

m / mol·kg ⁻¹	$10^3\Delta\rho$ /g·cm ⁻³	V_ϕ^b /cm ³ ·mol ⁻¹	$10^3\Delta\sigma/\sigma$	c_p /J·K ⁻¹ ·g ⁻¹	$C_{p\phi}^b$ /J·K ⁻¹ ·mol ⁻¹
CoSO₄					
0.00988	1.606 (4)	-8.05 ± 0.59	-0.522(23)	4.1724 (1)	-254.5 ± 11.6
0.02064	3.326(3)	-6.62 ± 0.38	-1.034(4)	4.1631 (1)	-236.9 ± 3.5
0.02673	4.295(4)	-6.15 ± 0.37	-1.291 (4)	4.1580(1)	-227.6 ± 2.9
0.04798	7.670(4)	-5.31 ± 0.33	-2.169(2)	4.1404 (1)	-211.1 ± 2.1
0.07637	12.130(6)	-4.27 ± 0.33	-3.310(13)	4.1174(1)	-198.9 ± 2.0
0.1057	16.721(8)	-3.69 ± 0.32	-4.444(5)	4.0941(1)	-191.2 ± 1.8
0.2058	32.179(8)	-1.75 ± 0.31	-7.888(2)	4.0186(1)	-167.4 ± 1.6
0.3495	54.096(6)	0.23 ± 0.30	-12.06 (2)	3.9183(1)	-145.3 ± 1.5
0.5343	81.756(7)	1.42 ± 0.28	-16.67(2)	3.8000(1)	-124.6 ± 1.4
0.6826	103.662(8)	2.44 ± 0.28	-19.52 (3)	3.7136 (1)	-109.6 ± 1.4
0.8781	132.253(7)	3.49 ± 0.27	-21.94(4)	3.6106(2)	-90.3 ± 1.3
0.9937	148.792(8)	4.20 ± 0.26	-24.34(5)	3.5498(2)	-85.3 ± 1.3

1.2241	181.716(8)	5.18 ± 0.25	-26.83(2)	3.4418(1)	-70.6 ± 1.2
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NiSO₄

0.01021	1.683(4)	-10.59 ± 0.58	—	—	—
0.01957	3.215(6)	-10.02 ± 0.47	-1.066 (13)	4.1634(1)	-269.5 ± 4.6
0.03408	5.578(2)	-9.38 ± 0.34	-1.645(8)	4.1512 (1)	-240.9 ± 2.6
0.05156	8.407(3)	-8.74 ± 0.33	-2.352 (2)	4.1366(1)	-227.1 ± 2.1
0.07709	12.529(6)	-8.18 ± 0.33	-3.404 (20)	4.1154(1)	-218.6 ± 2.2
0.1079	17.438(2)	-7.22 ± 0.32	-4.551(3)	4.0907(1)	-206.3 ± 1.8
0.2103	33.712(7)	-5.89 ± 0.31	-8.144(16)	4.0116(1)	-186.3 ± 1.7
0.3649	57.758(7)	-3.80 ± 0.30	-12.60(1)	3.9025(1)	-160.0 ± 1.5
0.5735	89.784(5)	-2.09 ± 0.29	-17.90(1)	3.7672(1)	-139.0 ± 1.4
0.8417	130.079(6)	-0.22 ± 0.28	-22.66 (2)	3.6149(1)	-113.5 ± 1.4
1.014	155.730(7)	0.62 ± 0.27	-25.36 (2)	3.5247(1)	-102.1 ± 1.3
1.211	184.320(6)	1.73 ± 0.26	-27.80 (2)	3.4308(1)	-89.0 ± 1.2
1.525	230.274(9)	2.70 ± 0.25	-30.95 (6)	3.2917(2)	-74.0 ± 1.2

