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Critical evaluation of CuSO$_4$-H$_2$O system up to solubility limit, from eutectic point to 373.15 K

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**Highlights**
- CuSO$_4$-H$_2$O system is modelled from freezing point to boiling point.
- The behaviour of the electrolyte solution is described by Pitzer model.
- Several parameter sets with different temperature dependency were evaluated.
- Only four parameters with eight temperature dependent terms are required.
- Model is tested against independent vapour pressure and electrochemical cell data.

**Abstract**

The solubility of copper(II) sulfate in water as a function of temperature and ionic strength is successfully modelled using Pitzer formalism. Four types of experimental data from the literature were implemented for the assessment, namely activity and osmotic coefficients, freezing point depression and solubility of CuSO$_4$ in water. This work proved that four Pitzer parameters with eight terms are sufficient to create a consistent thermodynamic model of the CuSO$_4$-H$_2$O system up to 5 mol/kg-H$_2$O of CuSO$_4$, from the eutectic point to 373.15 K. The whole optimization study included a critical deviation analysis to sort out less reliable experimental data. To verify the results of this work, comparisons were carried out with experimental data which were not included in the assessment, i.e. the vapour pressure of the saturated solution, thermodynamic values of the cell reaction as well as electrochemical cell potential (EMF).

**1. Introduction**

Copper sulfate is the most important compound of copper. Metallic copper of over 99.997% purity, necessary for good conductivity, is produced through an electrorefining method from acidic copper sulfate solution (Schlesinger, 2011). Beside electrochemistry (Nikolic et al., 2008), acidic copper sulfate solutions are used in the flotation cells of mining industries (Bai et al., 2019), other hydrometallurgy industries (Schranz et al., 1997; Wayne Richardson, 2003) and agriculture (Kühne et al., 2017).

In the case of a mining flotation system, dissolved copper ion is a tough and costly impurity that needs to be removed in water recycling (Bai et al., 2019; López et al., 2003; Milic´evic´ et al., 2020). The importance of this system is highlighted in places such as Finland where mining companies depend heavily on an effective water recycling system because the surface water contains too much organic matter that degrades flotation performance (Teollisuustaito Oy, 2016). The aim of this paper is to critically evaluate the thermodynamic properties of the CuSO$_4$-H$_2$O system in...
the stability area of CuSO₄·5H₂O as a preliminary step in the assessment of the CuSO₄·H₂SO₄·H₂O system.

Publications regarding the comprehensive thermodynamic modelling of the phase equilibria of the binary CuSO₄·H₂O system are limited in number. The latest study was published by Höfler and Steiger (2018) covering a temperature range from 268 to 377 K. Several models at 298.15 K have been made by Pitzer and Mayorga (1974); Downes and Pitzer (1975), Baes et al. (1993); Miller et al. (1980) and Guendouzi et al. (2003).

2. Thermodynamic theory and Pitzer method

2.1. Chemical potential in aqueous solution

In aqueous solutions the molality is generally used as a composition variable for solutes:

\[ \mu_i = \mu_i^0 + RT \ln(m_i \cdot \gamma_i) \] (1)

where \( \mu_i \) is the chemical potential, \( m_i \) is the molality of the species, \( \gamma_i \) is its activity coefficient and superscript \(^0\) refers to the hypothetical standard state, which is a 1 molal ideally diluted solution.

In aqueous solution, strong electrolytes dissociate completely into ions based on stoichiometry (Fletcher, 1993):

\[ M_i^{-}X_m^{-} = v^+ \cdot M^+ + v^- \cdot X^- \] (2)

where \( M^+ \) is the cation and \( X^- \) is the anion of the electrolyte \( M_i^{-}X_m^{-} \), \( v \) is the stoichiometric coefficient and \( z \) is the charge of the corresponding ion. Therefore, the concentration of the ions is proportional to the concentration of the original compound (MX):

\[ m_{MX} = v^+ \cdot m_{M^+} + v^- \cdot m_{X^-} \] (3)

and the properties of the electrolyte are proportional to the properties of its component ions:

\[ \mu(M_i^{-}X_m^{-}) = v^+ \cdot \mu(M^+) + v^- \cdot \mu(X^-) \]

\[ \mu'(M_i^{-}X_m^{-}) = v^+ \cdot \mu'(M^+) + v^- \cdot \mu'(X^-) \] (4)

\[ a_{MX} = m_{MX} \cdot \gamma_{MX} = (m_{M^+} \cdot \gamma_{M^+})^{v^+} \cdot (m_{X^-} \cdot \gamma_{X^-})^{v^-} \] (5)

The following notations are introduced for the electrolyte:

\[ v = v^+ + v^- \]

\[ (v^+) = (v^+)^{v^+} \cdot (v^-)^{v^-} \] (7)

\[ (\gamma^+) = (\gamma^+)^{v^+} \cdot (\gamma^-)^{v^-} \] (8)

When these new notations are substituted into Eqs. (4) and (5), the equation for the properties of the completely dissociated electrolyte can be expressed as:

\[ a_{MX} = (v^+ \cdot m_{MX} \cdot \gamma_{MX})^{v^-} \]

\[ \mu_i = \mu_i^0 + RT \cdot v^- \ln(v^+ \cdot m_i \cdot \gamma_i) \] (10)

The notation \( \gamma_i \) is called the mean activity coefficient of an electrolyte or a salt. The osmotic coefficient \( \phi \) is generally used in aqueous systems instead of the activity of water defined as:

\[ \phi = \frac{1000}{M_W \cdot \sum m_i} \ln a_w \] (11)

where \( \phi \) is the osmotic coefficient, \( M_W \) is the molecular weight of water in g/mol and \( a_w \) is the water activity.

2.2. Chemical potential and phase equilibrium

In phase equilibrium, the chemical potentials of the substance are equal in both phases. Thus, for the vapour pressure over aqueous solution at pressure \( p \), we obtain:

\[ \mu_i(g, T, p) = \mu_i^0(g, T, p) + RT \ln \frac{f_i}{p} = \mu_i^0(l, T, p) + RT \ln \left( \frac{l}{p} \right) \] (12)

where \( f_i \) is the fugacity consisting of the fugacity coefficient and the pressure, \( g \) is the gas phase, and \( l \) stands for the liquid phase. For pure water, this reduces to:

\[ \mu_i^0(g, T, p) + RT \ln \frac{f_i}{p} = \mu_i^0(l, T, p) \] (13)

where \(^*\) indicates a pure substance.

