Some Solution Equilibria Involving Calcium Sulfite and Carbonate

II. The Equilibrium between Calcium Sulfate and Calcium Sulfite in Aqueous Solutions

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The equilibrium constant for the reaction $\text{CaSO}_4(\text{H}_2\text{O})_2(s) + \text{SO}_3^{2-} \rightleftharpoons \text{CaSO}_4(\text{H}_2\text{O})_2(s) + \text{SO}_3^{2-} + 1.5 \text{ H}_2\text{O}$ has been determined at 25°C, 35°C, and 75°C, with $\text{Na}^+$ concentrations 1 m and 3.5 m, and $\text{ClO}_4^-$ as neutral anion. The average values for log $K$ are, for both $\text{Na}^+$ concentrations; at 25°C 1.88; at 35°C 1.96; and at 75°C 2.23; thus $K = [\text{SO}_3^{2-}] [\text{SO}_3^{2-}]^1 = 76, 91, \text{ and } 170$ at the three temperatures.

The measurements suggest log $K = -6.5 \pm 0.2$ for the activity solubility product of $\text{CaSO}_4(\text{H}_2\text{O})_2$ at 25°C.

The present paper will describe studies of the equilibrium

$$\text{CaSO}_4(s) + \text{SO}_3^{2-} = \text{CaSO}_4(s) + \text{SO}_3^{2-}; \quad K = [\text{SO}_3^{2-}] / [\text{SO}_3^{2-}]$$ (1)

The available literature data that could be used for estimating $K$ are in very bad agreement, giving values of $K$ ranging from about 1 to several hundreds.

ESTIMATION OF $K$ FROM LITERATURE DATA

The equilibrium constant $K$ in (1) is the ratio of the concentrations of two binegative ions of practically the same size. The activity factors of these ions can be expected to be approximately equal although their values will, of course, vary very much with the ionic medium. If this is so, the apparent $K$ in any aqueous solution will not be far from the real activity constant, and $K$ will be fairly independent of ionic strength.

We made an attempt to estimate $K$ from the relevant literature data, summarized in Table 1. The solubility of $\text{CaSO}_4(\text{H}_2\text{O})_2$ in water at temperatures below 100°C has been very accurately measured by several workers, whose results agree well. The last column in Tab. 1 gives the concentration of the saturated aqueous solutions in mM.

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Table 1. Literature data on the solubilities of CaSO₄(H₂O)₄ in water and in saturated CaSO₄(H₂O)₂, expressed in mg CaSO₄ per 1 000 g solution.

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>CaSO₄ in pure water</th>
<th>CaSO₄ in saturated CaSO₄ solutions</th>
<th>CaSO₄ in water mM</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>1 670</td>
<td>99.5 (29)</td>
<td>14.177</td>
</tr>
<tr>
<td>15</td>
<td>2 000</td>
<td>99.5 (29)</td>
<td>14.817</td>
</tr>
<tr>
<td>18</td>
<td>2 300</td>
<td>99.5 (29)</td>
<td>15.295</td>
</tr>
<tr>
<td>20</td>
<td>2 600</td>
<td>99.5 (29)</td>
<td>15.361</td>
</tr>
<tr>
<td>25</td>
<td>2 900</td>
<td>99.5 (29)</td>
<td>15.413</td>
</tr>
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<td>3 200</td>
<td>99.5 (29)</td>
<td>15.510</td>
</tr>
<tr>
<td>35</td>
<td>3 500</td>
<td>99.5 (29)</td>
<td>14.765</td>
</tr>
<tr>
<td>40</td>
<td>3 800</td>
<td>99.5 (29)</td>
<td>14.200</td>
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<tr>
<td>45</td>
<td>4 100</td>
<td>99.5 (29)</td>
<td>13.575</td>
</tr>
<tr>
<td>50</td>
<td>4 400</td>
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<td>11.900</td>
</tr>
<tr>
<td>55</td>
<td>4 700</td>
<td>99.5 (29)</td>
<td>11.900</td>
</tr>
<tr>
<td>60</td>
<td>5 000</td>
<td>99.5 (29)</td>
<td>11.900</td>
</tr>
<tr>
<td>65.3</td>
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<td>99.5 (29)</td>
<td>11.900</td>
</tr>
<tr>
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<td>5 600</td>
<td>99.5 (29)</td>
<td>11.900</td>
</tr>
<tr>
<td>75</td>
<td>5 900</td>
<td>99.5 (29)</td>
<td>11.900</td>
</tr>
<tr>
<td>80</td>
<td>6 200</td>
<td>99.5 (29)</td>
<td>11.900</td>
</tr>
<tr>
<td>90</td>
<td>6 500</td>
<td>99.5 (29)</td>
<td>11.900</td>
</tr>
<tr>
<td>100</td>
<td>6 800</td>
<td>99.5 (29)</td>
<td>11.900</td>
</tr>
</tbody>
</table>

R = Robart 1913.
L = van der Linden 1916 (The values in parentheses are the original data, expressed as mg of "CaSO₄(H₂O)₂" per 1 000 g solution).
W + S = Wurz and Swoboda 1948.