CuSO₄

0.00993	1.656(1)	-7.61 ± 0.45	-0.370(1)	4.1728(1)	-187.3 ± 6.1
0.04968	8.102(2)	-3.94 ± 0.33	-1.624(16)	4.1409(1)	-153.1 ± 2.4
0.1000	16.167(2)	-2.51 ± 0.32	-2.916(7)	4.1026(1)	-132.3 ± 1.7
0.1161	18.670(9)	-1.65 ± 0.33	-3.345(11)	4.0907(1)	-127.3 ± 1.7
0.2478	39.399(3)	0.14 ± 0.31	-5.859(14)	3.9988(1)	-98.3 ± 1.5
0.2996	47.460(18)	0.7 ± 0.31	-6.725(5)	3.9645(1)	-91.0 ± 1.5
0.4999	78.404(16)	2.14 ± 0.29	-9.103(18)	3.8412(1)	-67.3 ± 1.4
0.5818	90.684(31)	3.01 ± 0.29	-9.848(8)	3.7950(1)	-58.3 ± 1.3
0.6501	101.012(14)	3.43 ± 0.28	-10.22(2)	3.7578(1)	-51.6 ± 1.3
1.000	152.948(34)	5.40 ± 0.27	-11.30(1)	3.5842(1)	-25.0 ± 1.2
1.035	157.799(24)	5.80 ± 0.27	-11.24(2)	3.5694(1)	-21.5 ± 1.2
1.078	163.996(12)	6.05 ± 0.26	-11.50(1)	3.5494(1)	-19.7 ± 1.2

^a Standard uncertainties u are $u_r(m) = 0.002 \text{ mol}\cdot\text{kg}^{-1}$, $u(T) = 0.01 \text{ K}$, $u(p) = 0.001 \text{ MPa}$. Numbers in parentheses are the standard uncertainties u in the quantities calculated as the standard deviations of replicate measurements. ^b Average \pm combined standard uncertainty u_c .

3.1 Apparent Molar Volumes. The present values of V_ϕ for $\text{CoSO}_4(\text{aq})$, $\text{NiSO}_4(\text{aq})$ and $\text{CuSO}_4(\text{aq})$ are plotted against concentration (as \sqrt{m}) in Figures 1, 2 and 3 respectively, along with the available literature data. For $\text{CoSO}_4(\text{aq})$ the present results (Figure 1) are in excellent agreement with those of Lo Surdo and Millero,¹⁹ also obtained by vibrating tube densimetry (vtd), with an average difference of better than $\pm 0.2 \text{ cm}^3\cdot\text{mol}^{-1}$. The older data of Cantelo and Phifer,²⁰ measured using the less precise pycnometric method, are clearly in error. For $\text{NiSO}_4(\text{aq})$ the present results (Figure 2) are in good agreement with the values reported both by Lo Surdo and Millero¹⁹ and by Isono (also using vtd)²¹ with average differences of ± 0.1 and $\pm 0.5 \text{ cm}^3\cdot\text{mol}^{-1}$, respectively, over the studied concentration range. The situation for $\text{CuSO}_4(\text{aq})$ is slightly more complicated (Figure 3). There are three data sets: that of Pearce and Pumplin²² obtained by pycnometry and the more recent values of Lo Surdo and Millero,¹⁹ using a magnetic float, and of Puchalska et al.²³ using vtd. While the present data are in good agreement

with the older values and those of Lo Surdo and Millero,¹⁹ differing on average by $\pm 0.4 \text{ cm}^3 \cdot \text{mol}^{-1}$, the results reported by Puchalska et al.²³ differ by $\sim 2 \text{ cm}^3 \cdot \text{mol}^{-1}$ over most of the common concentration range. Similar deviations of V_ϕ values reported by Puchalska et al. from those of other investigators have also been observed for $\text{ZnSO}_4(\text{aq})$.²⁴ It is interesting to note that $V_\phi(m^{1/2})$ for all three of the present systems become almost linear, and with the same slopes, when $m^{1/2} \gtrsim 0.2 \text{ (mol} \cdot \text{kg}^{-1})^{1/2}$ (see also Section 3.4. below).