In a saturated solution, the solid phase is in equilibrium with the aqueous solution (aq). Up to moderate pressure the pressure effects on condensate phases can be neglected. Thus, the chemical potential for \( n \)-hydrate MX\(^n\)H\(_2\)O in saturated solution can be written as follows:

\[ \mu_{MX-nH_nO}(T) = \mu_{MX}(aq, T) + RT \ln(a_{MX}) + \eta \mu_{H_nO}(aq, T) \] (14)

\[ + nRT \ln(a_{H_nO}) \]

2.3. Pitzer model

The Pitzer equation (Pitzer, 1973; Pitzer, 1975; Pitzer and Kim, 1974; Pitzer and Mayorga, 1973; Pitzer and Mayorga, 1974) was selected to describe the non-ideal behaviour of aqueous copper sulfate solution. It has been confirmed over decades that this semi-empirical model is flexible yet can accurately predict the activity coefficients of solutions in a wide range of ionic strength and temperature (Rowland et al., 2015).

For a binary system, from three to four temperature-dependent parameters are used to model the activity and the osmotic coefficient depending on the type of electrolyte, whereas in a ternary system, a total number of from four to eight temperature-dependent parameters has been sufficient to create decent models of some sulfate systems (Baes et al., 1993; Kobylin et al., 2011; Pitzer and Kim, 1974).

In the 1970s, Pitzer (1991) constructed the following equation for excess Gibbs energy similar to the virial equation introduced for gases:

\[ \frac{C_{a}}{w_0RT} = f(I) + \sum_{l} \sum_{j} \sum_{i} m_i m_j \mu(l) + \sum_{l} \sum_{k} \sum_{i} m_i m_j m_k \mu(l) + \cdots \]

(15)

where \( w_0 \) is the weight of kilograms of water, \( m \) is the molality of the corresponding solute species and \( f \) is the function of ionic strength.

Pitzer recombinined the virial coefficients into new interaction parameters \( B, C, \Phi, \lambda, \psi \) and re-wrote the equation for excess Gibbs energy:

\[ \frac{C_a}{w_0RT} = f(I) + 2 \sum_{l} \sum_{m} m_i m_j [C_{a} + (\sum_{m} m_j) C_{a}] + \sum_{l} \sum_{m} m_i m_j \mu[l] + \sum_{l} \sum_{m} m_i m_j [\mu[l] + \sum_{l} \sum_{m} m_i m_j \mu[l]] + 2 \sum_{l} \sum_{m} m_i m_j \mu[l] + \cdots \]

(16)

where subscript \( n \) stands for neutral species, \( c \) for cation and \( a \) for anion.

The first term \( f(I) \) covers the electrostatic forces between ions. Pitzer parameters describe the short-range interactions between ions in the solution. They can be imagined as balls moving ran-
domly in a 3D space due to combinations of repelling forces (like-sign ions) and attraction forces (unlike-sign ions) (Fletcher, 1993). Meanwhile, solvent water is assumed to be a structureless medium with a temperature- and pressure-dependent dielectric constant. Pitzer parameters describing these interactions are obtained through assessment of experimental data.

After appropriate derivation, the following equations are obtained for the activity and osmotic coefficients for a single electrolyte:

\[
(\phi - 1) = |z_M z_A| f^e + 2m(v_M v_A)/v B_{MX}^e + 2m^2 (v_M v_A)^{1/2} / v C_{MX}^e \]

(17)

\[
\ln \gamma_{MX} = |z_M z_A| f^e + 2m(v_M v_A)/v (B_{MX}^e + B_{AX}^e) + 3m^2 (v_M v_A)^{3/2} / v C_{MX}^e \]

(18)

where \( f^e \) is defined as:

\[
f^e = -A_o \left[ \frac{1}{1 + b f^{1/2}} \right] \]

(19)

and \( f' \) as:

\[
f' = -A_o \left[ \frac{1}{1 + b f^{1/2}} + \frac{2b}{B} \ln(1 + bf^{1/2}) \right] \]

(20)

where \( A_o \) is the Debye-Hückel constant and \( b \) is a pre-determined constant (Pitzer, 1973).

The Debye-Hückel constant is calculated from the following equation:

\[
A_o = \left( \frac{1}{2} \right) \left( \frac{2\pi N d_w}{1000} \right)^{1/2} \left( \frac{e^2}{kT} \right)^{3/2} \]

(21)

where \( d_w \) is the density and \( c \) is the dielectric constant of pure water. The constant \( N_a \) is the Avogadro number, \( e \) is the electric charge and \( k \) is the Boltzmann constant.

\( C^o \) is assumed to be independent of ion strength but binary interaction parameters are functions of ionic strength and are defined as:

\[
B^o = b^{(0)} + b^{(1)} \exp(-\alpha_1 f^{1/2}) + b^{(2)} \exp(-\alpha_2 f^{1/2}) \]

(22)

\[
B = b^{(0)} + b^{(1)} g(\alpha_1 f^{1/2}) + b^{(2)} g(\alpha_2 f^{1/2}) \]

(23)

where \( b \), \( \alpha_1 \) and \( \alpha_2 \) are constants, and \( g(x) \) is defined as:

\[
g(x) = \frac{2}{\pi} \left[ 1 - (1 + x) \exp(-x) \right] \]

(24)

The values of constants \( b \), \( \alpha_1 \) and \( \alpha_2 \) depend on the electrolyte type, and are listed in Table 1.

2.4. Precipitation and dissociation of copper(II) sulfate salts

\( \text{CuSO}_4 \) precipitates from aqueous solution as hydrates at lower temperatures and at room temperature. Its thermodynamically stable form is chalcanthite (\( \text{CuSO}_4 \cdot 5\text{H}_2\text{O} \)), which also exists as a mineral. At elevated temperature, it dehydrates into bonattite (\( \text{CuSO}_4 \cdot 3\text{H}_2\text{O} \)), then poitevite (\( \text{CuSO}_4 \cdot \text{H}_2\text{O} \)), until eventually becoming anhydrous copper sulfate.

