

Thermodynamic model for CoSO₄(aq) and the related solid hydrates in the temperature range from 270 to 374 K and at atmospheric pressure.

Tuomas Vielma

Research Unit of Sustainable Chemistry, University of Oulu, P. O. Box 3000, 90014 University of Oulu, Oulu, Finland.

ABSTRACT

Available literature on the thermodynamic properties of binary CoSO₄ – H₂O system has been reviewed and used to derive a model for calculating the solution properties and phase equilibria in a thermodynamically consistent manner. The solution model is based on the Pitzer ion interaction approach and, with 10 adjustable parameters, is able reproduce the available literature data with good accuracy from 270 to 374 K. The length and exact form of temperature dependence of the model was optimised using the "structural optimisation" scheme. Properties of the solid hydrates have been included in the model for calculation of solubilities. The model has been validated by successfully predicting metastable solubilities and solid–liquid–vapor equilibrium pressures.

1. INTRODUCTION

Cobalt is an important metal for modern society, mainly used nowadays in lithium-ion batteries and high quality alloys, but its essential role in human biochemistry is also widely recognized [1]. Its global production has amounted to approximately 120 000 tons of refined cobalt per year in the last couple of years [1], mainly as a side-product of nickel and copper-refining [2]. Due to the nature of these processes, usually involving leaching with sulfuric acid, properties of aqueous CoSO₄ play a significant role in cobalt recovery. Cobalt sulfate solutions are also typically used in precipitation of Co-containing carbonates or hydroxides, key-ingredients to some Li-ion batteries [1]. Cobalt is also a key-impurity in hydrometallurgical production of zinc, and must be carefully removed by cementation before the electrowinning stage [3].

The available experimental data for CoSO₄(aq) paint a picture with great similarities to other chemically similar MSO₄ (M = Mn²⁺, Fe²⁺, Ni²⁺, Cu²⁺, Zn²⁺). That is, most of the data was measured around the midpoint of the previous century, followed by a sharp drop in the interest (and possibly, ability) to study the thermodynamic properties of these solutions. This is of course a bit surprising,

given the economic and industrial interest in $\text{CoSO}_4(\text{aq})$ solutions. Despite the fact that some laterite ore leaching processes can operate even at 523 K [2], no high temperature data seems to exist for binary $\text{CoSO}_4(\text{aq})$ solutions, not to mention the ternary $\text{CoSO}_4 - \text{H}_2\text{SO}_4(\text{aq})$ solutions, as most of the available data have been measured at 298.15 K. The few exceptions are two isopiestic studies [4,5] and some freezing point depression [6,7,8] and boiling point elevation [6] measurements. Solubility data for the different CoSO_4 hydrates apparently cover the whole domain of stability of $\text{CoSO}_4(\text{aq})$, from the eutectic point at around 270 K up to 473 K, above which the solubility tends to insignificant levels. The available literature is described in more detail below (see Section 2. Selected data).

This work reviews the available experimental data and presents the first Pitzer model parametrisation for $\text{CoSO}_4(\text{aq})$, covering essentially the available experimental range, in a simple format that is compatible with most commercial software, and thus fit for modelling the aqueous solution properties and solubility of CoSO_4 .

2. SELECTED DATA

All literature data discussed here has been summarised in Table 1 for convenience. Three studies that reported experimental osmotic coefficients ϕ for $\text{CoSO}_4(\text{aq})$ were found. These studies cover the temperature range 298.15 – 373.15 K and molalities from 0.1 – 0.2 $\text{mol}\cdot\text{kg}^{-1}$ to near-saturation [9, 4, 5]. These reported measurements apparently followed rather standard measurement protocols (as described by Rard and Platford [10]). Sturch [11] reported activity coefficients based on EMF measurements with cobalt amalgam electrodes. The results, however, contain clear anomalies and were not included in the optimisation. Malatesta et al. [12] reported activity coefficients measured with the "liquid membrane" cells at 298.15 K. The results appear reasonable and internally consistent, however, it should be mentioned that some criticism by Albright et al. [13] has been directed at the employed measurement technique, at least concerning their results for $\text{ZnSO}_4(\text{aq})$.

Heats of dilution have been reported on two occasions, by Brodale and Giauque [14] and Schreiber et al. [15]. Additionally, NBS Tables [16] lists a few values for heat of formation of $\text{CoSO}_4(\text{aq})$ at 298.15 K and finite concentration, which can be converted relative apparent molar enthalpies. Brodale and Giauque [14] and Goldberg et al. [17] have reported some heats of solution measurements for cobalt sulfate heptahydrate and hexahydrate at low concentrations and near ambient conditions. Solution heat capacities have been reported only by Akilan et al [18].

Freezing points (or freezing point depressions) were reported early-on by Kahlenberg (along with some boiling point elevations) [6] and Rohmer [7]. Brown and Prue [8] also performed some extremely precise measurements in their study about ion-pair formation. On a whole, the measurements extend from 0.005 $\text{mol}\cdot\text{kg}^{-1}$, to the eutectic composition 1.49 $\text{mol}\cdot\text{kg}^{-1}$, as given by

Rohmer [7].

Three cobalt sulfate hydrates can exist in stable equilibrium with its aqueous solution; heptahydrate, hexahydrate and monohydrate. Most comprehensive study of their solubilities is that of Rohmer [7]. Brodale and Giauque [14] reported solubilities for the heptahydrate and hexahydrate in excellent agreement with Rohmer's results. In addition to these two datasets, various small scale studies exist [19–28], usually reporting measurements at just one temperature. These results lay around the two first mentioned data sets, but appear to be of poorer quality and were thus left out of further treatment. Additionally, Bruhn et al. [29] measured solubility of the monohydrate up to 473 K. Their quality is hard to assess, since there is no other data to compare with, but they seem consistent with Rohmer's results at lower temperatures [7]. However, as modelling the solubilities beyond 373 K becomes increasingly uncertain due to lack of solution data, these data were not included in the optimisation.