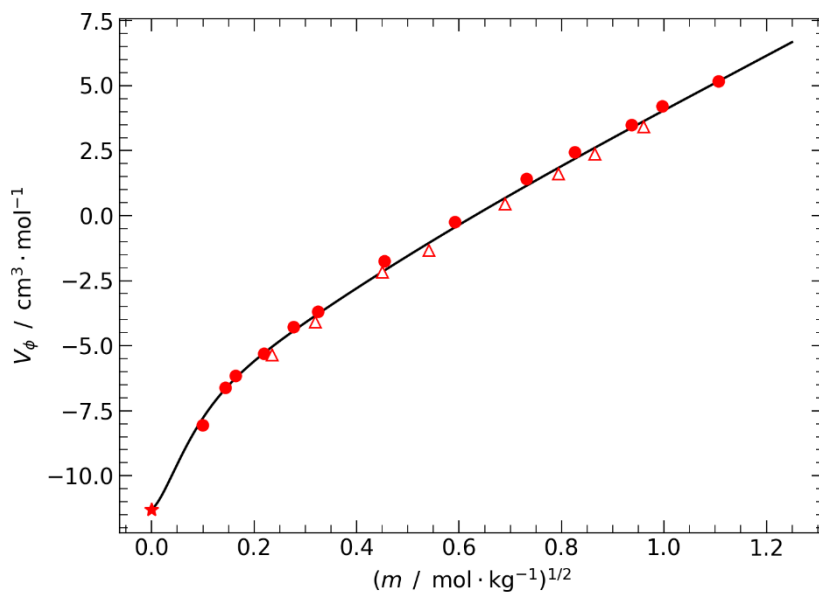


Figure 1. Present and literature values for the apparent molar volume, V_ϕ , of $\text{CoSO}_4(\text{aq})$ as a function of solute concentration (as \sqrt{m}) at 298.15 K and 0.1 MPa: ●, this work; Δ, Lo Surdo and Millero;¹⁹ ★, V° calculated using Marcus's ionic values.²⁵ The solid line was calculated from the present Pitzer model (Section 3.4.) using both data sets.

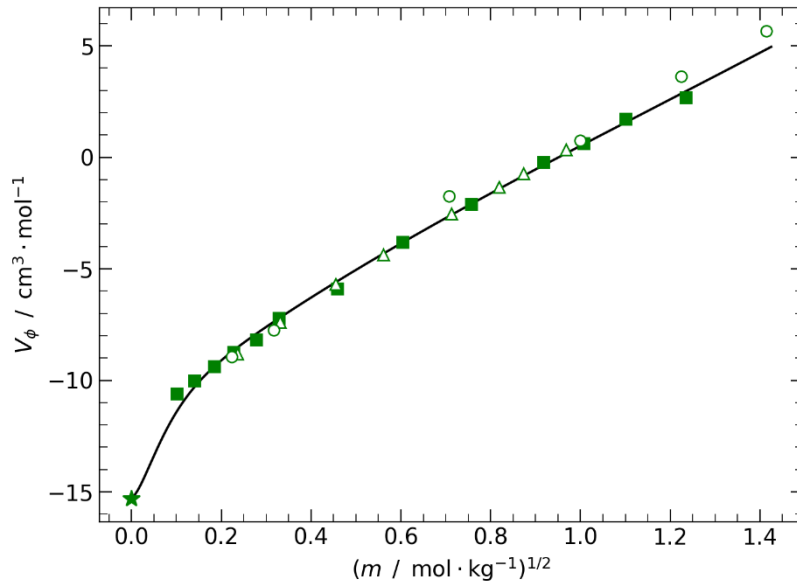


Figure 2. Present and literature values for the apparent molar volume, V_ϕ , of $\text{NiSO}_4(\text{aq})$ as a function of solute concentration (as \sqrt{m}) at 298.15 K and 0.1 MPa: ■, this work; ○, Isono;²⁰ Δ, Lo Surdo and Millero;¹⁹ ★, V° calculated from Chen's value for $\text{Ni}^{2+}(\text{aq})$ ¹⁴ and Marcus's value for $\text{SO}_4^{2-}(\text{aq})$.²⁵ The solid line was calculated from the present Pitzer model (Section 3.4.) using both data sets.