According to Wayne Richardson (2003), \( \text{CuSO}_4 \cdot 5\text{H}_2\text{O} \) decomposes in air rapidly to \( \text{CuSO}_4 \cdot 3\text{H}_2\text{O} \) at 361 K, then further to \( \text{CuSO}_4 \cdot \text{H}_2\text{O} \) at 387 K, and finally to anhydrous \( \text{CuSO}_4 \) at 518 K. However, since water is released in decomposition, the decomposition pressure depends on the prevailing activity of water (vapour pressure). Widjaja et al. (2010) have studied the decomposition of \( \text{CuSO}_4 \cdot 5\text{H}_2\text{O} \) by thermo-Raman spectroscopy and by thermogravimetric analysis (TGA). They found that thermo-Raman spectroscopy indicates that \( \text{CuSO}_4 \cdot 5\text{H}_2\text{O} \) will decompose at a temperature range of 312–334 K. According to TGA analysis, however, the dissociation occurs in the temperature range of 339–340 K. Using variable temperature diffuse reflection infrared Fourier transform spectroscopy (VT-DRIFTS), White (2012) has determined the decomposition temperature of \( \text{CuSO}_4 \cdot 5\text{H}_2\text{O} \) to \( \text{CuSO}_4 \cdot 3\text{H}_2\text{O} \) in air to be 318–331 K and to \( \text{CuSO}_4 \cdot \text{H}_2\text{O} \) at a temperature range of 355–368 K. He also noticed that the decomposition continues gradually if there is a constant purge of argon instead of static air. None of these experiments disclose the prevalent pressure or partial pressure of water.

The situation is different when \( \text{CuSO}_4 \cdot 5\text{H}_2\text{O} \) dehydrates into \( \text{CuSO}_4 \cdot 3\text{H}_2\text{O} \) in aqueous solution. At moderate pressure in the \( \text{CuSO}_4 \cdot 5\text{H}_2\text{O} \) system there is an invariant point where \( \text{CuSO}_4 \cdot 5\text{H}_2\text{O} \) and \( \text{CuSO}_4 \cdot 3\text{H}_2\text{O} \) are in equilibrium and the activity of water is also fixed. The situation is similar between \( \text{CuSO}_4 \cdot 3\text{H}_2\text{O} \) and \( \text{CuSO}_4 \cdot \text{H}_2\text{O} \) in recent research Höfler and Steiger (2018) have found the dehydration temperatures to be 366.9 K and 390.9 K, respectively. Their results were mostly based on the vapour pressure of dissociation reaction measurements.

Eq. (25) shows the solubility reaction of \( \text{CuSO}_4 \cdot 5\text{H}_2\text{O} \) and Eqs. (26) and (27) the Gibbs energy change and the equilibrium constant for the solubility reaction with relation \( \Delta G_{sol} = -RT \ln(K_{sol}) \):

\[
\text{CuSO}_4 \cdot 5\text{H}_2\text{O}(s) = Cu^{2+}(aq) + SO_4^{2-}(aq) + 5\text{H}_2\text{O}(l) 
\]

(25)

\[
\Delta G_{sol} = \mu_{\text{Cu}^{2+}}(aq) + 5\mu_{\text{SO}_4^{2-}}(aq) - \mu_{\text{CuSO}_4 \cdot 5\text{H}_2\text{O}(s)} = -RT \ln(K_{sol}) 
\]

(26)

\[
K_{sol} = \frac{\gamma_{cu}^{\infty} \cdot \gamma_{so}^{\infty} \cdot \gamma_{w}^{5}}{\gamma_{cuSO_4-5H_2O}} 
\]

(27)

The activity of solids can be assumed to be one at moderate pressures. Thus, in equilibrium the equilibrium constant \( K_{sol} \) is equal to the solubility product, \( K_{sol} = K_{sp} \).

3. Thermodynamic experimental data

The experimental data used in the assessment were isopiestic measurements, freezing point measurements and the mean activity coefficient as well as solubility data. All osmotic coefficient data were converted to the activity of water (Eq. (11)).

All isopiestic measurements are related to the vapour pressure inside the isopiestic apparatus used. Rard and Platford have derived the following equation for the error in the osmotic coefficient at 298.15 K when there is 0.001 K fluctuation in the temperature inside the apparatus (Rard and Platford, 1991):

\[
\Delta \phi = \frac{0.0033}{\sum \mu_{m_i}} 
\]

(28)

For 0.1 molal copper sulfate solution this would lead to an error of 0.0165, which is a serious error. The osmotic coefficient tends to first decrease as function of molality and later to increase. Around the minimum the osmotic coefficient is almost invariant, as can be seen in Fig. 1.

The term \( B^o \) in the Pitzer equation describes the interactions between a cation and an anion (Eq. (22)) and is a function of Pitzer
parameters $\beta^0$, $\beta^1$ and $\beta^2$. In the copper sulfate concentration range of 0.5–1.0 mol/kg, the latter is practically zero and the value of $B^\phi$ is a function of the two first ones. At 0.5 molal solution, the share of the $\beta^1$ is about 60%, decreasing to about 40% at 1.0 solution of copper sulfate (Fig. 2). The Pitzer parameter $\beta^0$ changes accordingly from 40% to 60%, respectively. The concentration range where both Pitzer parameters $\beta^0$ and $\beta^1$ have a significant effect is crucial for the assessment. However, the osmotic coefficient is almost invariant in this important range as far as experimental error caused by temperature fluctuation is concerned. Moreover, the activity of water will decrease steadily with increasing concentration. Thus, the activity of water was used in the assessments.

Fig. 1. The osmotic coefficient of copper sulfate in the concentration range of 0.5–1.0 molality at 298.15 K. The error lines are calculated using Eq. (28) and the experimental points are calculated using the Pitzer parameters by Downes and Pitzer (1975).

Fig. 2. Percentage sections of $B^\phi$ in the concentration range of 0.5–1.0 molality of copper sulfate at 298.15 K. Pitzer parameters values are taken from the model of Downes and Pitzer (1975).
instead of the osmotic coefficient (Sippola, 2012; Sippola and Taskinen, 2014; Sippola and Taskinen, 2018).

The freezing point depression data were also converted into activity of water according to the equation by Sippola and Taskinen (2018). Most of the freezing point data were included, except data by Chambers and Frazer (1900) which deviated clearly from other data as well as data by de Coppet (Timmermans, 1960), which were scattered and less accurate. However, the data by de Coppet include the lowest freezing temperature measurement so it can be used to test the extrapolation capacity of the model. All activity coefficients of copper sulfate were converted to the activity of aqueous copper sulfate (Eq. (9)).

Solubility data was modelled as the activity of a solid ($a_s$) in saturated solution:

$$a_s = \frac{K_{sp}}{K_{sol}}$$

(29)

where $K_{sp}$ is calculated using the assessed mean activity coefficient, and the molality and $K_{sol}$ from the assessed $\Delta G^\circ$ of the solubility reaction. In equilibrium the activity of the solid will be one, in supersaturation more than one and in undersaturation less than one.