Table 1. Literature data used in the parameter optimisation.

| Property | $m / \text{mol kg}^{-1}$ | T / K | p / MPa | Number of data points ^a | Reference |
|---|--------------------------|----------------------------|------------------|------------------------------------|-----------|
| ϕ | 0.1264–2.4693 | 298.15 | p_{sat} | 28 | [9] |
| ϕ | 0.1262–3.2482 | 323.15 | p_{sat} | 20 | [4] |
| ϕ | 0.2173–2.3346 | 373.15 | p_{sat} | 11 (1) | [5] |
| $\ln \gamma_{\pm}$ | 0.003–0.23 | 298.15 | 0.1 | 19 (19) | [11] |
| $\ln \gamma_{\pm}$ | 0.00005–1.000 | 298.15 | 0.1 | 19 | [12] |
| $\Delta_{\text{dil}}H$ | 0.05–2.4 | 298.15–317.8 | 0.1 | 6 | [14] |
| $\Delta_{\text{dil}}H$ | 0.2048–1.7219 | 298.15 | 0.1 | 28 | [15] |
| $\Delta_f H(\text{aq})$ | 0.056–2.381 | 298.15 | 0.1 | 4 | [16] |
| $\Delta_{\text{sol}}H(\text{CoSO}_4 \cdot 7\text{H}_2\text{O})$ | 0.07–0.08 | 298.15–317.25 | 0.1 | 4 (4) | [14] |
| $\Delta_{\text{sol}}H(\text{CoSO}_4 \cdot 7\text{H}_2\text{O})$ | 0.021 | 298.15 | 0.1 | 2 (2) | [17] |
| $\Delta_{\text{sol}}H(\text{CoSO}_4 \cdot 6\text{H}_2\text{O})$ | 0.08–0.095 | 298.15–319.75 | 0.1 | 4 (4) | [14] |
| $\Delta_{\text{sol}}H(\text{CoSO}_4 \cdot 6\text{H}_2\text{O})$ | 0.027 | 298.15 | 0.1 | 3 (3) | [14] |
| $C_{p\phi}$ | 0.00988–1.2241 | 298.15 | 0.1 | 13 | [18] |
| θ_m | 0.095–1.063 | 0.209–1.587 ^b | 0.098 | 5 (5) | [6] |
| θ_m | 0.00563–0.09724 | 0.0166–0.2090 ^b | 0.1 | 18 | [8] |
| θ_m | 0.638–1.494 | 0.9–2.7 ^b | 0.1 | 4 (4) | [7] |
| θ_b | 0.1389–3.1549 | 0.068–1.055 ^c | 0.098 | 12 (12) | [6] |
| $s(\text{CoSO}_4 \cdot 7\text{H}_2\text{O})$ | 1.49–3.94 | 270.45–316.45 | 0.1 | 11 (2) | [7] |
| $s(\text{CoSO}_4 \cdot 7\text{H}_2\text{O})$ | 2.39–3.19 | 298.37–317.68 | 0.1 | 12 | [14] |
| $s(\text{CoSO}_4 \cdot 7\text{H}_2\text{O})$ | 2.466 | 298.15 | 0.1 | 1 (1) | [19] |
| $s(\text{CoSO}_4 \cdot 7\text{H}_2\text{O})$ | 2.472 | 298.15 | 0.1 | 1 (1) | [20] |

| | | | | | |
|--|-------------|---------------|-----|---------|------|
| $s(\text{CoSO}_4 \cdot 7\text{H}_2\text{O})$ | 2.392 | 298.15 | 0.1 | 1 (1) | [21] |
| $s(\text{CoSO}_4 \cdot 7\text{H}_2\text{O})$ | 3.149 | 313.15 | 0.1 | 1 (1) | [22] |
| $s(\text{CoSO}_4 \cdot 7\text{H}_2\text{O})$ | 2.526 | 298.15 | 0.1 | 1 (1) | [23] |
| $s(\text{CoSO}_4 \cdot 7\text{H}_2\text{O})$ | 2.526 | 298.15 | 0.1 | 1 (1) | [25] |
| $s(\text{CoSO}_4 \cdot 7\text{H}_2\text{O})$ | 2.25–3.134 | 293.15–318.15 | 0.1 | 4 (1) | [26] |
| $s(\text{CoSO}_4 \cdot 6\text{H}_2\text{O})$ | 3.16–5.19 | 316.45–368.15 | 0.1 | 13 (11) | [7] |
| $s(\text{CoSO}_4 \cdot 6\text{H}_2\text{O})$ | 3.16–3.70 | 316.67–335.38 | 0.1 | 12 | [14] |
| $s(\text{CoSO}_4 \cdot 6\text{H}_2\text{O})$ | 3.436 | 323.15 | 0.1 | 1 (1) | [19] |
| $s(\text{CoSO}_4 \cdot 6\text{H}_2\text{O})$ | 3.436 | 323.15 | 0.1 | 1 (1) | [20] |
| $s(\text{CoSO}_4 \cdot 6\text{H}_2\text{O})$ | 3.613 | 313.15 | 0.1 | 1 (1) | [27] |
| $s(\text{CoSO}_4 \cdot 6\text{H}_2\text{O})$ | 3.316–4.058 | 323.15–348.15 | 0.1 | 2 (2) | [23] |
| $s(\text{CoSO}_4 \cdot 6\text{H}_2\text{O})$ | 3.313–4.051 | 323.15–348.15 | 0.1 | 2 (1) | [24] |
| $s(\text{CoSO}_4 \cdot 6\text{H}_2\text{O})$ | 3.316–4.058 | 323.15–348.15 | 0.1 | 2 (2) | [25] |
| $s(\text{CoSO}_4 \cdot 6\text{H}_2\text{O})$ | 3.32–3.55 | 323.15–333.15 | 0.1 | 4 (2) | [26] |
| $s(\text{CoSO}_4 \cdot 6\text{H}_2\text{O})$ | 3.313–4.051 | 323.15–348.15 | 0.1 | 2 (2) | [24] |
| $s(\text{CoSO}_4 \cdot 6\text{H}_2\text{O})$ | 2.99 | 313.15 | 0.1 | 1 (1) | [28] |
| $s(\text{CoSO}_4 \cdot \text{H}_2\text{O})$ | 2.41–3.87 | 334.45–374.35 | 0.1 | 8 (1) | [7] |
| $s(\text{CoSO}_4 \cdot \text{H}_2\text{O})$ | 0.06–1.47 | 393.15–473.15 | 0.1 | 5 (5) | [29] |
| $s(\text{CoSO}_4 \cdot \text{H}_2\text{O})$ | 2.700–3.535 | 343.15–369.65 | 0.1 | 2 (2) | [19] |
| $s(\text{CoSO}_4 \cdot \text{H}_2\text{O})$ | 2.854 | 373.15 | 0.1 | 1 (1) | [25] |
| $s(\text{CoSO}_4 \cdot \text{H}_2\text{O})$ | 3.47 | 333.15 | 0.1 | 1 (1) | [26] |

^aNumbers in parentheses are the number of data points discarded from the optimisation. ^bReported freezing point depression. ^c Reported boiling point elevation.