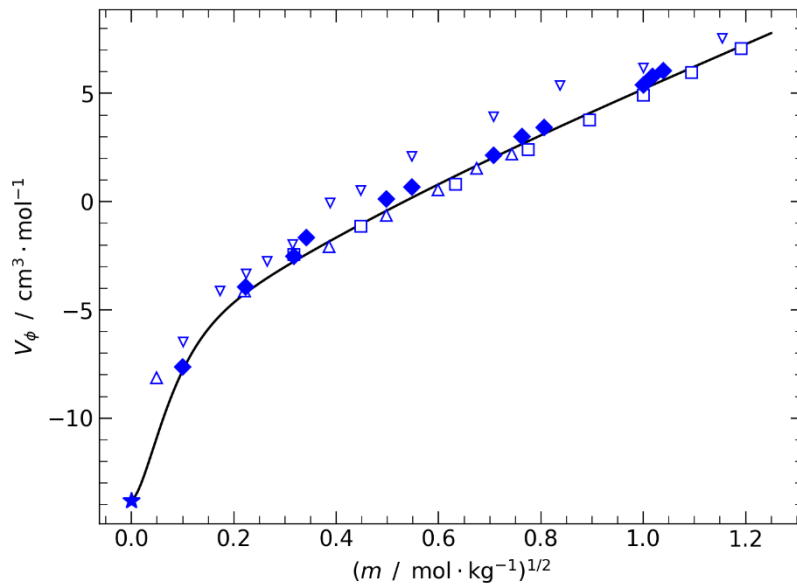


Figure 3. Present and literature values for the apparent molar volume, V_ϕ , of $\text{CuSO}_4(\text{aq})$ as a function of solute concentration (as \sqrt{m}) at 298.15 K and 0.1 MPa: ◆, this work; Δ, Lo Surdo and Millero;¹⁹ □, Pearce and Pumplin;²² ▽, Puchalska et al.;²³ ★, V° calculated from the Spitzer

et al. value for $\text{Cu}^{2+}(\text{aq})$ ²⁶ and Marcus's value for $\text{SO}_4^{2-}(\text{aq})$.²⁵ The solid line was calculated from the present Pitzer model (Section 3.4.) using all data except those of Puchalska et al.²³

3.2 Apparent Molar Heat Capacities. The apparent molar isobaric heat capacities, $C_{p\phi}$, for the present salts (Table 2) are plotted together in Figure 4 as a function of the solute concentration (as \sqrt{m}). As noted in the Introduction there are, to the best of our knowledge, no reliable literature data with which to compare our values. A partial exception is the batch calorimetry study of $\text{CuSO}_4(\text{aq})$ by Kapustinskii et al.²⁷ However, these values have been rejected as being seriously in error in a critical review of thermodynamic data for $\text{CuSO}_4(\text{aq})$ by Höffler and Steiger.²⁸

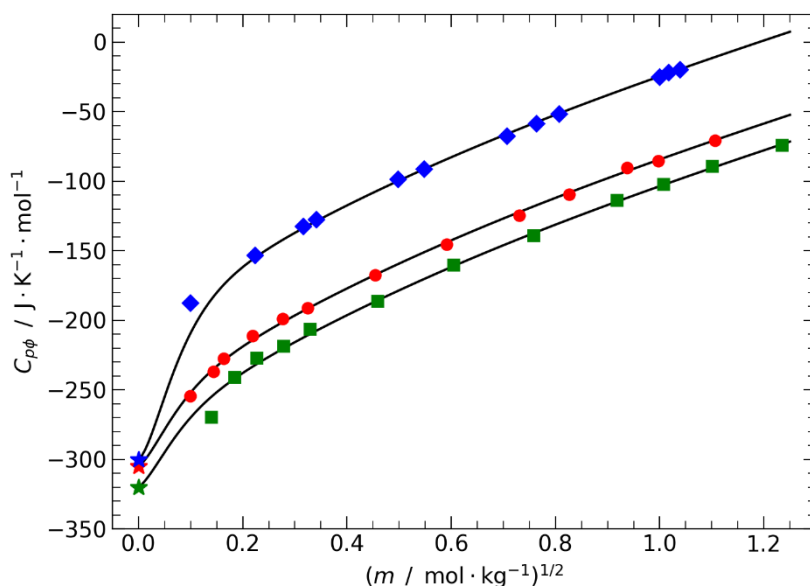


Figure 4. Present values for the apparent molar heat capacities, $C_{p\phi}$, of divalent metal sulfates as a function of solute concentration (as \sqrt{m}) at 298.15 K and 0.1 MPa: blue \blacklozenge , $\text{CuSO}_4(\text{aq})$; red \bullet , $\text{CoSO}_4(\text{aq})$; green \blacksquare , $\text{NiSO}_4(\text{aq})$; \star , C_p° calculated from Marcus's ionic values.²⁵ The solid lines were calculated from the present Pitzer models (Section 3.4.).