On the other hand, the data on CaSO₃ (really CaSO₃(H₂O)₄) are scarce and contradictory as seen from Table 1 where the data of Robart, van der Linden and Wurz and Swoboda are compared. The constant K could be estimated from them in two ways.

From the solubilities of CaSO₃ and CaSO₄ in pure water, we calculated the solubility products, making reasonable assumptions regarding the activity factors; K was then obtained as the ratio of the solubility products of CaSO₄ and CaSO₃. For both salts we used the activity factors for ZnSO₄ as given by Harned and Owen on the basis of data of Cowperthwaite and LaMer and Bray; the activity factors for all metal(II) sulfates seem to vary with concentration in practically the same way.

In this way we obtained the following very approximate values for K:

- from Robart’s data 1.2(15°C) to 0.8(100°C)
- from van der Linden’s data 200(30°C) to 6 000(100°C)
- from Wurz and Swoboda’s data 70(20°C) to 140(80°C)

If, instead, one uses Kielland’s activity factor tables, the constants in the two latter cases will be multiplied with a factor of about 1.5, and thus become 300 to 9000, and 100 to 200; however, the ZnSO₄ values seem preferable.

We may also use the solubility of CaSO₃ in saturated calcium sulfate solutions. In these experiments one may expect [SO₄²⁻] to be practically the same.
as in a saturated solution of \( \text{CaSO}_4(\text{H}_2\text{O})_2 \) in pure water; since the two binega-
tive ions are in the same solution no activity factor correction is needed, and
the constant \( K \) is obtained as the ratio \( \text{SO}_4^{2-}/\text{SO}_3^2- \) in the solution. The values
so obtained are approximately

from van der Linden’s data \[ 80(30^\circ\text{C}) \text{ to } 300(100^\circ\text{C}) \]
from Wurz and Swoboda’s data \[ 65(20^\circ\text{C}) \text{ to } 40(80^\circ\text{C}) \]

Not only do van der Linden’s and Wurz-Swoboda’s values disagree with
each other; in each paper the two sets of data seem to lead to disagreeing
results.

Robart’s solubility values are so much higher than those given in the two
other papers that one may suspect they are misquoted; since, however, Latimer
and Hildebrand \(^{10}\) had selected Robart’s data we felt we should not discard
them without making experiments of our own.

EXPERIMENTAL

The equilibrium (1) was studied in solutions with 1 m \( \text{Na}^+ \) at 25°C, 35°C, and 75°C,
and with 3.5 m \( \text{Na}^+ \) at 25°C and 35°C (with one stray experiment at 75°C).

At the two lower temperatures, the solutions were shaken to equilibrium in 100 ml
glass bottles in a water thermostat. At 75°C the solution was kept in an Erlenmeyer flask
with a magnetic stirrer; the flask was kept in an air thermostat at 75°C.

The solutions were generally made up by adding to a sodium sulfite solution an excess
of \( \text{CaSO}_4(\text{H}_2\text{O})_2 \). In one case, the equilibrium was approached from the other direction,
solid \( \text{CaSO}_4(\text{H}_2\text{O})_2 \) being added to a sodium sulfate solution. As in part \(^{1}\) the solutions
contained perchlorate ions as balance.

Especially at the lower temperatures, the time of contact was very long, 5—38 days,
to assure that equilibrium was obtained. — At the end of an experiment, the stirring was
stopped but the flask was still left in the thermostat. After a few hours, the solids had
settled, and samples of the solution were sucked out through a glass filter-stick. The
samples were weighed and analysed for sulfate and sulfite ions.

Sulfite was determined iodometrically (part 1). Since the sulfite concentration in
our solutions was low, the accuracy was only about 5% at the lowest concentrations.

For determining sulfite the standard gravimetric method could not be used here
because of the fear of the coprecipitation of sodium owing to the high \( \text{Na}^+ \) concentration in
the solutions. Instead, a volumetric method with the following principle \(^{11}\) was used. The
sulfite ions are first bound as a formalin complex and then sulfite precipitated with barium
chloride at room temperature after adding acetic acid. The precipitate of \( \text{BaSO}_4 \) is washed,
centrifuged, and then converted to \( \text{BaCO}_3 \) by means of a strong sodium carbonate solu-
tion. This reaction takes about 1 h at 100°C. The barium carbonate precipitate is washed
till the reaction is neutral, and then the carbonate content determined by dissolving in a
known excess of hydrochloric acid, and back-titrating with sodium hydroxide. The
accuracy of the sulfate determination is better than 1%, which is satisfactory consider-
ing the much larger uncertainty in the sulfite determination.