3. MODEL AND PARAMETER OPTIMISATION

3.1. Pitzer equations. Multiple more-or-less empirical models have been used to describe thermodynamic properties of aqueous electrolyte solutions, with varying levels of success [30]. Probably the best known and the most established one is the Pitzer ion interaction approach [31–33]. Several variants of the model equations exist [30], however, most commercial thermodynamic calculation software contain only the original model equations [31–33]. For full description of the equations, reader is referred to the original papers and only a short summary is given here. The equations for osmotic coefficient and mean activity coefficient for a 2:2 electrolyte (here CoSO_4) are [33]

$$\phi - 1 = 4 f^\phi + m B_{\text{CoSO}_4}^\phi + m^2 C_{\text{CoSO}_4}^\phi \quad (1)$$

$$\ln \gamma_{\pm} = 4 f^\gamma + m B_{\text{CoSO}_4}^\gamma + m^2 C_{\text{CoSO}_4}^\gamma \quad (2)$$

where

$$f^\phi = -A_\phi \frac{I^{1/2}}{1 + bI^{1/2}} \quad (3)$$

$$f^\gamma = -A_\phi \left[\frac{I^{1/2}}{1 + bI^{1/2}} + \frac{2}{b} \ln(1 + bI^{1/2}) \right] \quad (4)$$

are the Debye–Hückel type terms describing and A_ϕ is the Debye–Hückel slope for osmotic coefficient, calculated in this work from the IAPWS-95 equation of state for water [34,35], b is an empirical parameter with a fixed value $1.2 \text{ (kg} \cdot \text{mol}^{-1})^{1/2}$, and I is the stoichiometric ionic strength, calculated as $I = 0.5 \sum z_i^2 m_i$. The ternary interaction coefficients C^ϕ and C^γ , which are related by $C^\gamma = 3C^\phi/2$, are independent of ionic strength, but the binary terms B^ϕ and B^γ have the following ionic strength dependences

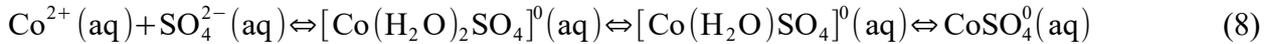
$$B^\phi = \beta^{(0)} + \beta^{(1)} e^{-\alpha_1 I^{1/2}} + \beta^{(2)} e^{-\alpha_2 I^{1/2}} \quad (5)$$

$$B^\gamma = 2\beta^{(0)} + \beta^{(1)} g(\alpha_1 I^{1/2}) + \beta^{(2)} g(\alpha_2 I^{1/2}) \quad (6)$$

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

where $\beta^{(i)}$ are the empirical interaction parameters, specific to the electrolyte, and α_1 and α_2 are common constants to all 2:2 electrolytes, $1.4 \text{ (kg} \cdot \text{mol}^{-1})^{1/2}$ and $12 \text{ (kg} \cdot \text{mol}^{-1})^{1/2}$, respectively.

$\text{CoSO}_4(\text{aq})$, like the related $\text{MSO}_4(\text{aq})$ ($M = \text{Mn}^{2+}, \text{Fe}^{2+}, \text{Ni}^{2+}, \text{Cu}^{2+}, \text{Zn}^{2+}$), shows significant ion-pairing even in dilute solutions [36], with formation of both solvent-separated and contact ion-pairs [37,38], according to the Eigen-Tamm mechanism [39,40]



To avoid the inclusion of explicit association equilibria in the calculations, Pitzer model contains the $\beta^{(2)}$ parameter, acting as a *de facto* over-all stability constant. Furthermore, it can actually be shown that, at the limit of infinite dilution, $\beta^{(2)}$ and the over-all stability constant are exactly related [33]. It thus follows that the various derivatives of $\beta^{(2)}$ with respect to temperature or pressure can be related by standard thermodynamic relationships to changes in thermodynamic properties upon ion pairing, at infinite dilution.

Analogous equations for relative apparent molar enthalpy L_ϕ and isobaric apparent molar heat capacity $C_{p\phi}$ can be derived from the temperature derivatives of equations 1 and 2

$$L_{\phi} = \frac{4A_L}{b} \ln(1 + bI^{1/2}) - 2RT^2 \left(m B_{\text{CoSO}_4}^L + 2m^2 C_{\text{CoSO}_4}^L \right) \quad (9)$$

$$C_{p\phi} = C_p^{\circ} + \frac{4A_J}{b} \ln(1 + bI^{1/2}) - 2RT^2 \left(m B_{\text{CoSO}_4}^J + 2m^2 C_{\text{CoSO}_4}^J \right) \quad (10)$$

where A_L and A_J are the Debye–Hückel slopes for enthalpy and heat capacity, respectively, R is the gas constant, and $B^{L/J}$ and $C^{L/J}$ are the interaction parameters, which can be calculated from the temperature derivatives of the corresponding terms in equations 1 and 2 [31]. C_p° is the apparent molar heat capacity of the electrolyte at infinite dilution.

3.2. Temperature dependence. No theoretically implied form of temperature or pressure dependence exists for the terms in the Pitzer equations, with the exception of the DHLL term. As such, the following general temperature dependence, compatible with FactSage and ChemSheet software [41,42], was assumed for the interaction parameters $\beta^{(i)}$ and C^{ϕ}

$$Q = q_0 + q_1 T + q_2 T^2 + q_3 \ln T + q_4 T^{-1} + q_5 T^{-2} \quad (11)$$

where T is the thermodynamic temperature in K, and q_i are the adjustable parameters. No explicit pressure dependence was assumed due to lack of the requisite data, ie. apparent molar volumes in the considered temperature range (see Section 4.3 for further discussion), and hence all variation with pressure stems from the pressure dependence of A_{ϕ} . Interestingly, at least some of the popular commercial software cannot handle pressure dependent Pitzer equations at the moment [41, 42]. This is rather unfortunate since many of the geochemical and industrial processes [2] of great interest operate under considerable pressure with significant effects on the thermodynamic properties of the system.

Equation 11 leads to equations 12 and 13 for the coefficients of enthalpy and heat capacity, respectively,

$$Q^L = q_1 + 2q_2 T + q_3 T^{-1} - q_4 T^{-2} - 2q_5 T^{-3} \quad (12)$$

$$Q^J = 2q_2 - q_3 T^{-2} + 2q_4 T^{-3} + 6q_5 T^{-4} + 2T^{-1} Q^L \quad (13)$$

To model heat capacity of the solution, a value for the isobaric partial molar heat capacity C_p° is needed. For this work a constant value $-305 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ calculated from the ionic values given by Marcus [43], was adopted. As heat capacities of ions are known to vary rather slowly in the considered temperature range, errors in solubility calculations stemming from this approximation tend to be small and can be absorbed into the refined standard enthalpies and entropies of the solid phases [44]. For the heptahydrate and hexahydrate, simple linear heat capacity functions were fitted

to the results of Rao and Giaque [45]. Heat capacity function for the monohydrate was estimated as suggested by De Kock [46]. These functions are given below in Equations 14–16, for the hepta-, hexa- and monohydrate, respectively. The standard enthalpies of formation $\Delta_f H^\circ$ and standard entropies S° at 298.15 K were refined using the first optimised solution model and the solubility data given in Table 1. $\Delta_f H^\circ(\text{CoSO}_4(\text{aq})) = -967.47 \text{ kJ}\cdot\text{mol}^{-1}$ and $S^\circ(\text{CoSO}_4(\text{aq})) = -94.2 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ were again calculated from Marcus [43]. Properties of pure water, ice and water vapor were calculated from the IAPWS-95 equation of state for water [34].