3.3 Standard Molar Values. Standard state (infinite dilution) values of the volumes and heat capacities, V° and C_p° , for the present salts can in principle be obtained by fitting $Y_\phi(m)$ data ($Y = V$ or C_p) with an appropriate theoretical model and extrapolating it to infinite dilution.²⁹ The most common models used for this purpose are the (extended) Redlich-Rosenfeld-Meyer equation(s)^{30,31} and the Pitzer equation(s).³² Both of these models are semi-empirical but, while they can provide excellent fits of $Y_\phi(m)$ data at moderate and high concentrations, it is well known that they do not provide reliable estimates of Y° for 2:2 electrolytes.^{33,34} A major reason for this unfortunate characteristic is the presence of significant self-association (ion pairing), which occurs in such systems even at low solute concentrations. The nature of ion pairs formed in divalent metal sulfate solutions is complicated^{35,36} and their presence in appreciable amounts can have substantial effects on observed $Y_\phi(m)$ values at low m , producing an unreliable extrapolation to infinite dilution.^{32,33,37}

While attempts have been made to quantitatively incorporate ion association into the estimation of Y° values,^{38,39} the extra (mostly unknown) parameters required and the numerical

correlations among them have discouraged their widespread application. For the present salts, the Y^0 was instead obtained by summation of literature values for $M^{2+}(\text{aq})$ and $\text{SO}_4^{2-}(\text{aq})$ ions. These values are based on measurements of appropriate 1:2 and 2:1 electrolytes, for which ion pairing effects are less problematic (albeit not entirely absent). Values of $Y^0(\text{ion})$ were taken from Marcus²⁵ except where more reliable estimates were available.

3.4 Pitzer modelling. The Pitzer ion-interaction model has been widely employed for correlating the various thermodynamic properties of aqueous electrolyte solutions. The Pitzer equations for V_ϕ and $C_{p\phi}$ of a binary electrolyte solution are:³²

$$V_\phi = V_{\text{MX}}^0 + \nu |z_{\text{M}} z_{\text{X}}| A_V \frac{\ln(1+1.2 \cdot I^{1/2})}{2.4} + 2\nu_{\text{M}} \nu_{\text{X}} RT [m B_{\text{MX}}^V + \nu_{\text{M}} z_{\text{M}} m^2 C_{\text{MX}}^V] \quad (4)$$

$$C_{p\phi} = C_{p,\text{MX}}^0 + \nu |z_{\text{M}} z_{\text{X}}| A_J \frac{\ln(1+1.2 \cdot I^{1/2})}{2.4} - 2\nu_{\text{M}} \nu_{\text{X}} RT^2 [m B_{\text{MX}}^J + \nu_{\text{M}} z_{\text{M}} m^2 C_{\text{MX}}^J] \quad (5)$$

where ν_{M} and ν_{X} are the stoichiometric numbers of cations M and anions X per formula unit, with $\nu = \nu_{\text{M}} + \nu_{\text{X}}$. The quantities z_{M} and z_{X} are the (algebraic) charge numbers of the ions and A_V and A_J are the Debye-Hückel slopes for volumes and heat capacities, respectively, calculated from the formulation of Fernandez et al.⁴⁰

The second virial coefficients B_{MX}^Y , ($Y = V$ or J) are empirical functions; for 2:2 electrolytes they are given by

$$B_{\text{MX}}^Y = \beta_{\text{MX}}^{(0)Y} + \beta_{\text{MX}}^{(1)Y} g(1.4 \cdot I^{1/2}) + \beta_{\text{MX}}^{(2)Y} g(12 \cdot I^{1/2}) \quad (6)$$

where

$$g(x) = \frac{2(1-(1+x))e^{-x}}{x^2} \quad (7)$$

and $\beta_{\text{MX}}^{(i)Y}$ are empirical parameters, normally determined by fitting to experimental data. In this work, inclusion of the third virial coefficients, C_{MX}^Y , was found to be unnecessary due to the limited concentration range of the data. The model parameters for eq 4 were fitted using the present volumetric data combined with the results of Pearce and Pumplin,²² Lo Surdo and Millero¹⁹ and Isono.²¹ The values reported by Puchalska et al.²³ for $\text{CuSO}_4(\text{aq})$ were excluded because of their large deviations from all other data, as discussed above. For heat capacities the Pitzer parameters for eq 5 were obtained by fitting only the present results.