The isopiestic measurements and freezing point data considered in this work are listed in Table 2.

Numerous CuSO$_4$ solubility data were found in very old literature sources, dated earlier than 1950. In fact, not many publications were found after that year, apart from Bruhn et al. (1965) and Urréjola et al. (2011) (Table 3). As preliminary screening of the solubility data, all copper sulfate solubility data have been plotted on a chart (Fig. 3).

Most of the old data are quite consistent with each other. Data which were observed to deviate significantly from the majority of trends were excluded and not used in the assessment, as notified in Table 3. Data by Foote (1919) and Urréjola et al. (2011) were both eliminated from the assessment due to the observed general inconsistency with the majority of the data, as well as one data point at 273.15 K from Crockford and Webster (1930).

The solubility data by Etard (1894) and Patrick and Aubert (1896) are in agreement, but the former are more scattered. Moreover, Patrick and Aubert (1896) measured parallel data at each temperature confirming consistency, so we consider their data more reliable. To reduce the effect of experimental error in the assessment we decided to exclude Etard’s data (Fig. 4). Additionally, articles that only have one experimental data point relevant to the studied system were rejected and consequently are not listed in the references.

Above 343.15 K the experimental data starts to diverge. All efforts to obtain satisfactory assessment which would model more than a few points for CuSO$_4$3H$_2$O and CuSO$_4$H$_2$O failed, so we decided to postpone the modelling of solubility for these hydrates in the ternary system CuSO$_4$–H$_2$SO$_4$–H$_2$O, where they also exist at lower temperatures. Besides, Tilden and Shenstone (1983) mentioned in their publication that green basic copper sulfate was observed during the experiment above 393 K. Thus, the experimental solubility of CuSO$_4$H$_2$O in pure water above 393 K was compromised. Consequently, our model is limited to 373.15 K and therefore existing boiling point data are excluded.

There is also a discrepancy between the data of Miles and Menzies (1937) and Patrick and Aubert (1896) on the solubility of CuSO$_4$5H$_2$O above 343.15 K. The experiment by Miles and Menzies (1937) was based on an excess amount of liquid water from a saturated solution which was used to estimate the amount of water in the saturated solution (Menzies, 1936). Since the vapour pressure of water is increased by temperature, the calculated molality must be corrected by the amount of water in the gas phase. In addition, some water could have condensed on the walls of the apparatus. The total amount of water used was only about 1 g, so, despite careful gas phase correction, we considered that the obtained results for solubility were too high at the higher temperatures. Moreover, their focus was on solubility in heavy water, and they made only four solubility measurements in ordi-

| Property | Temperature [K] | Concentration molality | Data Points | Reference |
|----------|-----------------|------------------------|-------------|-----------|
| $\phi$ (iso) | 298.15 | 0.1–1.4 | 12(12) | Robinson and Stokes (1949) |
| $\phi$ (iso) | 298.15 | 0.1–1.6 | 13(13) | Downes and Pitzer (1975) |
| $\phi$ (hygro) | 298.15 | 0.2–1.4 | 10(10) | Guendouzi et al. (2003) |
| $\phi$ (iso) | 298.15 | 0.0001–1.4199 | 24(24) | Miller et al. (1980) |
| $\phi$ (iso) | 298.15 | 0.1445–1.3392 | 8(8) | Libuš et al. (1980) |
| $\phi$ (iso) | 323.15 | 0.1289–2.056 | 15(15) | Yang et al. (2014) |
| $\phi$ (iso) | 373.15 | 0.2132–4.8707 | 17(17) | Yang et al. (2016) |
| $\omega$ (p/p$^*$) | 292.15–369.15 | 0.385–1.052 | 49(48) | Emden (1887) |
| $\Upsilon$ (iso) | 298.15 | 0.1–1.4 | 12(12) | Robinson and Stokes (1949) |
| $\Upsilon$ (iso) | 298.15 | 0.1–1.6 | 13(13) | Downes and Pitzer (1975) |
| $\Upsilon$ (iso) | 298.15 | 0.2–1.4 | 10(10) | Guendouzi et al. (2003) |
| $\Upsilon$ (iso) | 298.15 | 0.1050–1.4417 | 24(24) | Miller et al. (1980) |
| $\omega$ (fpd) | 273.13–272.94 | 0.000458–0.10355 | 23(23) | Brown and Prue (1955) |
| $\omega$ (fpd) | 272.85–271.59 | 0.1150–0.8903 | 5(2) | Kahlenberg et al. (1901) |
| $\omega$ (fpd) | 272.44–271.41 | 0.476–1.19 | 4(0) | Chambers and Frazer (1900) |
| $\omega$ (fpd) | 273.14–273.12 | 0.00023–0.014625 | 22(22) | Hausrath (1902) |
| $\omega$ (fpd) | 272.97–271.41 | 0.072–1.19 | 2(2) | Jones and Getman (1904) |
| $\omega$ (fpd) | 272.94–272.30 | 0.1–0.5 | 3(3) | Klein and Svanberg (1918) |
| $\omega$ (fpd) | 273.14–273.13 | 0.001–0.01 | 6(6) | Hovorka and RowePugh (1925) |
| $\omega$ (fpd) | 272.50–271.35 | 0.386–1.018 | 8(8) | Reddish (1873) |
| $\omega$ (fpd) | 269.25–272.14 | 0.368–1.699 | 7(0) | De Coppet 1872 |

* Thermodynamic property, iso stands for isopiestic vapour pressure measurement, hygro stands for hygrometric measurement, fpd stands for freezing point depression.