$$C_p/\text{J}\cdot\text{mol}^{-1}\text{K}^{-1} = 1.0187 T/\text{K} + 87.523 \quad (14)$$

$$C_p/\text{J}\cdot\text{mol}^{-1}\text{K}^{-1} = 0.9656 T/\text{K} + 64.737 \quad (15)$$

$$C_p/\text{J}\cdot\text{mol}^{-1}\text{K}^{-1} = 0.4184 T/\text{K} + 42.954 \quad (16)$$

4. RESULTS AND DISCUSSION

4.1. Solution properties. The optimised parameter values for $\beta^{(i)}$ and C^ϕ corresponding to equation 11 are given in Table 2. Using a Pitzer model implementation of the "structural optimisation" developed by Setzmann and Wagner [47], the model structure with the listed 10 fitting parameters was found and shown to properly describe the selected literature data, essentially to within their experimental uncertainties. All parameter optimisations were carried out with the PyMC3 Python-package for Bayesian statistics [48]. The estimated uncertainties of the different datasets were taken from the original references and used in the parameter optimisation. The root mean square deviations of the calculated results from the experimental values for the different properties are given in Table 3. A graphical comparison of the results is given in Figures 1–4.

The largest deviations are observed for the isopiestic results of Yang et al. [5] at 373.15 K. Closer inspection of the high-temperature isopiestic data revealed this lack of fit to be due to inconsistency with the existing heat of dilution data. Increasing number of adjustable parameters in the model did not lead to an improved fit, but was observed to negatively affect model extrapolations, leading to erratic and unphysical behaviour outside the parameterized range, a classical sign of over-fitting. As the high-temperature isopiestic data are based on only a single reference, the current fit is determined more by the enthalpy data derived from three independent references [14-16].

Table 2. Optimised Pitzer interactions parameters for $\text{CoSO}_4(\text{aq})$, corresponding to equation 11.^a

| | $\beta^{(0)}$ | $\beta^{(1)}$ | $\beta^{(2)}$ | C^ϕ |
|-------|---------------|---------------|---------------|-------------|
| q_0 | 0.4534(20) | -1.1607(56) | -2588.76(98) | -0.1086(15) |

| | | | | |
|-------|------------|-------------|-------------|-----------|
| q_1 | - | - | -2.0540(32) | - |
| q_2 | - | - | - | - |
| q_3 | - | - | 552.14(19) | - |
| q_4 | -78.21(59) | 3439.95(99) | - | 40.11(49) |
| q_5 | - | -672812(1) | - | - |

^aNumbers in parenthesis are the estimated standard uncertainties in the last digits.

Table 3. Root mean square deviations between calculated and experimental results.

| ϕ^a | ϕ^b | $\ln \gamma_{\pm}$ | $\Delta_{\text{dil}}H$ | L_{ϕ} | $C_{p\phi}$ |
|----------|----------|--------------------|-----------------------------------|-----------------------------------|--|
| - | - | - | / $\text{kJ}\cdot\text{mol}^{-1}$ | / $\text{kJ}\cdot\text{mol}^{-1}$ | / $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ |
| 0.005 | 0.005 | 0.02 | 0.15 | 0.2 | 2.9 |

^bNot including data Yang et al. [5] at 373 K. ^aCalculated from freezing point depressions [7,8].

Since no solution enthalpy or heat capacity data exists at temperatures other than 298.15, extrapolation of these properties is constrained mainly by the osmotic coefficient and freezing point depression data. Nevertheless, the model seems to give physically reasonable extrapolations, qualitatively comparable to $\text{MgSO}_4(\text{aq})$, which apparently is the only 2:2 electrolyte for which high temperature enthalpy [49] and heat capacity [50] data exists. The "good" behaviour of the model can be at least partially attributed to the reasonably simple temperature dependence employed in this work.

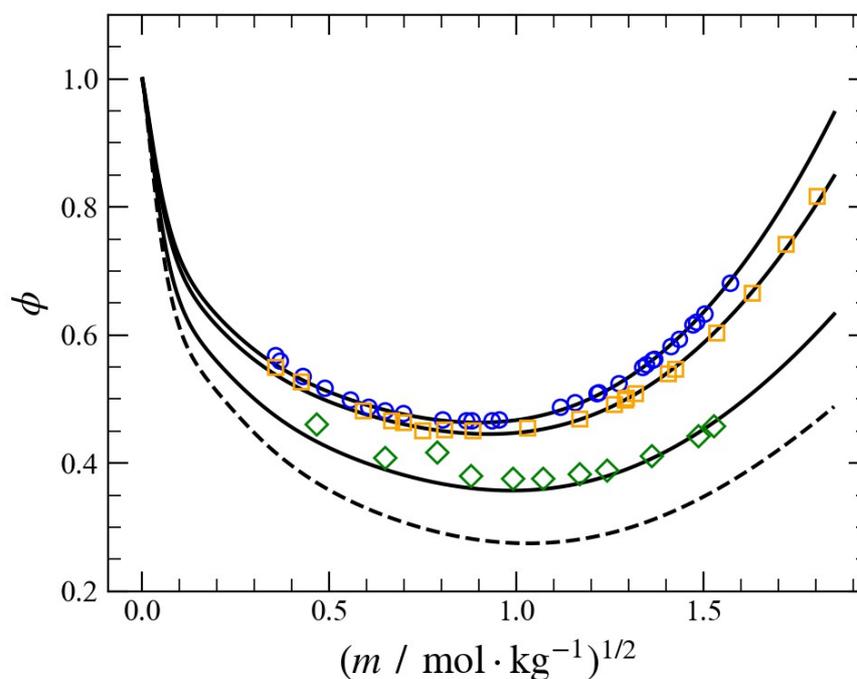


Figure 1. Osmotic coefficient ϕ of $\text{CoSO}_4(\text{aq})$ solution as a function of concentration (as $m^{1/2}$) at temperatures $T/\text{K} = 298.15, 323.15, 373.15, 403.15$ (from top to bottom). Circles [9]; squares [4], diamonds [5]. The dashed line is an extrapolation outside studied range.