The solid phases. In order to make sure in what form calcium sulfite and sulfate were
present, X-ray powder photographs were taken of the powder mixture in a number of the
equilibrium solutions at 25°C and 75°C and compared with photographs of synthetic spec-
cimens. Calcium sulfate proved to be present in the form of the dihydrate \( \text{CaSO}_4(\text{H}_2\text{O})_2 \),
gypsum. Calcium sulfite was present in one and the same form at 25°C and 75°C; this
phase was also prepared synthetically. The diffraction lines of this phase agreed very
well with the data of Matthews and McIntosh \(^{12}\); these authors state that the composition
of the phase is \( \text{CaSO}_4(\text{H}_2\text{O})_4 \).

Table 2. Experiments on the equilibrium

\[
\text{CaSO}_4(s) + \text{SO}_4^{2-} \rightleftharpoons \text{CaSO}_4(s) + \text{SO}_4^{2-}
\]

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>Na⁺ mole/kg H₂O</th>
<th>Time days</th>
<th>SO₄²⁻ mmole/kg solution</th>
<th>SO₄²⁻</th>
<th>K</th>
<th>log K</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
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<td>19</td>
<td>455</td>
<td>6.28</td>
<td>72.4</td>
<td>1.86</td>
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<tr>
<td>25</td>
<td>1.0</td>
<td>23</td>
<td>455</td>
<td>6.28</td>
<td>72.4</td>
<td>1.86</td>
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<tr>
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<td>3.61</td>
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</tr>
<tr>
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<td>35</td>
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<td>500</td>
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<td>144</td>
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</tr>
<tr>
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<td>0.1</td>
<td>743</td>
<td>4.31</td>
<td>172</td>
<td>2.24</td>
</tr>
</tbody>
</table>

RESULTS

Our results are given in Table 2. Since the equilibrium constant \( K \) of the reaction studied is a pure number, it is immaterial whether we express the concentrations in \( \text{m} \), in \( \text{M} \), or in mole/kg of solution. It is the latter unit we have chosen in the table, since it gives the easiest calculations, and thus the smallest chance of computation errors.

The columns of Table 2 are: temperature °C; concentration of Na⁺, in mole/kg of water; time of equilibration, days; final concentration of SO₄²⁻; final concentration of SO₃²⁻; equilibrium constant \( K \), and log \( K \).

The single experiment where the equilibrium was approached starting with calcium sulfite is marked with an asterisk.

The correction for the hydrolysis of the sulfite ion according to

\[
\text{SO}_3^{2-} + \text{H}_2\text{O} \rightleftharpoons \text{HSO}_3^- + \text{OH}^-
\]

can be shown to be negligible in comparison with the other experimental errors; it is less than 1 6\%.

The equilibrium constant \( K \) is found to increase with temperature. There may be a slight increase with increasing ionic strength, though the accuracy of the data does not allow a certain conclusion. We prefer to give an average \( K \) for both ionic strengths:

\[
\text{25}^\circ\text{C} \quad \log K = 1.88 \quad K = 76
\]
\[
\text{35}^\circ\text{C} \quad \log K = 1.96 \quad K = 91
\]
\[
\text{75}^\circ\text{C} \quad \log K = 2.23 \quad K = 170
\]

If we compare these values with the literature data given above, our data are found to be in complete disagreement with Robart’s. The best agreement...
is with the $K$ values from Wurz and Swoboda’s solubilities in pure water, and with those from van der Linden’s solubilities in calcium sulfate solutions. The accuracy of our values for log $K$ is, we hope, better than $\pm 0.10$.

If we assume that the log $K$ so obtained represents the true activity equilibrium constant, we can find the true activity solubility product for CaSO$_4$ by combination with the activity solubility product $^{13}$ $[\text{Ca}^{2+}] [\text{SO}_4^{2-}] = 10^{-4.63}$ at 25°C

$$[\text{Ca}^{2+}] [\text{SO}_4^{2-}] = K_s = 10^{-4.51}$$

The uncertainty in log $K_s$ is estimated as $\pm 0.2$.

From this value of $K_s$ we may calculate the solubility of CaSO$_4$(H$_2$O)$_2$ at 25°C in pure water to be around 0.76 mM or 91 mg CaSO$_4$/l.

REFERENCES


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