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Table 3
Solubility data description and sources.

| Temperature Kelvin | Data pointsa | Reference |
|--------------------|-------------|-----------|
| CuSO₄.5H₂O         |             |           |
| 272.15–367.15      | 22(0)       | Etard (1894) |
| 271.65–368.15      | 22(16)b     | Miles and Menzies (1937) |
| 293.15–308.15      | 2(1)c       | Massink (1917) |
| 285.15–298.15      | 2(0)        | Foote (1919) |
| 273.15–328.15      | 3(2)d       | Crockford and Brawley (1932) |
| 288.15–308.15      | 3(2)e       | Flöttmann (1928) |
| 273.15–298.15      | 2(1)f       | Crockford and Webster (1930) |
| 278.15–298.15      | 3(0)        | Urréjola et al. (2011) |
| 293.15–373.15      | 22(20)g     | Patrick and Aubert (1896) |
| 271.75–373.15      | 13(7)h      | Agde and Barkholt (1926) |
| 293.15–308.15      | 7(7)        | Ishikawa 1923 |
| 273.15–373.15      | 11(3)i      | Poggia1 (Poggiale, 1843) |
| 286.95–331.95      | 11(3)       | Lattey 1923 |
| 273.15–377.15      | 11(0)       | Mulder 1864, 18665 |
| 273.15–327.15      | 4(0)        | Tobler 1855 |
| 273.15–298.15      | 5(2)j       | Cohen et al. 1907 |
| 288.15–308.15      | 3(3)        | Schreinemakers (1911) |
| CuSO₄.3H₂O         |             |           |
| 369.15–438.15      | 13(0)       | Etard (1894) |
| 373.15–423.15      | 3(0)        | Bruhn et al. (1965) |
| 369.05–383.15      | 5(0)        | Miles and Menzies (1937) |
| CuSO₄.1H₂O         |             |           |
| 448.15–573.15      | 9(0)        | Bruhn et al. (1965) |
| 452.15–462.15      | 2(0)        | Etard (1894) |
| 393.15–461.15      | 5(0)        | Tilden and Shenstone (1883) |

* x(y) stands for the number of points (points used in the best model).

b except at 271.65 and all data from 348.15 K.
c except at 293.15 K.
d except at 273.15 K.
e actual experimental data is 10 solubility points consisting of 3 temperature points, although the author himself averaged them based on each temperature, except at 273.15 K.
f rejected 273.15–288.15 K.
g corresponding data were retrieved from (Timmermans, 1960) data compilation (Timmermans, 1960).

Fig. 3. Solubility of CuSO₄.5H₂O in H₂O as a function of temperature along with experimental solubility from multiple literature sources as listed in Table 3. The experimental data for solubility below 273.15 K, i.e., the freezing point depression data are not shown here. The hollow polygons indicate rejected data.
nary water using existing literature data at the time to generate the solubility values for ordinary water at rounded temperatures. Thus, data at 348.15 K and over by Miles and Menzies (1937) were excluded from the assessment.

All electrochemical cell measurements were reserved for model verification as well as all vapour pressures of saturated solutions and therefore they were not used in the assessment (Table 4). All excluded data are shown in Table 5.

4. Modelling

For thermodynamic properties we have used the same approach as Harvie et al. (Christov and Møller, 2004; Greenberg and Møller, 1989; Harvie et al., 1984; Møller, 1988), where all the chemical potentials of independent ions are set equal to zero. We also discovered that the Gibbs energy change of the solubility reaction can be expressed with three temperature dependency terms:

\[
\Delta G' = a + b(T) + c(T)\ln(T)
\]

which was converted to \(\Delta H\), \(\Delta S\) and \(\Delta C_p\) for the assessment. Thus, the initial values were readily obtained from pre-existing thermodynamic databases (Roine, 2018; Wagman et al., 1982) and the final values could be compared straightforwardly to the corresponding literature values.

The assessment was carried out using FactSage (Bale et al., 2016) software version 7.3 with the built-in optimization module called OptiSage. The allowed deviation from initial values manually assigned in the OptiSage module for the Gibbs energy of copper sulfate pentahydrate was 2000 J/mol for enthalpy, 20 J/K.mol for entropy and 20 J/K.mol for heat capacity. The initial value for delta enthalpy and entropy came from the average of the values in the HSC (Roine, 2018) and NBS (Wagman et al., 1982) databases. It was found that a large allowed-deviation value retained the modelled Gibbs energy very close to the initial value if the accepted experimental data fitted well.

Next, several Pitzer models were created, varying in the combination of temperature terms in each Pitzer parameter. Then, the deviation plot from the first tested model was made and analysed. We used an acceptance criterion of two per cent for deviation from the experimental data point, except for 0.5% for freezing point data. If a calculated point exceeded the deviation limit, that data point was omitted from the assessment. However, if this excluded data point deviated later less than 2% in the other tested Pitzer model.

![Fig. 4. Comparison of the solubility data of CuSO₄·5H₂O as a function of temperature by Etard (1894) and Patrick and Aubert (1896).](image)

Table 4
Data of saturated solution and electrochemical cell measurements.

| Property | Temperature (Kelvin) | Concentration | Data points | Reference |
|----------|----------------------|---------------|-------------|-----------|
| \(a_w\) (solv) | 298.15–368.15 | satd. solution | 9(0) | Collins and Menzies (1936) |
| \(a_w\) (solv) | 273.15–373.15 | satd. solution | 12(0) | Speranski (1911) |
| \(a_w\) (solv) | 293.15–313.15 | satd. solution | 5(0) | Ishikawa and Murooka (1933) |
| \(a_w\) (solv) | 282.98–303.94 | satd. solution | 14(0) | Apelblat (1993) |
| \(a_w\) (solv) | 292.15–306.95 | satd. solution | 8(0) | Diesnis (1935)* |
| \(a_w\) (solv) | 298.15–308.15 | satd. solution | 3(0) | Partington and Huntingford (1923) |
| \(\Upsilon\) (emf) | 298.15 | 0.005–0.1 | 5(0) | Getman (1930) |
| \(\Upsilon\) (emf) | 298.15 | 0.02–1 | 14(0) | Ajaye and Wigwe (1978) |
| \(\Upsilon\) (emf) | 298.15 | 0.02024–0.999 | 11(0) | Wetmore and Gordon (1937) |
| \(\Upsilon\) (emf) | 298.15 | 0.05–1.38 | 5(0) | Nielsen and Brown (1927) |

* corresponding data were retrieved from Apelblat (1993).
Table 5
List of rejected experimental data points. Completely rejected data sets are not listed.

| Property | Reference | Temperature Kelvin | CuSO₄ mol/kg | Water activity aw (p/p*) |
|----------|-----------|--------------------|--------------|-------------------------|
| a_w (p/p*) | Emden (1887) | 338.19 | 1.0512 | 0.9589 |
| a_w (fpd) | Kahlenberg et al. (1901) | 272.85 | 0.1150 | 0.9971 |
| | Rudorff (1873)* | 272.5 | 0.3865 | 0.9937 |
| | | 272.3 | 0.4586 | 0.9918 |
| | | 271.85 | 0.7468 | 0.9875 |
| | | 271.6 | 0.8836 | 0.9851 |
| | | 271.55 | 0.9181 | 0.9846 |
| | | 271.35 | 1.0183 | 0.9827 |
| Solubility CuSO₄·SH₂O | Miles and Menzies (1937) | 271.65 | 0.85 | |
| | | 348.15 | 3.21 | |
| | | 353.15 | 3.51 | |
| | | 358.15 | 3.84 | |
| | | 363.15 | 4.23 | |
| | | 368.15 | 4.7 | |
| | | 373.15 | 4.9630 | |
| | | 376.15 | 4.0371 | |
| | | 379.15 | 4.2527 | |
| | | 383.15 | 4.3107 | |
| | | 387.15 | 4.1390 | |
| | | 393.15 | 2.4330 | |
| | | 397.15 | 2.8229 | |
| | | 403.15 | 3.8699 | |
| | | 407.15 | 1.1074 | |
| | | 411.15 | 1.2068 | |

* data taken from (Timmermans, 1960).