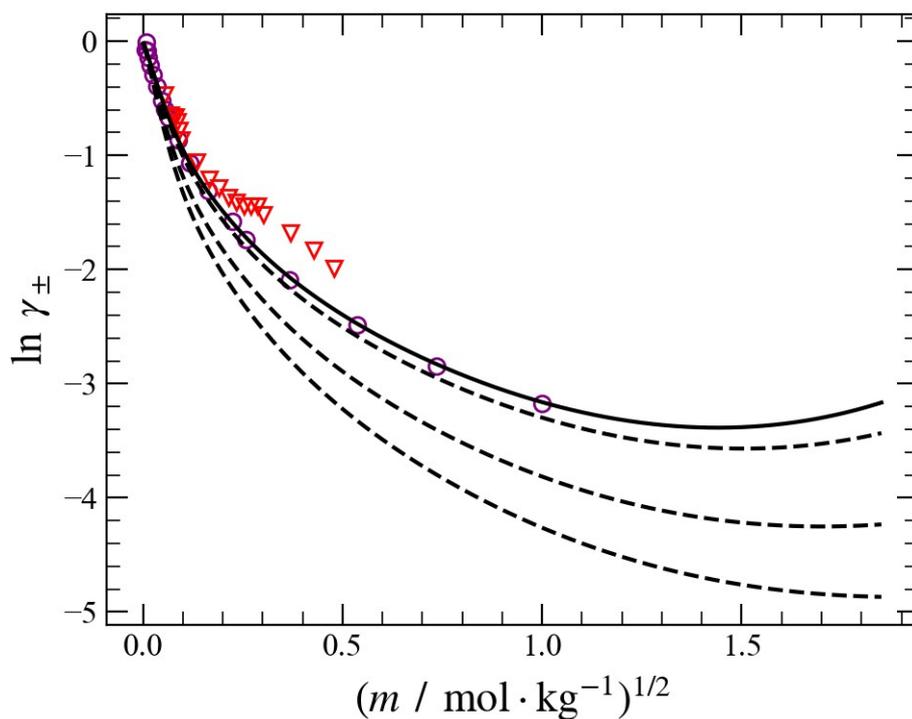


Figure 2. $\ln \gamma_{\pm}$ of $\text{CoSO}_4(\text{aq})$ as a function of concentration (as $m^{1/2}$) at temperatures $T/\text{K} = 298.15, 323.15, 373.15, 403.15$ (from top to bottom). Circles [12]; downward triangles [11] (not included in optimisation). Dashed lines are extrapolations outside the studied range.

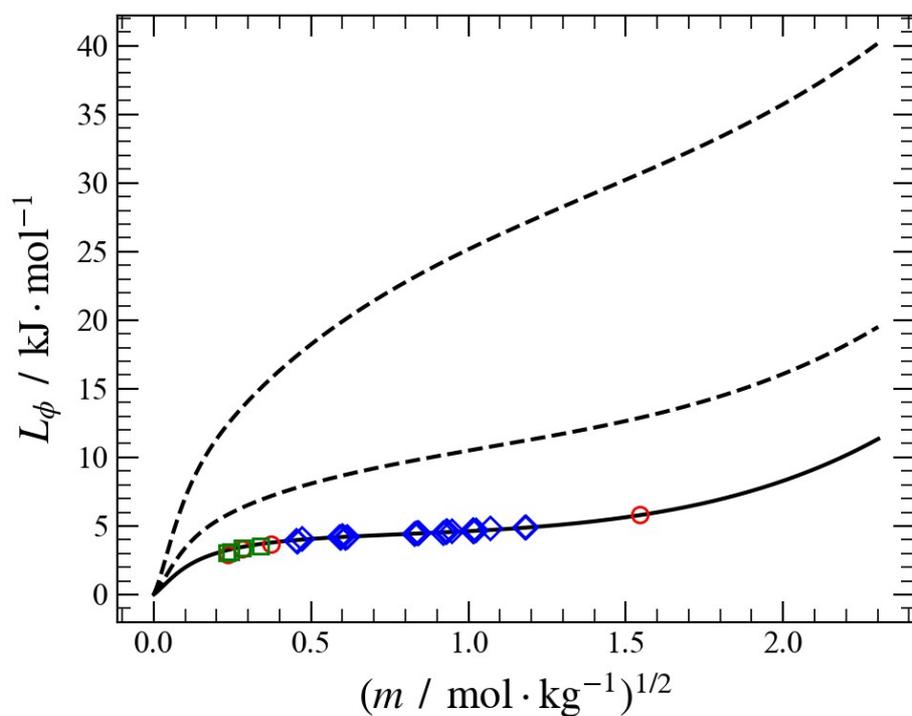


Figure 3. Relative apparent molar enthalpy L_{ϕ} of $\text{CoSO}_4(\text{aq})$ solution as a function of concentration (as $m^{1/2}$) at temperatures $T/\text{K} = 298.15, 323.15, 373.15$ (from bottom to top). Circles [16]; squares [14], diamonds [15]. Dashed lines are extrapolations outside the studied range.

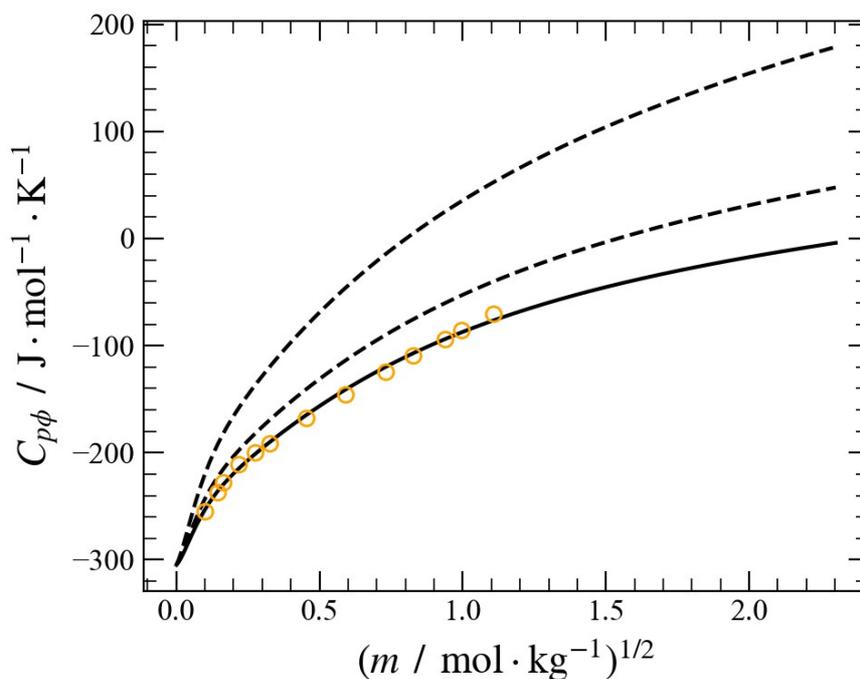


Figure 4. Isobaric apparent molar heat capacity $C_{p\phi}$ of $\text{CoSO}_4(\text{aq})$ solution as a function of concentration (as $m^{1/2}$) at temperatures $T/\text{K} = 298.15, 323.15, 373.15$ (from bottom to top). Circles [18]. Dashed lines are extrapolations outside the studied range.