During the fitting process remarkable similarities in the trends of $V_\phi(m)$ and $C_{p\phi}(m)$ for the studied metal sulfates, became apparent (see below). Close inspection of the data shows that the behavior of the different salts differs only at low concentrations ($\lesssim 0.04 \text{ mol} \cdot \text{kg}^{-1}$), where $\beta_{\text{MX}}^{(2)Y}$ has a significant effect. It was therefore decided, for comparison purposes, to fit the Pitzer equations using common values of $\beta_{\text{MX}}^{(0)Y}$ and $\beta_{\text{MX}}^{(1)Y}$ for all three salts, in addition to individual fits.

No significant differences were found between the results of the two fitting strategies, and as such, only the Pitzer parameters of the preferable (simpler) fit are given here (Table 3). This set of parameters reproduces the selected V_ϕ data with an average deviation of $\pm 0.25 \text{ cm}^3 \cdot \text{mol}^{-1}$, corresponding to $\pm 0.02 \%$ (relative) in ρ ; the smallest deviations occur for $\text{CoSO}_4(\text{aq})$ and the largest for $\text{CuSO}_4(\text{aq})$, for which the experimental data scatter is also greatest. For the heat

capacity data, after excluding the most dilute (and most uncertain) point for $\text{CuSO}_4(\text{aq})$ and $\text{NiSO}_4(\text{aq})$, the average deviation was $\pm 1.2 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ in $C_{p\phi}$ and $\pm 0.02 \%$ (relative) in c_p . Such differences are well within the experimental uncertainties.

Table 3. Debye–Hückel Slopes, Selected V° and C_p° and Fitting Parameters for Eqs 4 and 5 at 298.15 K and 0.1 MPa^{a,b}

A_V	1.8978	A_J	31.77
$V_{\text{CoSO}_4}^\circ$	-11.3	$C_{p,\text{CoSO}_4}^\circ$	-305
$V_{\text{NiSO}_4}^\circ$	-15.3	$C_{p,\text{NiSO}_4}^\circ$	-320
$V_{\text{CuSO}_4}^\circ$	-11.1	$C_{p,\text{CuSO}_4}^\circ$	-300
$\beta_{\text{MSO}_4}^{(0)V}$	0.0004625	$\beta_{\text{MSO}_4}^{(0)J}$	$-1.557 \cdot 10^{-5}$
$\beta_{\text{MSO}_4}^{(1)V}$	0.002386	$\beta_{\text{MSO}_4}^{(1)J}$	$-8.086 \cdot 10^{-5}$
$\beta_{\text{CoSO}_4}^{(2)V}$	0.1725	$\beta_{\text{CoSO}_4}^{(2)J}$	-0.008598
$\beta_{\text{NiSO}_4}^{(2)V}$	0.2009	$\beta_{\text{NiSO}_4}^{(2)J}$	-0.007885
$\beta_{\text{CuSO}_4}^{(2)V}$	0.2317	$\beta_{\text{CuSO}_4}^{(2)J}$	-0.01936

^a Units for the quantities presented here correspond to Eqs 4 and 5 expressed in $\text{cm}^3\cdot\text{mol}^{-1}$ and $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$, respectively. ^b See text for details of V° and C_p° values.

3.5 Comparative Behaviour of the Divalent Metal Sulfates. A well-known feature of the aqueous solutions of the divalent metal sulfates is their similarities to each other. This behaviour includes association constants and other thermodynamic data,⁵ spectroscopic behaviour⁴² and even dielectric properties.^{35,36} For the divalent first-row transition metal salts this peculiarity persists in spite of the differing sizes and electronic configurations of their cations. The origin of this behaviour is generally thought to be the attenuation of the differences among the M^{2+} ions caused by their strongly-bound hydration shell(s). Although the present values of $V_\phi(m^{1/2})$ and $C_{p\phi}(m^{1/2})$ differ among the three salts, their shape is virtually the same. This can be seen most clearly in Figures 5 and 6 which plot all the selected V_ϕ and $C_{p\phi}$ values for the present divalent metal sulfates, adjusted with arbitrary (empirical) fixed addends. The average spread among the values so adjusted is of the order of $\pm 0.4 \text{ cm}^3\cdot\text{mol}^{-1}$ for V_ϕ and $\pm 1 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ for $C_{p\phi}$.