Table 6
Pitzer models based on combination of terms.

| No. of terms | b(0) | b(1) | C(0) | b(2) | C(1) | C(2) |
|---------------|------|------|------|------|------|------|
| Model 1 | 8 | v | v | v | v | v |
| Model 2 | 8 | v | v | v | v | v |
| Model 6 | 8 | v | v | v | v | v |
| Model 7 | 8 | v | v | v | v | v |
| Model 8 | 12 | v | v | v | v | v |

Table 7
Pitzer parameters of the final version of each model as a function of temperature.

| b(0) | a/T | B | dT |
|------|------|---|----|
| Model 1 | −11.6467 | 0.40843 | −5.51E−04 |
| Model 2 | −12.5928 | 0.47563 | −7.22E−04 |
| Model 6 | −12.8432 | 0.20470 | 1.65E−04 |
| Model 7 | −15.4492 | 0.28214 | 4.51E−05 |
| Model 8 | −11.5773 | 0.41615 | −5.84E−04 |

| b(1) | a/T | b | dT |
|------|------|---|----|
| Model 1 | −56.717 | −56.717 | −0.06791 | −1.61E−04 |
| Model 2 | −55.951 | 7.40306 | −0.001312 | |
| Model 6 | −56.395 | 1.09895 | 0.09895 | −2.77E−04 |
| Model 7 | −54.483 | 10.80493 | −0.04053 | |
| Model 8 | 2917.8 | 81.808 | 0.03869 | −1.17E−04 |
then that experimental data point was re-approved. These steps were repeated until the final set of accepted experimental data was reached.

After that, the Pitzer models were re-assessed using only the valid experimental data to create a final version of each model. All models were then compared once more based on their deviation plot to determine the best one. The list of the best models with only eight Pitzer parameter terms is given in Table 6. Model 8 with 12 terms was retained for comparison purposes.

The Pitzer parameters obtained after layered deviation analysis are listed in Table 7 and a comparison of the parameter values with literature data at 298.15 K is given in Table 8. The Pitzer parameter values at 298.15 K of models 2 and 6 are considered closer to the literature values than the rest, especially to the work of Baes et al. (1993). The quality of assessment of each model is discussed in the next section.

5. Results

5.1. Model comparison

This work proved that thermodynamic modelling of the CuSO₄-H₂O system is sufficient with four (4) Pitzer parameters and eight (8) adjustable terms. In an attempt to find the most reliable model,
several models were made and compared regarding how well they fitted the experimental data (Table 9) and how well the obtained thermodynamic values for the solubility reaction agreed with the literature values (Table 10). The quality of the model was estimated separately for each type of experimental data using the root mean square error defined as:

$$\text{RMSE} = \sqrt{\frac{1}{N} \sum_{i=1}^{N} (M_i - E_i)^2},$$

where $M$ denotes calculated values, $E$ experimental values and $N$ the amount of data in the population. As can be seen from Table 9, models 8, 6 and 2 are the best as far as the RMSE is concerned.

However, the thermodynamic properties of the solubility reaction for model 6 differ from the NBS (Wagman et al., 1982) and CODATA (Cox et al., 1989) values (Table 10), whilst the values of model 2 are close to those obtained with 12 terms (model 8). Thus, we concluded that model 2, having fewer Pitzer parameters than model 8, was the best of the models under consideration.

The calculated solubility of copper sulfate pentahydrate by model 2 is compared to the literature data in Fig. 5 and the corresponding deviation plot is given in Fig. 6. Experimental data by Miles and Menzies (1937), Patrick and Aubert (1896), Agde and Barkholt (1926) and Poggiale (1843) are the four literature sources which have the most data compared to others. Apart from Poggiale's alienated data up to 343.15 K, our assessed values agree well with most literature sources at below 353.15 K. Agde and Barkholt's work only matched the assessed values in a medium temperature range but deviated at low (below 283.15 K) and high (above 353.15 K) temperature. Having a deviation range roughly around ±0.05 molal, our assessed values agree well with Miles-Menzies' work and Patrick-Aubert's work up to 343.15 K. Beyond this point, our assessment inclined more toward Patrick-Aubert's work, Poggiale's work and Agde-Barkholt's work below 366.15 K.

A comparison with freezing point data is displayed in Fig. 7. As can be seen from the figure, our model can extrapolate the extended scattered data surprisingly well. The assessed values agree well with dilute solutions such as in Brown and Prue (1955), Haußrath (1902) and Hovorka and Rodebush (1925). At higher ionic strength, the gaps between our results and works by Chambers and Frazer (1900) and by Kahlenberg et al. (1901) are

**Table 10**

Thermodynamic values of the solubility reaction of copper sulfate pentahydrate at 298.15 K.

| Source                        | No. of terms | $\Delta H_{298}$ J/mol | $\Delta S_{298}$ J/K mol | $\Delta C_p,298$ J/K mol |
|-------------------------------|--------------|------------------------|-------------------------|-------------------------|
| CODATA (Cox et al., 1989)     | 5            | 980                    | -30.95                  | -205.14                 |
| NBS (Wagman et al., 1982)     | 6            | 600.00                 | -30.35                  | -178.61                 |
| HSC 9 (Roine, 2018)           | 5            | 688.32                 | -30.67                  | -187.65                 |
| Höfler and Steiger (2018)     | 11           | 618.46                 | -31.86                  | -232.65                 |
| Model 1                       | 8            | 714.38                 | -31.41                  | -171.36                 |
| Model 2                       | 8            | 749.39                 | -31.32                  | -171.49                 |
| Model 6                       | 8            | 316.89                 | -36.07                  | -169.16                 |
| Model 7                       | 8            | 818.21                 | -37.80                  | -168.64                 |
| Model 8                       | 12           | 645.06                 | -31.64                  | -171.71                 |

**Fig. 5.** Calculated solubility of CuSO$_4$·5H$_2$O by model 2 (solid line) as a function of temperature compared to literature data (Agde and Barkholt, 1926; Crockford and Brawley, 1932; Crockford and Webster, 1930; Etard, 1894; Flöttmann, 1928; Massink, 1917; Miles and Menzies, 1937; Patrick and Aubert, 1896; Schreinemakers, 1911; Timmermans, 1960; Urréjola et al., 2011). Hollow polygons indicate omitted data.
obvious. Lastly, the solubility of ice and CuSO$_4$$\cdot$5H$_2$O are plotted together in Fig. 8, where the intersection shows the eutectic point. The calculated eutectic temperature of CuSO$_4$$\cdot$H$_2$O by model 2 is 271.62 K at 0.83669 mol/kg-H$_2$O of CuSO$_4$.