4.2. Phase equilibria. Standard state properties, $\Delta_f H^\circ$ and S° , at 298.15 K were optimised for each of the three hydrates, as detailed in Table 1. The optimised values are given in Table 4. Calorimetric values from Brodale and Giaque [14] and the derived values by Goldberg et al. [17] are shown for comparison. Using the present values and the optimised solution model, a phase diagram for the binary $\text{CoSO}_4 - \text{H}_2\text{O}$ system was calculated, shown in Figure 5. Selected literature data are shown for comparison.

Table 4. Standard enthalpies of formation $\Delta_f H^\circ$ and standard entropies S° of the solid hydrates at 298.15 K.

| | $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}(\text{s})$ | $\text{CoSO}_4 \cdot 6\text{H}_2\text{O}$ | $\text{CoSO}_4 \cdot \text{H}_2\text{O}(\text{s})$ |
|--|---|---|--|
| $\Delta_f H^\circ / \text{kJ} \cdot \text{mol}^{-1}$ | -2979.26 (-2977 ^a) | -2683.79 (-2681 ^a) | -1214.05 (-1198 ^a) |
| $S^\circ / \text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ | 403.51 (406.05 ^b) | 363.00 (367.62 ^b) | 127.40 (175 ^a) |

^aGoldberg et al. [17]. ^bCalorimetric values from Brodale and Giaque [14].

The following abbreviations are used in the discussion below: Co7, cobalt sulfate heptahydrate; Co6, cobalt sulfate hexahydrate; Co1, cobalt sulfate monohydrate; Aq, aqueous solution. Four isobaric invariant points (in addition to phase transitions of pure water) can be observed in the phase diagram. These are the $\text{Aq} + \text{H}_2\text{O}(\text{s}) + \text{Co7}$ eutectic point at $1.498 \text{ mol} \cdot \text{kg}^{-1}$ and 270.19 K, $\text{Aq} + \text{Co7}$

+ Co6 peritectic point at $3.203 \text{ mol}\cdot\text{kg}^{-1}$ and 318.07 K , Aq + Co6 + Co1 peritectic point at $3.754 \text{ mol}\cdot\text{kg}^{-1}$ and 337.18 K and the Aq + H₂O(g) + Co1 equilibrium at $2.395 \text{ mol}\cdot\text{kg}^{-1}$ and 373.90 K . These calculated points correspond fairly well with experimental values: $1.494 \text{ mol}\cdot\text{kg}^{-1}$ and 270.45 K for the eutectic point [7], and $3.741 \text{ mol}\cdot\text{kg}^{-1}$ and 337.35 K for the second peritectic point. The Aq + H₂O(g) + Co1 equilibrium temperature is in fairly good agreement with 374.22 K interpolated from Broers and Van Welie's vapor pressure data [51]. Rohmer [7] reported the first peritectic to lie at $3.938 \text{ mol}\cdot\text{kg}^{-1}$ and 316.45 K , but this point is most likely in severe error as it does not lie on the same curve as the rest of the data.

Since only the stable equilibrium data was used to optimise the model parameters, predicting metastable solubilities is a simple test to show the internal consistency of the model, and to some extent spot over- or under-parameterization issues. For this reason also the metastable solubilities of the hexahydrate, as reported by Rohmer [7], have been included in Figure 5. Overall, these data are reproduced to within 1 % by the current model, with increasing differences at higher temperatures.

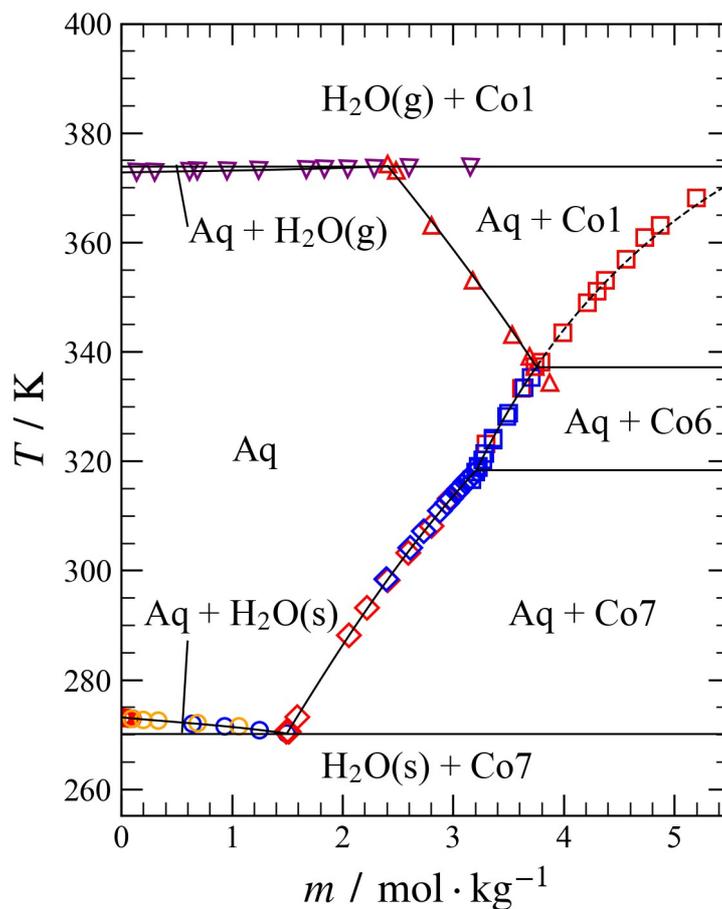


Figure 5. Isobaric phase diagram for the binary CoSO₄ – H₂O system. Solid lines were calculated from the present model. Open circles, ice curve [6,7, 8]; downward triangles, vapor curve [6]; diamonds, Co7 solubility [7, 14]; squares, Co6 solubility [7, 14]; triangles, Co1 solubility [7].