This singular behavior is of more than just academic interest: for example, it could be used to provide reliable estimates of the properties of difficult-to-measure sulfate systems, such as $\text{Fe}(\text{II})$ and $\text{Cr}(\text{II})$, with minimal experimental effort.

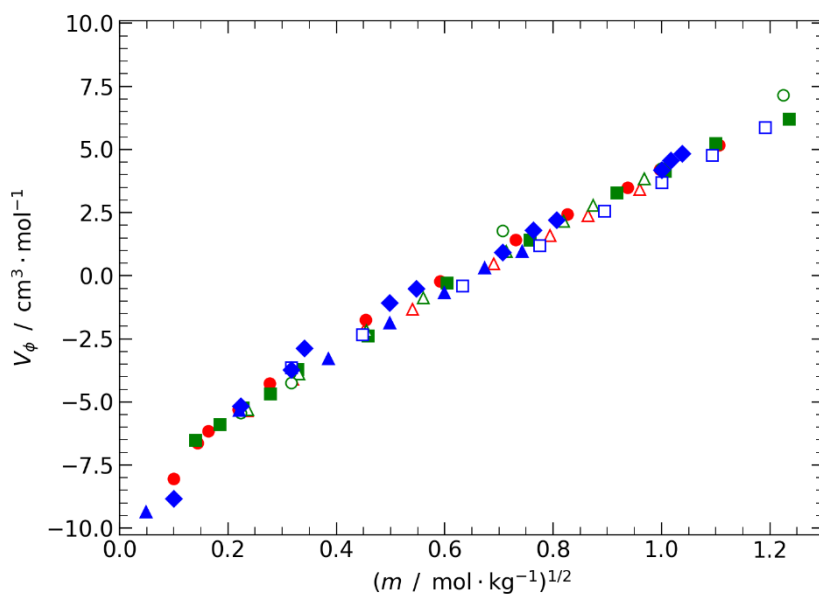


Figure 5. Apparent molar volumes V_ϕ of Co(II), Ni(II) and Cu(II) sulfates in aqueous solution at 298.15 K and 0.1 MPa. Present results: red \bullet , $\text{CoSO}_4(\text{aq})$; green \blacksquare , $\text{NiSO}_4(\text{aq})$; blue \blacklozenge , $\text{CuSO}_4(\text{aq})$; with fixed addends of -1.2 , 0 and $+3.5 \text{ cm}^3 \cdot \text{mol}^{-1}$, respectively. Other symbols refer to selected literature data (Figures 1, 2 and 3) with the same addends.

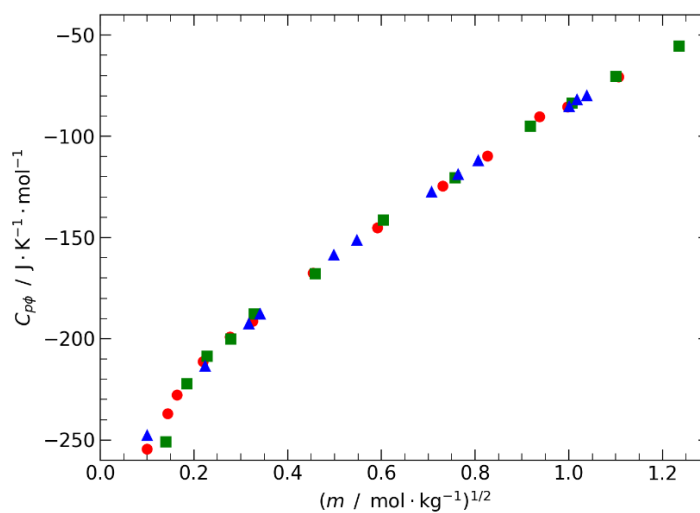


Figure 6. Apparent molar isobaric heat capacities, $C_{p\phi}$ of Co(II), Ni(II) and Cu(II) sulfates in aqueous solution at 298.15 K and 0.1 MPa: red \bullet , $\text{CoSO}_4(\text{aq})$; green \blacksquare , $\text{NiSO}_4(\text{aq})$; blue \blacklozenge , $\text{CuSO}_4(\text{aq})$; with fixed addends of -60.2 , 0 and $+18.7 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$, respectively.