The calculated mean activity and osmotic coefficients at 298.15 K compared to literature data are presented in Fig. 9 and Fig. 10, respectively. The result is consistent with most of the literature data, with a deviation of less than 0.001. It is apparent that the osmotic coefficient of this work is closer to that of Miller et al. (1980), Downes and Pitzer (1975) and Libuš et al. (1980) than to Robinson and Stokes (1949). Although assessed with more water activity data at various temperatures, the RMSE of water activity was still around $10^{-4}$ and 0.0037 for the osmotic coefficient. The same phenomenon occurs in the assessment of the mean activity data.

Fig. 6. Model 2 deviation plot for solubility of CuSO$_4$$\cdot$5H$_2$O as a function of temperature compared to literature data (Agde and Barkholt, 1926; Crockford and Brawley, 1932; Crockford and Webster, 1930; Flöttmann, 1928; Massink, 1917; Miles and Menzies, 1937; Patrick and Aubert, 1896; Schreinemakers, 1911; Timmermans, 1960). Hollow polygons indicate omitted data.

Fig. 7. Predicted freezing point of copper sulfate as a function of temperature compared to literature data (Brown and Prue, 1955; Chambers and Frazer, 1900; Hausrath, 1902; Hovorka and Rodebush, 1925; Jones and Getman, 1904; Kahlenberg et al., 1901; Klein and Svanberg, 1918; Timmermans, 1960). Hollow polygons indicate omitted data.
coefficient, where Robinson and Stokes’ work deviated the most from the calculated values. Nevertheless, most of the assessed osmotic coefficients deviate by less than 0.005 at 298.15 K. The calculated mean activity coefficient and osmotic coefficient from 273.15 K to 373.15 K at various CuSO₄ concentrations are tabulated in Appendix.

5.2. Model verification

To further examine the integrity of our model, we compared the predicted values with thermodynamically related properties excluded from the assessment, namely the vapour pressure of the saturated solution and electromotive force measurements, which were reserved for verifying the model.

5.2.1. Vapour pressure of saturated solution

We used FluidCal software (Wagner and Prub, 2002) to obtain the vapour pressure of pure water and the second virial coefficient for the gas phase to describe its real gas behaviour. The calculated vapour pressure over saturated solution is shown in Fig. 11 and the corresponding deviation plot in Fig. 12.

As can be seen, our model is in good agreement with the saturated pressure measurements up to 333 K but predicts higher pressures at higher temperatures. On the other hand, the RMSE from...
The vapour pressure of solution at concentrations of 0.386, 0.747 and 1.051 mol/kg-H$_2$O in a temperature range of 292.8–368.8 K by Emden (1887) is 0.04, 0.08 and 0.13 kPa, respectively.

5.2.2. Electromotive force

The electromotive force measurements for the Cu(Hg) | CuSO$_4$ (m) | Hg$_2$SO$_4$ | Hg cell were used to test the validity of model 2. The electromotive force $E$ of this cell is:

$$E = E^0 - \frac{RT}{F} \ln(m_{\text{CuSO}_4} \cdot \gamma_{\text{CuSO}_4})$$

where $F$ is the Faraday constant 96 485 C/mol and $E^0$ is the standard potential which is related to the Gibbs energy change ($\Delta G^o$) of the cell reaction: Cu(Hg) + Hg$_2$SO$_4$ = 2Hg(l) + CuSO$_4$(aq). We discovered that the temperature dependence of the $\Delta G^o$ of the cell reaction can be modelled using only two terms:

$$\Delta G^o = a + bT$$

Applying model 2, the following values for $a$ and $b$ were assessed from the literature data (Ajayi and Wigwe, 1978; Getman, 1930; Müller and Reuther, 1941; Nielsen and Brown, 1976).

Fig. 10. Calculated osmotic coefficient as a function of copper sulfate by model 2 at 298.15 K compared to literature data (Downes and Pitzer, 1975; Guendouzi et al., 2003; Libuš et al., 1980; Miller et al., 1980; Robinson and Stokes, 1949) and the profile of deviations from literature values.
The obtained electromotive force at 298.15 K is shown in Fig. 13.

The electrochemical force for saturated copper sulfate was also estimated. The RMSE for the calculated values is shown in Table 12.

As can be seen from the table, the obtained electrochemical cell potential is in excellent agreement with the values in Miller et al. (1980). Also, the calculated enthalpy and entropy changes for the cell reaction agree well with the literature data.

The RMSE of the data by Wetmore and Gordon (1937) is 0.344 mV and by Müller and Reuther (1941) is 0.426 mV. The obtained thermodynamic values for the cell reaction are listed below.
6. Conclusions

The thermodynamic properties of CuSO$_4$ solution up to a molal concentration of five were modelled in this research with the Pitzer equation using FactSage software through its assessment module OptiSage. Different Pitzer models were tested, varying the number of temperature terms in the Pitzer parameters. It was found that a model using four Pitzer parameters with only eight temperature-dependent terms can assess the freezing point depression, solubility of CuSO$_4$/$C_1$$_5$H$_2$O, mean activity and osmotic coefficients (activity of water) up to 373.15 K. The obtained thermodynamic properties $D_H$, $D_S$ and $D_Cp$ for the solubility reaction of CuSO$_4$/$C_1$$_5$H$_2$O are also in good agreement with the literature data (Table 10).

The quality of the model was verified using the vapour pressure of saturated solution as well as electrochemical cell data which were not included in the assessment. Our model can predict the vapour pressure of saturated solution within 0.4 kPa up to 333 K. At higher temperatures, the deviation increases to 2.7 kPa at 363.15 K. On the other hand, the model can predict the vapour pressure of a 1.05 m solution (Emden, 1887) in a temperature range of 292.8–368.8 K with an RMSE of 0.13 kPa.