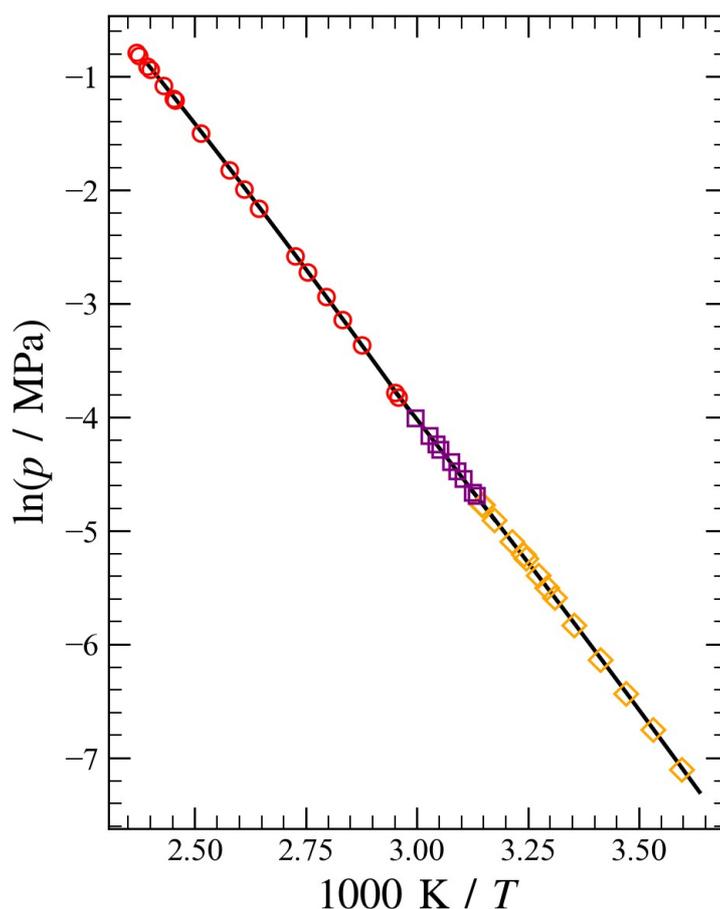


Figure 6. Equilibrium pressure of solid–liquid–vapor equilibria as a function of temperature (as $1/T$). Diamonds, Co7; squares, Co6; circles, C1. All experimental data are from Broers and van Welie [51]. Solid line is calculated from the present model.

This is of course not surprising, since only few high temperature data was available to parametrize the model, and all of it being constrained below $3.3 \text{ mol}\cdot\text{kg}^{-1}$. Nevertheless, the observed differences are likely bordering the true experimental errors. Further checks on the consistency of the model have been done by comparing calculated results with the experimental equilibrium pressures Broers and van Welie [51] reported for different solid–aqueous–vapor equilibria (Figure 6). The agreement is good.

4.3. Further developments. One of the main motivations for creating the present model, and others like it [52–57], have been without a doubt a need to model the multicomponent solutions of acid main drainage and hydrometallurgical processes. However, for such concentrated solutions with multiple major solutes, it is usually necessary to include mixing parameters to the model [58]. It is customary to use solubilities in electrolyte mixtures for this purpose, but for the first row d-block sulfates this is much complicated by formation of solid solutions [27]. As such, experimental activity data is needed, which, unfortunately for these systems, does not appear to be available.

It has been noted previously that the thermodynamic properties of the bivalent sulfates show striking similarities, as evidenced by their ion-pairing stability constants [36], osmotic coefficients [59], heat capacities and volumetric properties [18] and dielectric relaxation behaviour [37,38], to give some examples. These all imply strong attenuation of the individual characteristics of the cation, both due to ion-pairing with the sulfate and the strong hydration, characteristic of highly charged ions. This suggests (but does not ensure) that the problem of lacking mixture data can be solved by employing the so-called *mixing rules* [60], such as the *Zdanovskii's rule* [61] for water activities or *Young's rule* for enthalpies, heat capacities and volumes [62]. Problem with the mixing rules is of course that commercial software do not support their explicit application. It is, however, straight-forward to show that for electrolytes of the same charge type Young's rule applied to Pitzer equations reduces to the Pitzer equation for a mixture with all the mixing terms set to zero. Other work-arounds can also be devised, eg. creating mock datasets from the mixing rules.

5. CONCLUSIONS

An internally consistent and physically reasonable thermodynamic model for the $\text{CoSO}_4 - \text{H}_2\text{O}$ system is presented. The model follows the Pitzer ion interaction approach and is based on the available literature data, covering physico-chemical properties of the aqueous solution and observed phase equilibria. The model was parametrized from the eutectic temperature near 270 K to the highest observable boiling point (at 0.1 MPa) near 374 K. With 10 adjustable parameters to describe the solution phase, the model reproduces most of the available literature within their experimental uncertainties. Solubilities of the different solid cobalt sulfate hydrates were modelled by combining the solution model with the thermodynamic properties of the solid phases, adjusted to the available solubility data. Model performance was confirmed by predicting metastable solubilities and saturation vapor pressures with good agreement with available literature.

Lack of high quality data, especially calorimetric and volumetric data outside 298 K, is a surprising but common problem for the first row transition metal sulfates. This is despite their relevance to hydrometallurgy, and their role as an archetype for symmetrical (relatively) highly charged electrolytes. Measuring these properties is of course not straight-forward, as it is time-consuming and demands the necessary equipment and special expertise. As such, one of the future research topics should be exploring whether the physico-chemical similarities between the different bivalent sulfates could be exploited also in modelling their properties.

Acknowledgements

Walter Ahlström Foundation is acknowledged for funding the author's visit to Murdoch University (Perth, Western Australia), where this work was brought to completion.

References

- [1] Cobalt Institute [accessed July 27, 2020]; <https://www.cobaltinstitute.org>.
- [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*, Spectrum Series volume 13, AUSSIM, Carlton, Australia, 2005.
- [4] H. Yang, D. Zeng, W. Voigt, G. Hefter, S. Liu, Q. Chen, *J. Chem. Eng. Data* 59 (2014) 97 – 102.
- [5] H. Yang, D. Zeng, W. Voigt, Y. Chen, Q. Zhou, *J. Chem. Eng. Data* 61 (2016) 3406 – 3412.
- [6] L. Kahlenberg, *J. Phys. Chem.* 5 (1901) 339–392.
- [7] R. Rohmer, *Ann. Chim.* 11 (1939) 611–725.
- [8] P.G.M. Brown, J.E. Prue, *Proc. R. Soc. Lond. A* 232 (1995) 320–336.
- [9] W. Libus, T. Sadowska, Z. Libus, *J. Solution Chem.* 9 (1980) 341 – 353.
- [10] J.A. Rard, R.F. Platford, "Experimental methods: Isopiestic" in *Activity Coefficients in Electrolyte Solutions*, 2nd edition, CRC Press, Boca Raton, 1991.
- [11] E. Sturch, *The standard potential of the cobalt amalgam and activity coefficients of aqueous solutions of cobalt sulfate*, Ph.D. Thesis, University of Oklahoma, 1956.
- [12] F. Malatesta, L. Carbonaro, N. Fanelli, S. Ferrini, A. Giacomelli, *J. Solution Chem.* 28 (1999) 593 – 619.
- [13] J.G. Albright, J.A. Rard, S. Serna, E.E. Summers, M.C. Yang, *J. Chem. Thermodynamics* 32 (2000) 1447–1487.
- [14] G. E. Brodale, W. F. Giauque, *J. Phys. Chem.* 69 (1965) 1268–1272.
- [15] D.R. Schreiber, K. DeWyse, L.C. Schreiber, T. Tung, *J. Solution. Chem.* 28 (1999) 567 – 573.
- [16] D.D. Wagman, et al., *J. Phys. Chem. Ref. Data* 11 (Supplement 2) (1982).
- [17] R.N. Goldberg, R.G. Riddell, M.R. Wingard, H.P. Hopkins, C.A. Wulff, L.G. Hepler, *J. Phys. Chem* 70 (1966) 706–710.
- [18] C. Akilan, T. Chen, T. Vielma, P.M. May, G. Senanayake, G. Hefter, *J. Chem. Eng. Data* (2020), article in press.
- [19] V.I. Zavitskaya, *Russ. J. Inorg. Chem.* 19 (1974) 605–606.
- [20] V.I. Zavitskaya, *Russ. J. Inorg. Chem.* 19 (1974) 607–608.