4. CONCLUSIONS

Apparent molar volumes and heat capacities of aqueous solutions of cobalt(II), nickel(II) and copper(II) sulfate have been determined at 298.15 K over wide concentration ranges using vibrating tube densimetry and flow calorimetry, respectively. For volumes the present results for all three salts are in good agreement with reliable literature data. No heat capacity data appear to have been reported previously for these systems. The values of V_ϕ and $C_{p\phi}$ over the entire concentration range investigated were well fitted using Pitzer equations by utilizing literature values of the standard quantities V° and C_p° . The three salts show remarkable similarities in the concentration dependence of both V_ϕ and $C_{p\phi}$, which can be made to lie on single curves over most of the studied concentration range by using empirical fixed addends.

ASSOCIATED CONTENT

Supporting Information

Empirical equations relating solution densities (ρ) and isobaric massic heat capacities (c_p) to solute molality (m) for $\text{CoSO}_4(\text{aq})$, $\text{NiSO}_4(\text{aq})$ and $\text{CuSO}_4(\text{aq})$.

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Notes

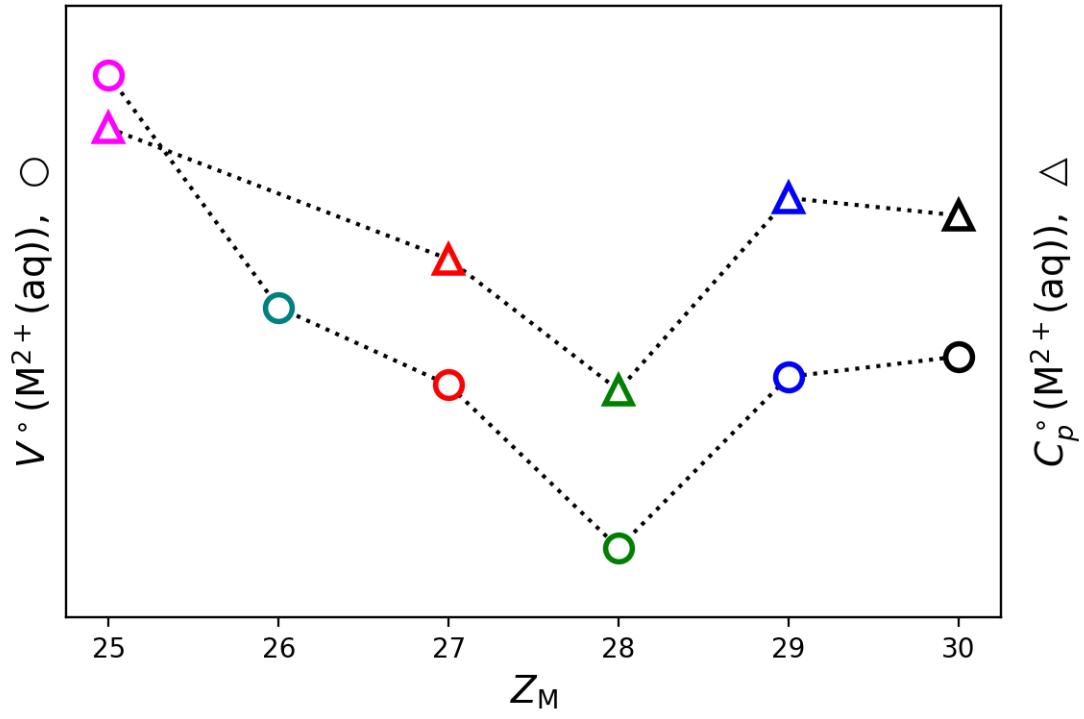
The authors declare no competing financial interest.

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