Moreover, the behaviour of the Cu(Hg) | CuSO$_4$(m) | Hg$_2$SO$_4$ | Hg electrochemical cell in the temperature range of 284–323 K up to saturated copper sulfate solution as well as the thermodynamics of cell reaction Cu(Hg) + Hg$_2$SO$_4$ = 2Hg(l) + CuSO$_4$(aq) are in good agreement with the literature data (Table 13).

We also concluded that it is best to model the data for solubilities and vapour pressures for three and one hydrates as part of the ternary system, CuSO$_4$-H$_2$SO$_4$-H$_2$O, building a more consistent and extensive database for hydrometallurgical purposes at ambient and elevated temperatures and pressures.

When comparing our model to the recent Höfler and Steiger model (Höfler and Steiger, 2018), some differences exist. Firstly, we have retained all the data for CuSO$_4$/$C_1$$_3$H$_2$O and CuSO$_4$/$C_1$$_H$$_2$Ot o to be modelled as part of the assessment of the CuSO$_4$-H$_2$SO$_4$-H$_2$O system. Secondly, our analysis of the most reliable solubility data is different. We have excluded some data by Miles and Menzies (1937) above 343 K and included older data which they considered

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### Table 11

RMSE of assessed electrochemical force from experimental values for the Cu(Hg) | CuSO$_4$(m) | Hg$_2$SO$_4$ | Hg cell.

| No. of Experiments | Temperature (K) | Molality (mol/kg) | RMSE (mV) | Reference |
|--------------------|----------------|-------------------|-----------|-----------|
| 29                 | 298.15         | 0.1–1             | 0.62      | Ajayi and Wigwe (1978) |
| 4                  | 298.15         | 0.05–1            | 1.13      | Nielsen and Brown (1927) |
| 9                  | 298.15         | 0.005–1.44        | 1.03      | Getman (1930) |
| 6                  | 288.21         | 0.02850–1.0000    | 0.41      | Wetmore and Gordon (1937) |
| 11                 | 298.15         | 0.02024–0.9990    | 0.31      | Wetmore and Gordon (1937) |
| 4                  | 308.15         | 0.02735–1.0000    | 0.20      | Wetmore and Gordon (1937) |
| 5                  | 318.10         | 0.02735–1.0000    | 0.60      | Wetmore and Gordon (1937) |
| 3                  | 284.65         | 0.506–1.253       | 0.56      | (Müller and Reuther (1941) |
| 3                  | 293.15         | 0.506–1.253       | 0.38      | (Müller and Reuther (1941) |
| 3                  | 298.15         | 0.506–1.253       | 0.03      | Müller and Reuther (1941) |
| 3                  | 303.15         | 0.506–1.253       | 0.20      | Müller and Reuther (1941) |
| 3                  | 313.15         | 0.506–1.253       | 0.28      | Müller and Reuther (1941) |
| 2                  | 323.15         | 0.506–1.253       | 0.30      | Müller and Reuther (1941) |

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**Fig. 13.** Calculated electromotive force for the Cu(Hg) | CuSO$_4$(m) | Hg$_2$SO$_4$ | Hg cell at 298.15 K in comparison with the literature values (Ajayi and Wigwe, 1978; Getman, 1930; Müller and Reuther, 1941; Nielsen and Brown, 1927; Wetmore and Gordon, 1937).
too low. Thus, instead of Miles and Menzies' (1937) data, our results at high temperature agree with the works of Patrick and Aubert (1896), Poggiale (1843) and part of Agde and Barkholt (1926).

Furthermore, instead of including electrochemical data at 298.15 K with fixed standard state potential, we have used EMF data with excellent results for validating our model. Our Pitzer model uses the same Pitzer parameters as Höfler and Steiger.

![Graph showing deviation of calculated electromotive force by model 2 from literature values (Ajayi and Wigwe, 1978; Getman, 1930; Müller and Reuther, 1941; Nielsen and Brown, 1927; Wetmore and Gordon, 1937) for the Cu(Hg) | CuSO4(m) | Hg2SO4 | Hg cell.]

**Table 12**

Deviation of assessed electrochemical force from experimental values for the Cu(Hg) | CuSO4(sat) | Hg2SO4 | Hg cell.

| Temperature (K) | Saturation (mol/kg) | Mean activity coefficient | Deviation (mV) | Reference |
|-----------------|---------------------|--------------------------|----------------|-----------|
| 288.21          | 1.178               | 0.0407                   | 0.08           | Wetmore and Gordon (1937) |
| 298.15          | 1.413               | 0.0369                   | −0.52          | Wetmore and Gordon (1937) |
| 308.15          | 1.675               | 0.0317                   | −0.22          | Wetmore and Gordon (1937) |
| 318.10          | 1.968               | 0.0280                   | 0.41           | Wetmore and Gordon (1937) |
| 284.65          | 1.100               | 0.0426                   | −0.04          | Müller and Reuther (1941) |
| 293.15          | 1.292               | 0.0383                   | −0.33          | Müller and Reuther (1941) |
| 298.15          | 1.413               | 0.0360                   | −0.12          | Müller and Reuther (1941) |
| 303.15          | 1.540               | 0.0338                   | 0.04           | Müller and Reuther (1941) |
| 313.15          | 1.817               | 0.0298                   | 0.46           | Müller and Reuther (1941) |
| 323.15          | 2.131               | 0.0262                   | 0.94           | Müller and Reuther (1941) |

**Table 13**

Thermodynamic values for the Cu(Hg) | CuSO4(sat) | Hg2SO4 | Hg cell at 298.15 K.

| ΔH° | ΔS° | ΔG° | E° | Reference |
|-----|-----|-----|----|-----------|
| J/mol | J/K mol | J/mol | mV | |
| −96 150 | −147 | −52 313 | 271.09 | NBS (Wagman et al., 1982) |
| −96 120 | −147 | −52 200 | 270.51 | CODATA (Cox et al., 1989) |
| −100 372 | −162 | −52 044 | 269.70 | Höfler and Steiger (2018) |
| −97 948 | −154 | −52 052 | 269.74 | This work |
|       |      |       | 269.70 | Miller et al. (1980) |
|       |      |       | 269.71 | Miller et al. (1980) |

a Values for Cu(Hg) are taken from NBS Tables.
b fixed value from Miller et al. (1980).
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