- [21] V.K. Filippov, S.I. Yakovleva, *Russ. J. Inorg. Chem.* 24 (1979) 112–113.
- [22] T. Oikova, D. Barkov, *Russ. J. Inorg. Chem.* 24 (1979) 278–280.
- [23] V.G. Shevchuk, N.M. Lazorenko, A.G. Dryuchko, V.M. Skorikov, *Russ. J. Inorg. Chem.* 24 (1979) 1890–1891.
- [24] V.G. Shevchuk, D.A. Storozhenko, N.N. Kisel, *Russ. J. Inorg. Chem.* 25 (1980) 466–469.
- [25] D.A. Storozhenko, V.G. Shevchuk, *Russ. J. Inorg. Chem.* 24 (1979) 1564–1565.
- [26] S. Bursa, M. Stanish-Levitska, *Russ. J. Inorg. Chem.* 25 (1980) 1400–1405.
- [27] C. Balarew, V. Karaivanpva, *Z. Anorg. Allg. Chem.* 422 (1976) 283–288.
- [28] G. Wollmann, W. Voigt, *Fluid Phase Equilib.* 291 (2010) 154–158.
- [29] G. Bruhn, J. Gerlach, F. Pawlek, *Z. Anorg. Allg. Chem.* 337 (1965) 68–79.
- [30] P.M. May, D. Rowland, *J. Chem. Eng. Data* 62, (2017) 2481–2495.
- [31] K.S. Pitzer, "Ion interaction approach: Theory and data correlation" in *Activity Coefficients in Electrolyte Solutions*, 2nd edition, CRC Press, Boca Raton, 1991.
- [32] K.S. Pitzer, *J. Phys. Chem.* 77 (1973) 268–277.
- [33] K.S. Pitzer, G. Mayorga, *J. Solution. Chem.* 3 (1974) 539–546.
- [34] W. Wagner, A. Pruss, *J. Phys. Chem. Ref. Data*, 31 (2002) 387–535.
- [35] D.P. Fernandez, A.R.H. Goodwin, E.W. Lemmon, J.M.H. Levelt Sengers, R.C.A. Williams, *J. Phys. Chem. Ref. Data*, 26 (1997) 1125–1166.
- [36] K.S. Pitzer, *J. Chem. Soc., Faraday Trans. 2*, 68 (1972) 101–113.
- [37] T. Chen, G. Hefter, R. Buchner, *J. Solution. Chem.* 34 (2005) 1045–1066.
- [38] C. Akilan, G. Hefter, N. Roman, R. Buchner, *J. Phys. Chem. B* 110 (2006) 14961–14970.
- [39] M. Eigen, K. Tamm, *Z. Elektrochem.* 66 (1962) 93–107.
- [40] M. Eigen, K. Tamm, *Z. Elektrochem.* 66 (1962) 107–121.
- [41] C.W. Bale, E. Bélisle, P. Chartrand, S.A. Decterov, G. Eriksson, K. Hack, I.H. Jung, Y.B. Kang, J. Melancon, D.A. Pelton, C. Robelin, S. Petersen, *Calphad* 33 (2009) 295–311.
- [42] P. Koukkari, K. Penttilä, K. Hack, S. Petersen in *Microstructures, Mechanical Properties and Processes Computer Simulation and Modelling*, Volume 3, Wiley, Weinheim, 2000.
- [43] Y. Marcus, *Ion Properties*, Dekker, New York, 1997.

- [44] E. Königsberger, *Monatsh. Chem.* 132 (2001) 1363–1386.
- [45] R.V.G. Rao, W. F. Giauque, *J. Phys. Chem.* 69 (1965) 1272–1277.
- [46] C.W. De Kock, *Information Circular*, 8910, U.S. Bureau of Mines, 1982.
- [47] U. Setzmann, W. Wagner, *Int. J. Thermophys.* 10 (1989) 1103–1126.
- [48] J. Salvatier, T.V. Wiecki, C. Fannesbeck, *PeerJ Comput. Sci.* 2 (2016) e55.
- [49] J.E. Mayrath, R.H. Wood, *J. Chem. Eng. Data* 28 (1983) 50–59.
- [50] R.C. Phutela, K.S. Pitzer, *J. Phys. Chem.* 90 (1986), 895–901.
- [51] P.M.A. Broers, G.S.A. van Welie, *Recueil des Travaux Chimiques des Pays-Bas*, 84 (1965) 789–798.
- [52] P.M. Kobylin, *Proceedings of the European Metallurgical Conference* 3 (2011) 957–974.
- [53] P.M. Kobylin, P.A. Taskinen, *Calphad* 38 (2012) 146–154.
- [54] P.M. Kobylin, P.A. Taskinen, *Calphad* 35 (2011) 499–511.
- [55] F. Höffler, M. Steiger, *Monatsh. Chem.* 149 (2018) 369–379.
- [56] F. Höffler, I. Müller, M. Steiger, *J. Chem. Thermodynamics* 116 (2018) 279–288.
- [57] T. Vielma, J. Salminen, U. Lassi, *Calphad* 60 (2018) 126–133.
- [58] K.S. Pitzer, J.J. Kim, *J. Chem. Soc.* 96 (1974) 5701–5707.
- [59] R.A. Robinson, R.H. Stokes, *Electrolyte Solutions*, 2nd ed., Butterworths, London, 1970.
- [60] D. Rowland, P.M. May, *J. Solution Chem.* 47 (2018) 107–126.
- [61] A.B. Zdanovskii, *Trudy Solvanoj Laboratorii (Trans. Salt Lab.)* No. 6. Akad. Nauk. SSSR, 1936.
- [62] T.F. Young, M.B. Smith, *J. Phys. Chem.* 58 (1954) 716 – 724.